



# Conference Guide and Abstracts



Nancy  
FRANCE

9 -12 May 2016

21<sup>st</sup> International Symposium on  
Analytical and Applied Pyrolysis



CDS Analytical has manufactured Pyrolyzers for almost 50 years and has been a regular sponsor of this symposium. We are happy to be participating in Nancy, France and look forward to a successful conference.

**CDS** Analytical



Benvenuto  
TereTulemast  
Bienvenido  
Welcome  
欢迎  
Welkom  
Svāgat  
Aloha  
yākoso  
l'ovozlet  
Valkommen  
Wilkommen  
Velkommen  
HoanNghiēnh  
BaruchHaba  
DobroPozhalovat  
YinDeeUllinZap  
AhlanWaSahlan  
SooDjowow  
HoşGeldin  
vaangha  
Dobrodošli  
BemVindo  
Fūnyhng  
Bienvenue  
SelamatDatang  
HwangyongHamnida  
Padhāro  
VítámeTě

Our pyrolyzers use a unique-resistively heated filament system that offers the widest range in heating profiles and temperature control. In addition, our systems are built on a modular platform, so you can add options as they are needed to meet your future needs.

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- First Pyrolysis Reactor System Commercially Available
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- Polymer and Additive Libraries Available; No special software needed

We look forward to meeting you in Nancy and to hear about your unique area of research!



# CONTENTS

|  |       |
|--|-------|
| Welcome to PYRO2016 .....                            | p 3   |
| Scientific Committee.....                            | p 4   |
| Sponsorship & support.....                           | p 5   |
| Conference information.....                          | p 6   |
| Social events.....                                   | p 8   |
| Keynote speakers.....                                | p 10  |
| Special session in honor of Michael Antal.....       | p 12  |
| Specialists workshops.....                           | p 13  |
| Floor plans.....                                     | p 13  |
| Program Overview.....                                | p 14  |
| Detailed Program.....                                | p 15  |
| Poster sessions.....                                 | p 19  |
| Full abstracts listing.....                          | p 31  |
| Keynote speaker abstracts.....                       | p 33  |
| Special session abstract.....                        | p 43  |
| Analytical Pyrolysis – oral presentations.....       | p 45  |
| Analytical Pyrolysis – poster presentations.....     | p 55  |
| Biomass / Catalysis – oral presentations.....        | p 99  |
| Biomass / Catalysis – poster presentations.....      | p 109 |
| Biomass / Fast Pyrolysis – oral presentations.....   | p 133 |
| Biomass / Fast Pyrolysis – poster presentations..... | p 141 |
| Biomass / Kinetics – oral presentations.....         | p 153 |
| Biomass / Kinetics – poster presentations.....       | p 159 |
| Biomass / Reactors – oral presentations.....         | p 177 |
| Biomass / Reactors – poster presentations.....       | p 185 |
| Biomass / Slow Pyrolysis – oral presentations.....   | p 197 |
| Biomass / Slow Pyrolysis – poster presentations..... | p 205 |
| Bio-Oil – oral presentations.....                    | p 223 |
| Bio-Oil – poster presentations.....                  | p 229 |
| Fossil Fuels – oral presentations.....               | p 245 |
| Fossil Fuels – poster presentations.....             | p 249 |
| Hydrocarbons / Kinetics – oral presentations.....    | p 263 |
| Hydrocarbons / Kinetics – poster presentations.....  | p 269 |
| Instrumentation – oral presentations.....            | p 281 |
| Instrumentation – poster presentations.....          | p 289 |
| Organic Geochemistry – oral presentations.....       | p 297 |
| Organic Geochemistry – poster presentations.....     | p 309 |
| Waste / Reactors – oral presentations.....           | p 327 |
| Waste – poster presentations.....                    | p 333 |
| Authors’s index.....                                 | p 375 |

# HISTORY

## International Symposia on Analytical and Applied Pyrolysis

|     |      |                                  |
|-----|------|----------------------------------|
| #1  | 1965 | Paris, France                    |
| #2  | 1972 | Paris, France                    |
| #3  | 1976 | Amsterdam, The Netherlands       |
| #4  | 1979 | Budapest, Hungary                |
| #5  | 1982 | Vail, CO, USA                    |
| #6  | 1984 | Wiesbaden, Germany               |
| #7  | 1986 | Reading, UK                      |
| #8  | 1988 | Lund, Sweden                     |
| #9  | 1990 | Noordwijkerhout, The Netherlands |
| #10 | 1992 | Hamburg, Germany                 |
| #11 | 1994 | Nagoya, Japan                    |
| #12 | 1996 | Venice, Italy                    |
| #13 | 1998 | Munich, Germany                  |
| #14 | 2000 | Sevilla, Spain                   |
| #15 | 2002 | Leoben, Austria                  |
| #16 | 2004 | Alicante, Spain                  |
| #17 | 2006 | Budapest, Hungary                |
| #18 | 2008 | Lanzarote, Spain                 |
| #19 | 2012 | Linz, Austria                    |
| #20 | 2014 | Birmingham, UK                   |
| #21 | 2016 | Nancy, France                    |

## Organizing Committee of PYRO2016

**Anthony Dufour (Chairman)**

**Valérie Burklé-Vitzthum**

**Valérie Warth**

**Francis Billaud**

**Roda Bounaceur**

**Olivier Herbinet**

**Jacques Lédé**

**Guillain Mauviel**

**Gabriel Wild**



**CNRS, Université de Lorraine**

Reactions and Chemical Engineering Laboratory

LRGP, 1 rue Grandville 54000 Nancy, France



WELCOME

## Welcome to PYRO 2016!

This conference series was initiated by Prof. Guiochon in Paris in 1965. For the past 40 years, this symposium has been the premier forum for the pyrolysis community for sharing ideas and results from fundamentals to applied pyrolysis. We are pleased to bring back this prestigious symposium to France.

Our city has a long tradition on pyrolysis research: from coke in the 60's to petroleum and biomass in the 80's. An "image d'Epinal" illustrating the history of pyrolysis development in Nancy is included in the congress documents.

Around 1900, Nancy was one of the main « Art Nouveau » cities in Europe (Ecole de Nancy in French). The logo of this congress is a tribute to the « Ecole de Nancy » style, joining history, science and arts. Near the location of the congress, one can see the « Villa Bergeret » which is one of the best examples of the Art Nouveau architecture. One session of the congress will be held at the Musée des Beaux-Arts. The idea of a special session in a museum to link art, history and science was proposed by the late Michael Antal. He is much missed and his memory will be honoured during this special session.

The social programme has been organised to the best of our abilities. We hope that you will enjoy the different aspects of our beautiful city: from Renaissance (Lorraine Museum), to the 18<sup>th</sup> century (Place Stanislas) and the Art nouveau. We took special care in choosing (and testing!) the dishes and drinks.

Above all, we have done our best to propose a rich scientific program with a good balance between the different fields of application and the different methodologies. This conference should not be restricted to "applied biomass pyrolysis". Its tradition and success lies in the diversity of the topics and methods. Innovation requires an inter-disciplinary approach. It is very important to keep promoting the links between all disciplines related to pyrolysis.

Nevertheless, on the 340 submissions, 170 dealt with biomass. Therefore it was a difficult task to select the oral presentations, especially for biomass sessions, in order to ensure a balance of topics. We want to thank the members of the scientific committee for their important reviewing work of the abstracts (2 to 5 reviews per abstract) and for their advice and support.

We thank all our sponsors, exhibitors and partners. PYRO2016 has attracted a lot of interest from the sponsoring companies. Without their support, our symposium would not have been possible.

We will do our utmost possible to make your stay in Nancy pleasant. We hope that you will enjoy this conference and that our debates will be fruitful and intense, both in the scientific domain and in cultural matters, including the arts and food (a very important topic in France!).

The PYRO2016 Team

# SCIENTIFIC COMMITTEE

## Scientific Committee

**Françoise Behar**, TOTAL, France

**Franco Berruti**, University of Western Ontario, Canada

**Marianne Blazso**, Hungarian Academy of Sciences, Hungary

**Tony Bridgwater**, Aston University, UK

**Robert C. Brown**, Iowa State University, USA

**Daniele Fabbri**, University of Bologna, Italy

**Jose A. Gonzalez-Perez**, CSIC Seville, Spain

**Andreas Hornung**, Fraunhofer Umsicht, Germany

**Raymond Michels**, CNRS Nancy, France

**Hajime Ohtani**, Nagoya Institute of Technology, Japan

**R. Paul Philp**, The University of Oklahoma, USA

**Marie-Françoise Reyniers**, Ghent University, Belgium

**Clemens Schwarzinger**, Johannes Kepler University, Austria

**Colin E. Snape**, The University of Nottingham, UK

**Kent J. Voorhees**, Colorado School of Mines, USA

## Conference Secretariat

Maggy Aulon

Coralie Desgranges

Hélène Gueniot



**PROGEPI** – 1, rue Grandville  
BP 20451 – 54001 Nancy, France

**SPONSORSHIP  
& SUPPORT**

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for their invaluable support.**

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PyroLAB:



Frontier Laboratories:



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IFPEN:



The CNRS (French National Research Center), the Université de Lorraine (Lorraine University), the Région Lorraine (Region Lorraine) and the Ville de Nancy (City of Nancy)



# CONFERENCE INFORMATION

## Conference venue

The PYRO2016 conference will take place at the Faculty of Pharmacy, 20 rue Lionnois in Nancy.

The venue can easily be reached by bus from Nancy Center with the T2 bus (Bus stop: Hopital Central - Maternité).

The sessions will be held in the Parisot Amphitheater, the poster sessions, coffee breaks and lunch in the Parisot Foyer and the Salle des Sociétés Savantes on the 1st floor, the scientific exhibition in the hall of the Faculty.

## Registration desk

The registration desk is located in the Parisot Foyer. All delegates should register as soon as they arrive at the conference.

The registration desk will be staffed throughout the conference, so please go there if you have any questions or need any assistance.

Opening hours:

Monday 9 May: from 8:00 to 16:00

Tuesday 10 May: from 8:00 to 18:45

Wednesday 11 May: from 8:00 to 18:30

Thursday 12 May: from 8:00 to 18:30

## Conference team

Members of the conference team will wear **an orange scarf** to be easily recognisable. Please do not hesitate to ask them for any information you may require.

## Name badges

You should have been provided with a name badge when you registered. All delegates, staff and presenters **must wear** their name badges at all times **throughout the conference and the social events**.

This will identify you as a PYRO2016 delegate and give you access to the conference areas and catering.

## Lunch and refreshments

Refreshments are available for all PYRO2016 delegates in the Parisot Foyer and the Salle des Sociétés Savantes on the 1<sup>st</sup> floor during each of the timetabled breaks.

A buffet lunch will be served each day in the Parisot Foyer and in the Salle des Sociétés Savantes on the 1<sup>st</sup> floor.

Meal trays will be served to the delegates attending the specialist workshops in the workshop rooms.

We have sent to the catering services the dietary requirements based on the information you provided us with. For any questions, please ask the catering staff at the buffet lunch.

## Wifi and internet

There is free wifi provided by the University of Lorraine, for all PYRO2016 delegates throughout the conference areas. Login details:

Login: wifipyro2016

Password: pyro2016!!

There are few multi-sockets available to recharge your battery at tables in the Parisot Foyer.

## Fire and evacuation policy

If you hear the fire alarm sound, please quietly and calmly make your way to the nearest exit (via the stairs). Do not use the lifts.

If you are in the Parisot Amphitheater, the nearest fire exits will be the doors on each side of the stage.

If you are in the Parisot Foyer or in the hall of the Faculty, please go outside the building to rue Lionnois.

Members of the conference team will direct you where to go.

## Safety

For safety reasons, we recommend that delegates do not leave their personal computer or personal belongings in the Parisot Amphitheater even though it will be locked during the breaks.

**Please note that all delegates must leave the Faculty of Pharmacy before 18:50.**



## Information for presenters

Each presenter has been allocated a 12 minutes presentation slot which is followed by 3 minutes for questions. Please show respect for your fellow presenters by finishing on time so we can keep the conference running on schedule.

The presentation room will be set up with a laptop running Microsoft Windows 7 and Microsoft Office 2010 Professional (including Powerpoint) connected to a projector and presentation screen.

It won't be possible for presenters to directly connect their personal laptop. We strongly advise presenters to have their presentation on an USB drive in PDF or PPT format.

There will be a preview space with dedicated staff in the conference room where presenters will be asked to upload their presentation before their session starts.

## Poster sessions

Due to the high number of posters accepted, two sessions will be organized. Half of the posters will be displayed on Monday 9 May and Tuesday 10 May (1<sup>st</sup> session) and the others on Wednesday 11 May and Thursday 12 May (2<sup>nd</sup> session). Please refer to the list of posters to find out which topics will be displayed in each session.

Poster numbers starting with 1 will be in the 1<sup>st</sup> session while poster numbers starting with 2 will be in the 2<sup>nd</sup> session.

The times of the poster sessions in the program are as follows:

**Session 1:** Monday 9 May: 10:30-11:30

Tuesday 10 May: 10:15-11:15 + 16:30-18:30 (with local beer and sandwiches)

**Session 2:** Wednesday 11 May: 10:15-11:15

Thursday 12 May: 10:15-11:15 + 13:00-15:00

For the 1<sup>st</sup> session, posters should be put up before 10:00 on Monday 9 May and put off before 18:45 on Tuesday 10 May.

For the 2<sup>nd</sup> session, posters should be put up before 10:00 on Wednesday 11 May and put off before 18:45 on Thursday 12 May.

Poster clips will be provided for each poster.

### Young scientist best poster award:

Our partner Frontier Lab will give a prize for the best poster presented by a young scientist. Prizes will be awarded at the PYRO2016 gala dinner on Thursday 12 May.

## A few words about Nancy...

Nancy has many centres of interest and a great variety of tours to offer to the visitor as you will see thanks to our social events.



Very close to the Faculty of Pharmacy, you will be able to discover the Bergeret House which is one of the Art Nouveau villas in Nancy.

The Art Nouveau movement appeared and spread across the globe from 1880, forming neighbouring or sister schools. The School of Nancy was a part of the Art Nouveau movement and was born when the Alsace and Moselle regions were annexed by the Prussians in 1871. Nancy, a French border town, was home to much of the intelligentsia who refused the annexation. These conditions in particular, as well as the presence here of an established artistic community, industrialists and entrepreneurs, led to the establishment of the School of Nancy.

## Practical information

Shops are usually closed on Sunday, and open every other day from 10h00 to 19h00.

Banks are closed on Monday.

Stamps can be bought at the Post Office (closed on Saturday afternoon and Sunday), or at tobacconist ("tabacs") shops.

The tourism office situated on Place Stanislas opens everyday from 9:00 to 13:00 and from 14:00 to 19:00.

## Imagerie d'Épinal

**Épinal pictures** were prints on popular subjects rendered in bright sharp colours, sold in France in the 19<sup>th</sup> Century. They owe their name to the fact that the first publisher of such images — Jean-Charles Pellerin — was born in Épinal and named the printing house he founded in 1796, *Imagerie d'Épinal*.

The expression *image d'Épinal* has become a proverbial expression in French and refers to an emphatically traditionalist and naïve depiction of something which only shows the good aspects.

The PYRO2016 team has decided to create a specific « image » dedicated to the pyrolysis research history in Nancy and is very honoured to offer it to all the delegates attending the conference.

## Local products and gifts

L'Épicerie du Goût - 4 place Vaudémont 54 000 NANCY - offers you a wide range of high quality local products and gifts. A discount of 5% will be offered to all delegates (please wear your name badges).

## SOCIAL EVENTS

# Several social events will be organised in our UNESCO World Heritage city, notably on the marvellous **Place Stanislas**.

The conference will start with a welcome reception (8 May 2016 evening) and go on with several social events such as a visit to Fine Arts museum, the French gastronomy gala dinner (12 May 2016 evening), tours (13 May 2016), etc.

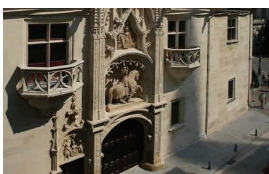
Sunday 8 May 2016—14:00-20:00:

### Welcome Reception at the Musée Lorrain

The Palace of the Dukes of Lorraine (also named Musée Lorrain) is located in the heart of the Old City of Nancy, just steps from the Place Stanislas, a recognized UNESCO World Heritage Site.

It consists of three sets with remarkable architecture.

#### The Palace of the Dukes of Lorraine

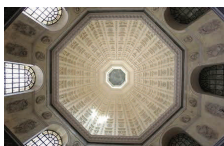


Built from the late fifteenth century onwards, the palace was an important symbol of power for the Dukes of Lorraine. Its gatehouse, hall of honour on the *Grande Rue*, is one of the first examples of Renaissance

art in the East of France. The Galerie des Cerfs, large ceremonial hall, is the only princely gallery of that time to have retained its original dimensions. The palace was heavily redesigned after a fire in 1871.

#### The Church and Convent of the Cordeliers

Founded in the late fifteenth century by Duke René II, after his victory over Charles the Bold, the church and convent of the Cordeliers together have a very strong symbolic aspect. The Church is a jewel of the Lorraine architecture, was built in the full Renaissance period and opens onto the "round Chapel". The latter, built in the early seventeenth century, still houses the graves of the ducal family of Lorraine.



#### The Government Palace



The Government Palace was built between 1751 and 1753 by Emmanuel Héré and is the architectural counterpart to the City Hall (*Mairie*) it faces. During the reign of Stanislas, the King of Poland and father-in-law of Louis XV, it was the residence of the representative of France in Lorraine. This building symbolizes the advent of the kingdom of Lorraine in France. The Government Palace retained a role of military residence until 2010 and today is part of the Musée Lorrain.

Monday 9 May 2016—17:00-21:00:

### Special Session at the Fine Arts Museum—Place Stanislas



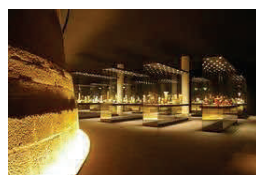
The Museum of Fine Arts of Nancy is located on the Place Stanislas, a UNESCO World Heritage of Humanity site. Since its creation in 1793, it has continued to expand and now offers courses in the heart of artistic creation in Europe of the late fourteenth century to today.

The reception of the museum is housed in a 18<sup>th</sup> century pavilion and is an exceptional piece of architecture designed in 1755 by Emmanuel Héré. Visitors entering this completely restored building discover the quality of the peristyle with its coloured stucco and the staircase, a sumptuous example of domestic 18<sup>th</sup> century architecture, decorated with ironwork by Jean Lamour. The cocktail will be served in this room.

This area provides access to the library and opens onto the ground floor of the first extension finished in 1936 by Jacques and Michel André, the sons of Emile André, the famous School of Nancy architect.



In 1999, a new extension doubled the museum's surface area and provided new rooms: an auditorium (where the keynote lecture will take place), temporary exhibition rooms, a graphic arts firm, a documentation center and a workshop for children. This project was entrusted to Laurent Beaudouin and his team who brought a style of contemporary architecture to the museum while respecting the exceptional site of the Place Stanislas.



In 2011, major work on lighting and accessibility for all was directed by the architect Luca Lotti. This enable a new museum tour to be set up including a room devoted to the work of Jean Prouvé,

from Nancy.

In the basement, the remains of the fortifications of the city (15<sup>th</sup> to 17<sup>th</sup> century), immerse the visitor in the heart of the history of the former Duchy of Lorraine. The basement also houses the illustrious collection of Daum glassware in a spectacular scenographical setting.

Tuesday 10 May 2016—19:30-22:30:

### Opéra National de Lorraine - Place Stanislas

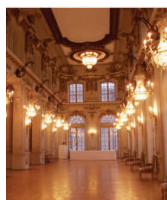


The Opera is part of the Place Stanislas and the Lorraine region's heritage. It was given the status of historical monument in 1923 and is registered with the entire Place Stanislas as a world heritage of humanity site by UNESCO in 1983.

« **Les Pêcheurs de perles** » is an opera in three acts by Georges Bizet with libretto by Eugène Cormon and Michel Carré, created on September 30<sup>th</sup> 1863 at the Théâtre - Lyrique (18 performances). It was reinterpreted in a new version after the composer's death in 1893 at the Opéra-Comique.

The story: situated in ancient times on the island of Ceylon, the book tells how the vow of eternal friendship between two men is threatened by their love for the same woman, herself caught between her love for the fisherman Nadir and her vow as a priestess.

A glass of champagne will be offered in the "foyer" of the Opera de Lorraine during the intermission. You will enjoy an exceptional view of the Place Stanislas.



Wednesday 11 May 2016—18:45-20:30:

### Visit with guides « From Ducal Nancy to Royal Nancy »

The tour especially includes the Place Stanislas and Place de la Carrière and measures the influence of the last Duke of Lorraine over the city.



The charm of the Old City, medieval and Renaissance, is revealed through its architectural highlights which are landmarks in the history of Lorraine region—the Ducal Palace, Mansions, Porte de la Craffe, Eglise Saint Epvre, etc....

**Little tourist train – hourly departures from Place de la Carrière - (except from 13:00 to 14:00).**

During your stay, you could choose your visiting date. The ticket is valid for any time during the symposium.



Discovering Nancy on the little train "**THE CAPITAL OF THE DUKES OF LORRAINE**" - a tour of the historical centre of the city.

You will be surprised by the many cultural treasures through the centuries which the city's buildings testify to. These include the Porte de la Craffe (14<sup>th</sup> century), Ducal Palace (16<sup>th</sup> century), private mansions ... and a whole 18<sup>th</sup> century architectural ensemble.

Highlight of your visit: Place Stanislas (entirely pedestrian) will reveal all its beauty and its richness—buildings, statues and the gilded Jean Lamour gates.

Nancy and its famous "Place Stanislas", fully restored in 2005, will seduce you...No hesitation...get on board the tourist train ...



Thursday 12 May 2016—20:00:

### Gala dinner at Nancy's City Hall (*Mairie*) on the Place Stanislas

Entirely renovated, embellished and returned to pedestrians, the Place Stanislas is considered one of the most beautiful squares in the world.

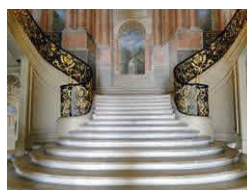


The works to beautify the square were completed in 2005 and an exceptional quality was achieved particularly in the gorgeous paving which is extremely close to the original.

The gates have been gilded while the buildings and their decorative elements have been finely restored. This square is a spectacular 18<sup>th</sup> century architectural gem and has been returned to its former glory.

The facade above the main entrance is decorated with the coats of arms of both Stanislas and the town of Nancy.

**The City Hall is the most important building on the square.**



The entrance starts at the foot of the stairs (Jean Lamour bannister) which leads to the square lounge with its superb mythological paintings.

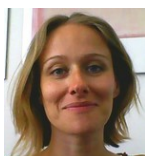
The Dinner will be served in the reception room and from its balconies you will be able to admire the magnificent view of Place Stanislas.

## KEYNOTE SPEAKERS

PYRO2016 is playing host to many distinguished speakers, including the following presenters.

### **Ilaria Bonaduce,**

Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Italy - [ilaria.bonaduce@unipi.it](mailto:ilaria.bonaduce@unipi.it)



Ilaria Bonaduce is lecturer and permanent researcher at the Department of Chemistry of the University of Pisa. Her research focuses on the development of analytical methods and models for the characterization of organic materials in works of art and the study of their ageing processes. [www.dcci.unipi.it/scibec/](http://www.dcci.unipi.it/scibec/)

### **Tiziano Faravelli,**

Politecnico di Milano, Italy - [tiziano.faravelli@polimi.it](mailto:tiziano.faravelli@polimi.it)



Tiziano Faravelli, Full professor at the Department of Chemistry, Materials and Chemical Engineering of Politecnico di Milano. Research activity: numerical fluid dynamics of reactive flows; turbulent/kinetics interactions. Chemical engineering of complex systems: pyrolysis, partial oxidation and combustion modelling of gas, liquid and solid fuels. Pollutant formation (NO<sub>x</sub>, PAH and soot) from combustion processes. Publications: Author of about 150 papers, review articles appeared as books chapters and 1 patent. <http://creckmodeling.chem.polimi.it/index.php>

### **Brian Horsfield,**

GFZ German Research Centre for Geosciences, Potsdam, Germany - [brian.horsfield@gfz-potsdam.de](mailto:brian.horsfield@gfz-potsdam.de)



Brian Horsfield is Full Professor of Organic Geochemistry and Hydrocarbon Systems at the Technical University of Berlin, Germany. He leads the research group Organic Geochemistry at the GFZ German Research Centre for Geosciences, Potsdam. He is director and Executive Chairman of the International Continental Scientific Drilling Program. He has more than thirty five years experience working with the petroleum industry. Brian is co-founder and CEO of GEOS4. He invented and developed the MSSV pyrolysis method. He has more than 200 publications. Brian was appointed to acatech, the German Academy of Science and Technology. [www.gfz-potsdam.de/en/section/organic-geochemistry/](http://www.gfz-potsdam.de/en/section/organic-geochemistry/)

### **Daniel Isler,**

Centre de Pyrolyse de Marienau, Forbach, France - [daniel.isler@cpmarienau.com](mailto:daniel.isler@cpmarienau.com)



Daniel Isler was graduated as Engineer in 1978 of the High School of Mines and Metallurgy (Nancy). He started working at Centre de Pyrolyse de Marienau (CPM) in Forbach in 1979 to carry out research work in the field of cokemaking. He was manager of a Research Group at CPM from 1984 to 1990 and particularly in charge of the construction, start-up and operation of the new pilot facilities of CPM. He is now deputy Director of CPM. In the course of the years Daniel Isler has been involved in various R&D projects: thermal control of coke oven battery, coke reactivity, coal blending and coal blend preparation, etc. He is a member of the European Cokemaking Committee since 1992. [www.cpmarienau.com/](http://www.cpmarienau.com/)

### **Mark R. Nimlos,**

National Renewable Energy Laboratory, Golden, Colorado, USA - [mark.nimlos@nrel.gov](mailto:mark.nimlos@nrel.gov)



I am a Principal Scientist and Section Leader in the National Bioenergy Center at the National Renewable Energy Laboratory (NREL) in Golden, Colorado, USA. I have worked at NREL for over 26 years and have been involved in a variety of renewable energy processes include biomass gasification and pyrolysis. Our current focus is on the catalytic upgrading of biomass pyrolysis vapors into transportation fuels and chemical co-products. [www.nrel.gov/biomass/](http://www.nrel.gov/biomass/)

### **Yrjö Solantausta,**

VTT Technical Research Centre of Finland, Espoo, Finland - [yrjo.solantausta@vtt.fi](mailto:yrjo.solantausta@vtt.fi)



Solantausta is a Principal Investigator at VTT. He has a PhD from Aston University, UK. He has been developing alternative liquid fuels for more than 35 years. Much of his effort lately has involved development of fast pyrolysis of biomass. [www.vttresearch.com/services/bioeconomy/liquid-biofuels1/](http://www.vttresearch.com/services/bioeconomy/liquid-biofuels1/)

## Jan J. Verstraete,

IFPEN, Solaize, France - [jan.verstraete@ifpen.fr](mailto:jan.verstraete@ifpen.fr)



Dr. Jan VERSTRAETE is a Senior Researcher at IFP Energies Nouvelles (IFPEN). He holds a PhD (1997) from the University of Ghent (Belgium), where he developed fundamental kinetic models for catalytic reforming

under the supervision of Prof. Dr. Gilbert Froment. He joined the IFPEN-Lyon in 1994, where he first worked on the modeling of various refining processes. From 1999 onwards, he was appointed R&D program manager for several applied research projects on various refining processes. He has also been deeply involved in basic research on feed composition modeling and reaction modeling, while leading a basic research project on Multi-Scale Modeling. [www.ifpenergiesnouvelles.fr](http://www.ifpenergiesnouvelles.fr)

## Guangwen Xu,

Institute of Process Engineering, Chinese Academy of Science, Beijing, China - [gwxu@ipe.ac.cn](mailto:gwxu@ipe.ac.cn)



Prof. Dr. Guangwen Xu, the director of Southwest Research & Design Institute of Chemical Industry, Adjunct Prof. of Institute of Process Engineering (IPE), Chinese Academy of Sciences (CAS). He had his college education in Tsinghua University and got his doctoral degree from IPE of CAS. He has worked in Japan and Germany for more than 10 years, published more than 200 journal papers and applied more than 90 patents. <http://english.ipe.cas.cn/>

## Toshiaki Yoshioka,

Tohoku University, Sendai, Japan - [yoshioka@env.che.tohoku.ac.jp](mailto:yoshioka@env.che.tohoku.ac.jp)



Toshiaki Yoshioka is Dean, Professor at Graduate School of Environmental Studies, Tohoku University. His scientific background is chemical engineering and industry related environmental issues. His researches have been focused on development of recycling processing of waste materials and waste water treatment. He was guest professor at Hamburg University (2001). He has won some awards, such as "Honda Award (2007)" on recycling technology development, and "Commendation for MEXT in the science and technology"(2013). [www.che.tohoku.ac.jp/~env/gaiyou-e.htm](http://www.che.tohoku.ac.jp/~env/gaiyou-e.htm)

## Keynote lectures

### Monday 9 May

#### 9h15—Mark R. Nimlos

*Biomass Pyrolysis Vapor as an Intermediate to Fuels and Chemicals*

#### 14h30—Daniel Isler

*Some steps in the development of coke manufacture in Europe*

#### 15h15—Guangwen Xu

*Keys to commercially successful coal pyrolysis for production of coal tar*

#### 18h00—Ilaria Bonaduce

*Analytical pyrolysis as a tool for the characterisation of organic materials in cultural heritage*

### Tuesday 10 May

#### 8h30—Tiziano Faravelli

*Kinetic modeling of pyrolysis reactions: from light gas to solids*

#### 11h15—Brian Horsfield

*Geochemical transformation and transport processes as revealed by kinetic determinations and molecular indicators*

### Wednesday 11 May

#### 8h30—Toshiaki Yoshioka

*Chemical processing for feedstock recycling of waste plastics*

#### 11h15—Yrjö Solantausta

*Supporting the industry in scaling up biomass fast pyrolysis technology by building on pioneering work*

### Thursday 12 May

#### 11h15—Jan J. Verstraete

*Monte-Carlo techniques for molecule-based kinetic modeling of heavy oil conversion*

## SPECIAL SESSION

# Soirée in the Fine Arts Museum of Nancy, 9 May 2016, 17:00-21:00 to honour the late Michael J. Antal Jr

*« I looked forward to your meeting more than  
any other in my life »*



**Michael J. Antal, Jr**, a leading biomass researcher, died on 21 October 2015.

He received his MS degree in Applied Physics (Quantum Mechanics and Electromagnetic Theory) from Harvard University followed by a PhD degree in Applied Mathematics (Numerical Analysis and Quantum Mechanics), also from Harvard University.

In 1973, he started his professional career at the Los Alamos National Laboratory as a staff member of the Thermonuclear Weapons Physics Group. However, his research interests soon turned to topics related to the sustainable future of mankind.

In 1976, he published his first pioneering work on the peaceful use of solar energy in the production of fuels from biomass and municipal wastes. After serving as an assistant professor at Princeton University, he was selected as the recipient of the Coral Industries Endowed Chair at the University of Hawaii in 1982, where he became a full professor and the Coral Industries Distinguished Professor of Renewable Energy Resources.

He achieved outstanding results in practically all areas of biomass research and development, including the pyrolysis of biomass materials, and the formation of charcoals through pyrolytic reactions.

Currently the Scopus database reports more than 10 600 citations for 175 articles published with his authorship. The corresponding h-index is 54.

During the planning period of PYRO2016, Michael suggested a special evening linking art, science and history together. However, he was already seriously ill when he received a request for an invited keynote lecture entitled “The art, archaeology, and history of wood pyrolysis” at PYRO2016.

That was when he answered: “I looked forward to your meeting more than any other in my life ”. Indeed he hoped to prepare his lecture but sadly Michael passed away before he could finish it.

His death changed the course of the special evening that was planned to take place in the Museum of Fine Arts. Now the focus is on a commemoration of Michael.

The first lecture will deal with the connections between pyrolysis and art by Ilaria Bonaduce, according to the original plans. Then two presentations will follow about the results that Michael achieved with his co-workers in two fruitful and long-lasting international collaborations which lasted until the end of his life.

### Program

17:00-18:00: Visit of the Fine Arts Museum

18:00-18:30: **Analytical pyrolysis as a tool for the characterization of organic materials in cultural heritage**, by Ilaria Bonaduce

18:30-18:40: **In remembrance of Prof. Michael Antal**, by Jacques Ledé

18:40-19:00: **Towards a realistic kinetics in the non-isothermal studies, 30 years of a US-Hungarian cooperation in biomass research**, by Gabor Varhegyi

19:00-19:20: **Towards the maximum theoretical yields of charcoal from biomass pyrolysis**, by Morten Gronli and Wang Liang

19h30: Cocktail

## SPECIALISTS WORKSHOPS

PYRO2016 is a good opportunity to organise specialists workshops, during a dedicated free time

Specialists workshops will be organised on:

**Tuesday 10 May from 16:30 to 18:30**

**Coke and biochar quality**, chaired by Colin Snape, [colin.snape@nottingham.ac.uk](mailto:colin.snape@nottingham.ac.uk)

**Pyrolysis compound specific isotopic analysis (Py-CSIA). Technique and applications**, chaired by José A. González Pérez, [jag@irnase.csic.es](mailto:jag@irnase.csic.es)

**Thursday 12 May from 13:00 to 15:00**

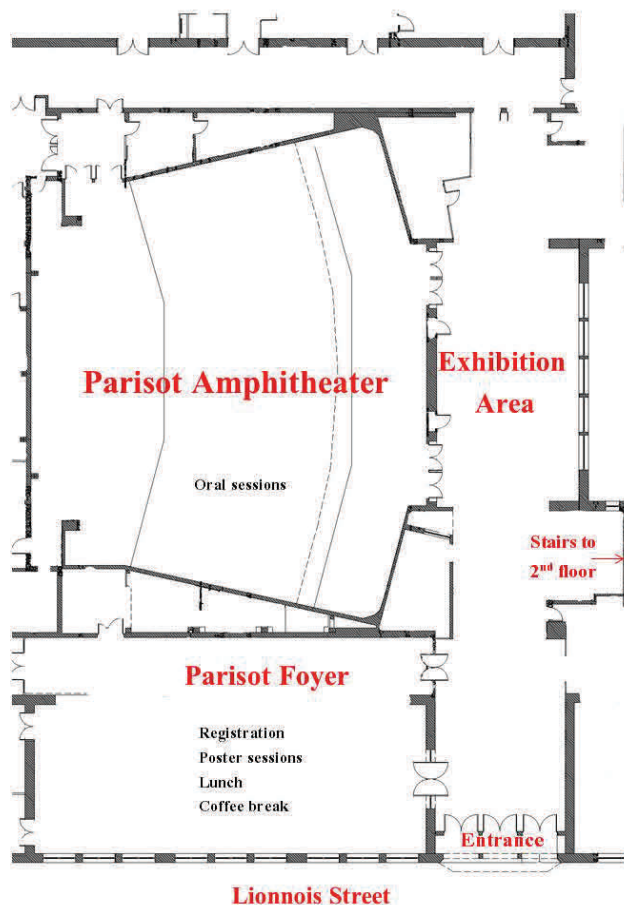
**Kinetic modelling of pyrolysis reactions**, chaired by Perrine Pepiot, [pp427@cornell.edu](mailto:pp427@cornell.edu)

**ESCAPE: AMDIS and Excel, a powerful combination in the development of an Expert System for Interpreting Py-GC/MS Data**, chaired by Henk van Keulen and by Michael Schilling: [h.van.keulen@cultureelerfgoed.nl](mailto:h.van.keulen@cultureelerfgoed.nl) / [MSchilling@getty.edu](mailto:MSchilling@getty.edu)

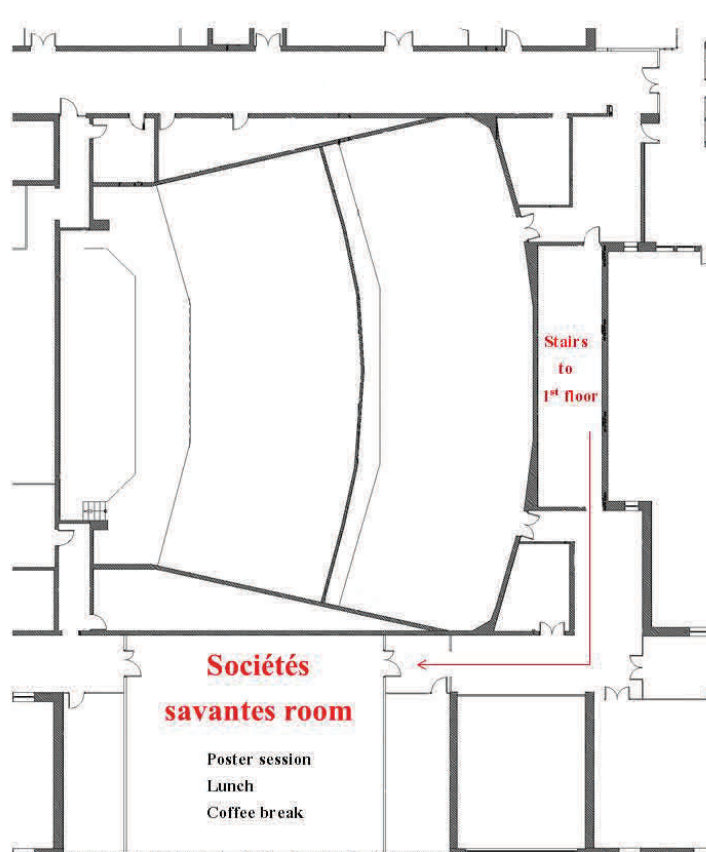
**Analytical pyrolysis of polymers**, chaired by Clemens Schwarzingger, [clemens.schwarzingger@jku.at](mailto:clemens.schwarzingger@jku.at)

## FLOOR PLAN

1<sup>st</sup> floor:



2<sup>nd</sup> floor:



The rooms for these specialist workshops will be indicated at the conference venue.

# PROGRAM

|       | Sunday 8 May 2016  | Monday 9 May 2016   | Tuesday 10 May 2016  | Wednesday 11 May 2016   | Thursday 12 May 2016  | Friday 13 May 2016 |
|-------|--|---|--|---|---|--------------------|
| 08h30 |  |   |  |   |   |                    |
| 09h00 |  | Registration  | Session 4: Biomass / Kinetics                                    | Session 7: Wastes / Reactors  | Session 11: Biomass / Reactors  |                    |
| 09h15 |  | Session 1: Biomass / Catalysis  | Coffee breaks, posters & exhibition                              | Coffee breaks, posters & exhibition   | Session 12: Hydrocarbons / Kinetics                                       | Technical Tours    |
| 09h45 |  |   |  |   |   |                    |
| 10h00 |  |   | Session 5: Organic Geochemistry                                  | Session 8: Bio-oil  |   |                    |
| 10h15 |  |   | Lunch, posters & exhibition                                      | Lunch, posters & exhibition // specialists workshops  | Session 13: Biomass / Slow Pyrolysis                                      |                    |
| 10h30 |  |   |  |   |   |                    |
| 10h45 |  | Session 2: Instrumentation  |  |   | Session 14: Biomass / Catalysis   |                    |
| 11h00 |  |   |  |   |   |                    |
| 11h15 |  |   |  |   |   |                    |
| 11h30 |  |   |  |   |   |                    |
| 11h45 |  |   |  |   |   |                    |
| 12h00 |  |   |  |   |   |                    |
| 12h15 |  |   |  |   |   |                    |
| 12h30 |  |   |  |   |   |                    |
| 12h45 |  |   |  |   |   |                    |
| 13h00 |  |   |  |   |   |                    |
| 14h00 |  |   |  |   |   |                    |
| 14h30 |  |   |  |   |   |                    |
| 14h45 |  |   |  |   |   |                    |
| 15h00 |  | Session 3: Fossil Fuels   | Session 6: Analytical pyrolysis                                  | Session 9: Biomass / fast pyrolysis   |   |                    |
| 15h15 |  |   |  | coffee breaks   |   |                    |
| 15h45 |  |   |  |   |   |                    |
| 16h00 |  |   |  | Session 10: Organic Geochemistry  |   |                    |
| 16h30 |  |   |  |   |   |                    |
| 17h00 | Registration & Welcome drink at the Musée Lorrain - 64, Grande Rue - 54000 Nancy |   |  |   |   |                    |
| 18h00 |  |   |  |   |   |                    |
| 18h30 |  |   |  |   |   |                    |
| 19h00 |  | Soiree to Honour Prof. Michael J. Antal Jr. at the Fine Arts Museum - Place Stanislas - 54000 Nancy |  | Visit of Nancy - meeting point in front of the Tourism Office - Place Stanislas - 54000 Nancy |   |                    |
| 19h30 |  |   |  |   |   |                    |
| 20h00 |  |   |  |   |   |                    |
| 21h00 |  |   |  |   |   |                    |
| 22h00 |  |   | Evening at the Opéra de Lorraine - Place Stanislas - 54000 Nancy |   | Gala Dinner - City Hall of Nancy - entrance Place Stanislas - 54000 Nancy |                    |
| 23h00 |  |   |  |   |   |                    |



## Monday 9 May 2016

08h00-08h45 Registration at the Faculté de Pharmacie - 18 rue Lionnois - 54000 Nancy  
08h45-09h15 Welcome by the Université de Lorraine's representatives and by Anthony Dufour, chairman of PYRO2016

### Session 1 Biomass / Catalysis

**Chairs:** Briens Cédric, Meier Dietrich

**9:15-9:45 KEYNOTE: BIOMASS PYROLYSIS VAPOR AS AN INTERMEDIATE TO FUELS AND CHEMICALS**

Mark Nimlos, National Renewable Energy Laboratory (United States)

**9:45-10:00 INTEGRATED CATALYTIC PYROLYSIS: TOWARDS RENEWABLE BUILDING BLOCKS FOR THE CHEMICAL INDUSTRY**

Andre Heeres, CSO BioBTX (Netherlands)

**10:00-10:15 PRODUCTION OF RENEWABLE AROMATIC COMPOUNDS BY CATALYTIC FAST PYROLYSIS OF LIGNOCELLULOSIC BIOMASS WITH CE-ZSM-5 AND V-ZSM-5 CATALYSTS**

Scott Banks, Bioenergy Research Group (United Kingdom)

**10:15-10:30 ACHIEVEMENTS AND CHALLENGES IN CATALYTIC FAST PYROLYSIS OF WOODY BIOMASS**

Güray Yildiz, Department of Biosystems Engineering, Ghent University (Belgium)

10:30-11:30 Coffee breaks, exhibition and posters

### Session 2 Instrumentation

**Chairs:** Ohtani Hajime, Varhegyi Gabor

**11:30-11:45 DEVELOPMENT OF TANDEM MICRO-REACTOR GC/MS SYSTEM WITH PRESSURE CONTROL MODULE SUITABLE FOR MEDIUM PRESSURE CATALYTIC REACTIONS**

Michael Soll, Frontier Laboratories Europe (Germany)

**11:45-12:00 INVESTIGATION OF EPOXY RESINS WITH DIFFERENT ANALYTICAL PYROLYSIS SYSTEMS**

Clemens Schwarzingler, Institute for Chemical Technology of Organic Materials, Johannes Kepler University (Austria)

**12:00-12:15 CHARACTERIZATION OF CRUDE OILS AND ASPHALTENES BY PYROLYSIS GC/MS AND THERMAL ANALYSIS COUPLED TO PHOTO IONIZATION MASS SPECTROMETRY**

Thorsten Streibel, Helmholtz Zentrum München (Germany), University of Rostock (Germany)

**12:15-12:30 PYROLYSIS STUDY OF PINE WOOD USING THERMOGRAVIMETRY /SYNCHROTRON VUV PHOTOIONIZATION MASS SPECTROMETRY**

Zhongyue Zhou, Shanghai Jiao Tong University [Shanghai] (China)

**12:30-12:45 KINETIC OF POLYSTYRENE PYROLYSIS IN MICROWAVE TGA**

Jamal Chaouki, Polytechnique Montréal (Canada)

**12:45-13:00 MODELING PHYSICAL PHENOMENA DURING FAST PYROLYSIS OF BIOMASS IN A HEATED FOIL REACTOR**

Konstantinos Anastasakis, TU Delft (Netherlands)

13:00-14:30 Lunch, exhibition and posters

### Session 3 Fossil Fuels

**Chairs:** Snape Colin, Michels Raymond

**14:30-15:00 KEYNOTE: SOME STEPS IN THE DEVELOPMENT OF COKE MANUFACTURE IN EUROPE**

Daniel Isler, Centre de Pyrolyse de Marienau (France)

**15:00-15:15 AUTHENTICATION AND QUALITY CONTROL OF COAL FOR COKE MAKING IN STEEL PRODUCTION BY MEANS OF PYROLYSIS ? GAS CHROMATOGRAPHY/MASS SPECTROMETRY**

Andreas Klingberg, Lablicate UG (Germany)

**15:15-15:45 KEYNOTE: KEYS TO COMMERCIALY SUCCESSFUL COAL PYROLYSIS FOR PRODUCTION OF COAL TAR**

Guangwen Xu, State Key Laboratory of Multi-phase Complex System, Institute of Process Engineering, Chinese Academy of Sciences (China)

**15:45-16:00 PYROLYSIS-DERIVED GAS STREAMS AS ALTERNATIVE FUELS FOR THE FUTURE ENERGY SECTOR**

Michel Moliere, Laboratoire d'Études et de Recherches sur les Matériaux, les Procédés et les Surfaces (France)

### Special session: Soiree to Honour Prof. Michael J. Antal Jr. at the Fine Arts Museum-Place Stanislas-54000 Nancy

**Chairs:** Lédé Jacques

17:00-18:00 Visit of the Fine Arts Museum

**18:00-18:30 KEYNOTE: ANALYTICAL PYROLYSIS AS A TOOL FOR THE CHARACTERISATION OF ORGANIC MATERIALS IN CULTURAL HERITAGE**

Ilaria Bonaduce, Dipartimento di Chimica e Chimica Industriale Università di Pisa (Italy)

**18:30-18:40 Introduction : In remembrance of Prof. Michael J. ANTAL**

Jacques Lédé, Laboratoire Réactions et Génie des Procédés, Nancy (France)

**18:40-19:00 TOWARDS A REALISTIC KINETICS IN THE NON-ISOTHERMAL STUDIES. 30 YEARS OF A US-HUNGARIAN COOPERATION IN BIOMASS RESEARCH**

Gabor Varhegyi, Institute of Materials and Environmental Chemistry (Hungary)

**19:00-19:20 TOWARDS THE MAXIMUM THEORETICAL YIELDS OF CHARCOAL FROM BIOMASS PYROLYSIS**

Morten Grønli, NTNU - The Norwegian University of Science and Technology - Wang Liang, SINTEF Energy Research (Norway)

## Tuesday 10 May 2016

### Session 4 Biomass / Kinetics

**Chairs:** Pepiot Perrine, Westmoreland Philip

- 8:30-9:00** **KEYNOTE: KINETIC MODELING OF PYROLYSIS REACTIONS: FROM LIGHT GAS TO SOLIDS**  
Tiziano Faravelli, Department of Chemistry, Materials and Chemical Engineering (Italy)
- 9:00-9:15 **EXPERIMENTAL AND KINETIC STUDY ON PYROLYSIS OF WOODY AND NON-WOODY BIOMASSES**  
Paola Giudicianni, Instituto Superior Tecnico [Lisboa] (Portugal)
- 9:15-9:30 **RECENT ADVANCES IN REACTION MECHANISMS AND MULTI-SCALE MODELLING OF BIOMASS PYROLYSIS**  
Andrés Anca-Couce, Graz University of Technology - Institute of Thermal Engineering (Austria)
- 9:30-9:45 **EVOLUTION OF CELLULOSE WITH DIFFERENT CRYSTALLIZATION MORPHOLOGY DURING PYROLYSIS BASED ON IN-SITU DIFFUSE REFLECTANCE FT-IR**  
Erwei Leng, State Key Laboratory of Coal Combustion (China)
- 9:45-10:00 **THE KINETICS OF CELLULOSE GLYCOSIDIC BOND CLEAVAGE**  
Paul Dauenhauer, University of Minnesota - Twin Cities (United States)
- 10:00-10:15 **R-OH HYDROXYL CATALYSIS OF PYROLYSIS REACTIONS**  
Phillip Westmoreland, Department of Chemical and Biomolecular Engineering, North Carolina State University (United States)
- 10:15-11:15 Coffee breaks, exhibition and posters

### Session 5 Organic Geochemistry

**Chairs:** Béhar Françoise, Burklé-Vitzthum Valérie

- 11:15-11:45** **KEYNOTE: GEOCHEMICAL TRANSFORMATION AND TRANSPORT PROCESSES AS REVEALED BY KINETIC DETERMINATIONS AND MOLECULAR INDICATORS**  
Brian Horsfield, GFZ German Research Centre for Geosciences (Germany)
- 11:45-12:00 **THE STUDY OF PETROLEUM GENERATION AND REACTIVITY BY ARTIFICIAL MATURATION: FROM EXPERIMENTATION TO GEOLOGICAL CONDITIONS**  
Raymond Michels, GéoRessources (France)
- 12:00-12:15 **SHORT-CHAIN KETONES IN REACTION NETWORKS OF HYDROUS PYROLYSIS EXPERIMENTS: METASTABLE PRECURSORS OF HYDROCARBON GASES AND NEW BUILDING BLOCKS FOR MATURING KEROGEN**  
Christian Ostertag-Henning, Federal Institute for Geosciences and Natural Resources (Germany)
- 12:15-12:30 **RELEASE OF MOLECULAR HYDROGEN (H<sub>2</sub>) FROM CARBONACEOUS ROCKS DURING LABORATORY PYROLYSIS EXPERIMENTS**  
Xiaoqiang Li, Energy and Mineral Resources Group (EMR), Institute of Geology and Geochemistry of Petroleum and Coal, RWTH Aachen University (Germany)
- 12:30-12:45 **EVALUATION OF SHALE GAS RESOURCES USING A HIGH PRESSURE WATER PYROLYSIS MATURATION METHOD: APPLICATION TO THE UK BOWLAND SHALE**  
Colin Snape, University of Nottingham (United Kingdom)
- 12:45-13:00 **ROLE OF WATER DURING PYROLYSIS OF CRUDE OIL: EVIDENCES FROM SYNTHETIC FLUID INCLUSIONS**  
Jacques Pironon, University of Lorraine / CNRS / CREGU, GeoRessources Laboratory (France)
- 13:00-14:30 Lunch, exhibition and posters

### Session 6 Analytical pyrolysis

**Chairs:** Schwarzingher Clemens, Bonaduce Ilaria

- 14:30-14:45 **DETAILED ANALYSIS OF LESS VOLATILE PRODUCTS FORMED DURING THERMALLY ASSISTED HYDROLYSIS AND METHYLATION OF POLYMER SAMPLES**  
Hajime Ohtani, Nagoya Institute of Technology (Japan)
- 14:45-15:00 **DIRECT ANALYSIS OF RESIDUAL CHROMOPHORES ON PULP FIBRES USING PY-GC/MS**  
Bruce Sithole, Council for Scientific and Industrial Research (South Africa)
- 15:00-15:15 **PYROLYSIS/GC-MS PROFILING AS A FAST PROCEDURE TO IDENTIFY THE INFLUENCE OF EXCESS CARBON AND LIMITED NITROGEN ON POLYHYDROXYALKANOATE MONOMER BIOSYNTHESIS BY *Bacillus thuringiensis***  
Sarisha Singh, University of KwaZulu-Natal (South Africa)
- 15:15-15:30 **VALUE-ADDED NITROGENOUS CHEMICALS EVOLUTION FROM THE PYROLYSIS OF CHITIN AND CHITOSAN**  
Chao Liu, Key Laboratory of Energy Thermal Conversion and Control of Ministry of Education, Southeast University (China)
- 15:30-15:45 **IMPROVEMENT OF AROMATICS COMPOUNDS PRODUCTION FROM PYROLYSIS OF SCRAPS TYRES RUBBER USING HETEROPOLYACIDS BASED CATALYSTS**  
Claudia Tavera, Universidad Industrial de Santander [Bucaramanga] (Colombia), Unité de Catalyse et de Chimie du Solide (France)
- 15:45-16:00 **PYROLYSIS OF TIRE TRACES TO HELP RECONSTRUCT TRAFFIC ACCIDENTS: STUDY OF THE VARIATION OF TIRE CHEMICAL PROFILES**  
Line Gueissaz, University of Lausanne - Ecole des Sciences Criminelles (Switzerland)
- 16:00-16:15 **BENEFITS OF THE USE OF PY-GCxGC/MS COMPARED TO PY-GC/MS: AN ILLUSTRATION THROUGH TWO EXAMPLES TAKEN FROM CULTURAL HERITAGE STUDIES**  
Michel Sablier, Centre de recherche sur la Conservation USR 3224 du CNRS, Muséum National d'Histoire Naturelle (France)
- 16:15-16:30 **AMDIS & EXCEL: A POWERFUL COMBINATION FOR EVALUATING PY-GC/MS RESULTS**  
Michael Schilling, Getty Conservation Institute (United States)

16:30-18:30 Posters sessions & Refreshments

**16:30-18:30 Specialists workshops (optional)**

**Evening at the Opéra de Lorraine - Place Stanislas - 54000 Nancy**

19:30 Meeting point at the Opéra de Lorraine Entrance

## Wednesday 11 May 2016

|   |  |
|---|--|
| <b>Session 7</b>  | <b>Waste / Reactors</b>  |
| <b>Chairs:</b>  | <b>Wu Chunfei, Hornung Andreas</b>   |
| 08:30-09:00   | <b>KEYNOTE: CHEMICAL PROCESSING FOR FEEDSTOCK RECYCLING OF WASTE PLASTICS</b><br>Toshiaki Yoshioka, Graduate school of Environmental Studies, Tohoku University (Japan)  |
| 9:00-9:15   | <b>CO-PRODUCTION OF HYDROGEN AND CARBON NANOTUBES FROM CATALYTIC PYROLYSIS OF WASTE PLASTICS ON NI-FE BIMETALLIC CATALYST</b><br>Dingding Yao, Huazhong University of Science and Technology (China),  |
| 9:15-9:30   | <b>PYROLYSIS OF MULTICOMPONENT PLASTIC WASTE DERIVED FROM END-OF-LIFE VEHICLES</b><br>János Bozi, Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences (Hungary),   |
| 9:30-9:45   | <b>PYROLYSIS - DECENTRALIZED RECOVERY OF HIGH-TECH METALS</b><br>Peter Hense, Fraunhofer Institute for Environmental, Safety, and Energy Technology UMSICHT, Institute Branch Sulzbach-Rosenberg (Germany)   |
| 9:45-10:00  | <b>DISINTEGRATION OF METAL-RICH COMPOSITE FRACTIONS FROM WEEE THROUGH PYROLYSIS</b><br>Peter Quicker, Unit of Technology of Fuels (RWTH Aachen University) (Germany)   |
| 10:00-10:15   | <b>CO-PYROLYSIS OF MUNICIPAL PLASTIC WASTE AND DIFFERENT HYDROCARBONS: REDUCTION OF CONTAMINANTS</b><br>Norbert Miskolczi, MOL Department of Hydrocarbon and Coal Processing, University of Pannonia (Hungary),  |
| 10:15-11:15   | Coffee breaks, exhibition and posters  |
| <b>Session 8</b>  | <b>Bio-oil</b>   |
| <b>Chairs:</b>  | <b>Boateng Akwasi, Nowakowski Daniel</b>   |
| 11:15-11:45   | <b>KEYNOTE: SUPPORTING THE INDUSTRY IN SCALING UP BIOMASS FAST PYROLYSIS TECHNOLOGY BY BUILDING ON PIONEERING WORK</b><br>Yrjö Solantausta, VTT (Finland)  |
| 11:45-12:00   | <b>FRACTIONATION AND ANALYSIS OF BIOMASS FAST PYROLYSIS OILS BY LIQUID CHROMATOGRAPHY</b><br>Nadege Charon, IFP Energies Nouvelles (France)  |
| 12:00-12:15   | <b>HOT GAS FILTRATION OF FLASH PYROLYSIS VAPOURS : A FIRST STEP FOR BIO-OIL UPGRADING</b><br>Miguel Ruiz Bailon, UR BioWooEB (France)  |
| 12:15-12:30   | <b>WOODY BIOMASS PYROLYSIS AND BIO-OIL UPGRADING BY HYDRODEOXYGENATION (HDO)</b><br>Charles Greenhalf, Institute for Chemicals and Fuels from Alternative Resources (Canada)   |
| 12:30-12:45   | <b>STUDY OF THE REACTIVITY OF PLATFORM MOLECULES IN AQUEOUS SOLUTION AND IN THE PYROLYSIS OIL DURING HYDROTREATMENT</b><br>Chiara Boscagli, Karlsruhe Institute of Technology, Institute of Catalysis Research and Technology (Germany)  |
| 12:45-13:00   | <b>EUROPEAN STANDARDIZATION OF FAST PYROLYSIS BIO-OILS: HEAT AND GREEN ELECTRICITY PRODUCTION</b><br>Alain Quignard, IFPEN (France)  |
| 13:00-14:30   | Lunch, exhibition and posters  |
| <b>Session 9</b>  | <b>Biomass / Fast pyrolysis</b>  |
| <b>Chairs:</b>  | <b>Prins Wolter, Mauviel Guillain</b>  |
| 14:30-14:45   | <b>PREDICTIVE MODELING OF SWITCHGRASS THERMOCHEMICAL PRODUCTS FROM BIOMASS COMPOSITIONAL FEATURES</b><br>Christopher Waters, University of Oklahoma (United States)  |
| 14:45-15:00   | <b>HEAT TRANSFER BETWEEN SOLID PARTICLES: APPLICATION TO FAST PYROLYSIS</b><br>Axel Funke, Karlsruhe Institute of Technology (Germany)   |
| 15:00-15:15   | <b>CHARACTERIZING THE ROLE OF INTRA-PARTICLE PROCESSES DURING BIOMASS THERMOCHEMICAL CONVERSION USING HIGH PERFORMANCE COMPUTING</b><br>Perrine Pepiot, Cornell University (United States)   |
| 15:15-15:30   | <b>FLASH PYROLYSIS CONVERSION TIMES AND KINETICS OF TORREFIED BIOMASS</b><br>Alexander Louwes, Thermal Engineering - University of Twente (Netherlands)  |
| 15:30-15:45   | <b>CHARACTERIZATION OF CHARS FROM FAST PYROLYSIS OF BIOMASS IN A FLUIDIZED BED REACTOR</b><br>Mathieu Morin, Laboratoire de génie chimique (France)  |
| 15:45-16:00   | <b>WOODY BIOMASS FAST PYROLYSIS IN A DROP TUBE REACTOR</b><br>Marine Peyrot, CEA/LITEN (France)  |
| 16:00-16:30   | Coffee breaks, exhibition and posters  |
| <b>Session 10</b>   | <b>Organic Geochemistry</b>  |
| <b>Chairs:</b>  | <b>Biache Coralie, Gonzalez-Pérez José</b>   |
| 16:30-16:45   | <b>VARIATION IN THE STABLE CARBONACEOUS FRACTION (BCHYPY) WITHIN BIOCHARS PRODUCED AT DIFFERENT TEMPERATURES</b><br>Colin Snape, University of Nottingham (United Kingdom)   |
| 16:45-17:00   | <b>EXPLORING THE MOLECULAR COMPOSITION OF TERRESTRIAL ORGANIC CARBON USING TETRAMETHYLAMMONIUM HYDROXIDE (TMAH) THERMOCHEMOLYSIS</b><br>Geoffrey Abbott, Newcastle University (United Kingdom)   |
| 17:00-17:15   | <b>ASSESSMENT OF THE SPATIO-TIME VARIABILITY OF ORGANIC MATTER IN THE UPSTREAM SECTION OF THE SEINE ESTUARY</b><br>Agnes Lattuati-Derieux, Milieux Environnementaux, Transferts et Interactions dans les hydrosystèmes et les Sols (France)  |
| 17:15-17:30   | <b>PALAEOCLIMATIC CONDITIONS IN CENTRAL IBERIAN PENINSULA IN THE SENONIAN EPOCH (C. 72 MYA) AS INFERRED BY PYROLYSIS COMPOUND SPECIFIC ISOTOPIC ANALYSIS (PY-CSIA) OF THE FOSSIL CONIFER (FRENELOPSIS OLIGOSTOMATA)</b><br>José A. González-Pérez, IRNAS-CSIC (Spain)  |
| 17:30-17:45   | <b>THERMOCHEMOLYSIS FOR THE SIMULTANEOUS ANALYSIS OF THE MAIN BIOMOLECULAR FAMILIES IN SOIL. APPLICATION TO THE MESUREMENT OF THE IMPACT OF INOVATIVE RENEWABLE PRACTICES FOR REFORESTATION IN A CLIMATE CHANGE CONTEXT.</b><br>Laurent Gasset, INSTITUT DE CHIMIE DES MILIEUX ET MATERIAUX DE POITIERS (France) |
| 17:45-18:00   | <b>A FAST AND NEW METHOD TO QUANTIFY PAHS IN CONTAMINATED SOILS BASED ON FLASH-PYROLYSIS COUPLED WITH MOLECULAR ANALYSIS</b><br>Coralie Biache, Laboratoire Interdisciplinaire des Environnements Continentaux (France)  |
| <b>Visit of Nancy - meeting point in front of the Turism Office - Place Stanislas - 54000 Nancy</b> |  |
| 19:00-20:30   | Visit of Nancy Old City with guides (meeting at 18h45 in front of the Turism Office)<br>Free evening   |

## Thursday 12 May 2016

### Session 11 Biomass / Reactors

**Chairs:** Xu Guangwen, Chaouki Jamal

- 8:30-8:45 **PYROLYSIS OF WOOD IN A LARGE-SCALE MECHANICALLY FLUIDIZED REACTOR**  
Cédric Briens, University of Western Ontario (Canada), Clément Villemont, Université de Québec à Trois Rivières (Canada)
- 8:45-9:00 **THERMO-CHEMICAL MODEL OF A SCREW PYROLYSIS REACTOR**  
Marco Tomasi Morgano, Karlsruhe Institute of Technology (Germany)
- 9:00-9:15 **CATALYTIC UPGRADING OF PINE WOOD PYROLYSIS VAPORS IN A DOWNER REACTOR: PRELIMINARY RESULTS WITH ZEOLITE**  
Daniele Castello, Sustainable Process Technology, Faculty of Science and Technology, University of Twente (Netherlands)
- 9:15-9:30 **PYRENA: PYROLYSIS EQUIPMENT FOR NEW APPROACHES IN CIRCULATING FLUIDISED BED CATALYTIC PYROLYSIS FOR BETTER BIO-OIL AS A PRECURSOR FOR FUELS AND CHEMICALS**  
Paul De Wild, Energy research Centre of the Netherlands (Netherlands)
- 9:30-9:45 **DESIGN OF A GAS-SOLID VORTEX REACTOR DEMONSTRATION UNIT FOR THE FAST PYROLYSIS OF LIGNOCELLULOSIC BIOMASS**  
Arturo Gonzalez Quiroga, Laboratory for Chemical Technology, Ghent University (Belgium)
- 9:45-10:00 **THERMO-CATALYTIC REFORMING PROCESS (TCR®): SCALE UP FROM PILOT PLANT TO DEMO-SCALE**  
Johannes Neumann, Fraunhofer UMSICHT (Germany)
- 10:00-10:15 **A FLEXIBLE THREE-STAGE THERMOCHEMICAL CONVERSION PROCESS - TSTC PROCESS**  
Vander Tumiatti, Sea Marconi Technologies (Italy)
- 10:15-11:15 Coffee breaks, exhibition and posters

### Session 12 Hydrocarbons / Kinetics

**Chairs:** Van Geem Kevin, Herbinet Olivier

- 11:15-11:45 **MONTE-CARLO MODELLING OF THERMAL CRACKING OF RESIDUE FRACTIONS**  
Jan Verstraete, IFPEN (France)
- 11:45-12:00 **AN HOMOGENEOUS AND HETEROGENEOUS DETAILED KINETIC MODEL OF ALKANE PYROLYSIS FOR SIMULATION OF C/C BRAKE DISKS DENSIFICATION BY CVI PROCESS**  
Cédric Descamps, HERAKLES Ceramics (France)
- 12:00-12:15 **EXPERIMENTAL STUDY OF HYDROCARBON PYROLYSIS IN A REGENERATIVE COOLING SYSTEM OF A COMBUSTOR**  
Lucio Taddeo, Institut National des Sciences Appliquées de Bourges (France)
- 12:15-12:30 **STEAM CRACKING OF BIOMASS-DERIVED C30- NORMAL AND BRANCHED ALKANES: AN EXPERIMENTAL AND FUNDAMENTAL KINETIC MODELING STUDY**  
Ruben De Bruycker, Laboratory for Chemical Technology, Ghent University (Belgium),
- 12:30-12:45 **PYROLYSIS OF DIMETHYL CARBONATE: PAH FORMATION**  
Fausto Viteri, Tecnológica Equinoccial University (Ecuador), Universidad de Zaragoza (Spain)
- 12:45-13:00 **HYDROCARBON AVIATION FUEL PYROLYSIS UNDER DIFFERENT PRESSURES**  
Guozhu Liu, Tianjin University (China)
- 13:00-15:00 Lunch, exhibition and posters sessions

13:00-15:00 **Specialists workshops (optional)**

### Session 13 Biomass / Slow pyrolysis

**Chairs:** Fabbri Daniele, Gronli Morten

- 15:00-15:15 **CONTAMINANT ISSUES IN PRODUCTION OF BIOCHAR**  
Ondřej Mašek, University of Edinburgh (United Kingdom)
- 15:15-15:30 **STUDY ON THE EFFECTS OF USING A CARBON DIOXIDE ATMOSPHERE ON THE PROPERTIES OF VINE SHOOTS-DERIVED BIOCHAR**  
Manuel Azuara, Institute of Nanoscience of Aragón (INA), University of Zaragoza, Spain (Spain)
- 15:30-15:45 **TORREFACTION OF VARIOUS WOODY AND AGRICULTURAL BIOMASSES AND OF THEIR EXTRACTED CELLULOSE, HEMICELLULOSE AND LIGNIN THROUGH TGA-GCMS**  
María González Martínez, CEA Grenoble (France)
- 15:45-16:00 **COKE/CHAR AND OTHER PRODUCTS FORMATION BEHAVIORS IN PYROLYSIS OF TEN SOFTWOOD/HARDWOOD SPECIES**  
Mohammed Yussuf Mohd Asmadi, Kyoto University (Japan), Universiti Teknologi Malaysia (Malaysia)
- 16:00-16:15 **EFFECT OF TORREFACTION ON PROPERTIES AND PYROLYSIS BEHAVIORS OF WOOD AND BARK**  
Eszter Barta-Rajnai, Institute of Materials and Environmental Chemistry (Hungary)
- 16:15-16:30 **FAST TORREFACTION VERSUS CLASSIC TORREFACTION: COMPARISON OF THE PRODUCTS ON A PILOT SCALE CONTINUOUS REACTOR**  
Jean-Michel Commandre, CIRAD (France)
- 16:30-17:00 Coffee breaks, exhibition and posters

### Session 14 Biomass / Catalysis

**Chairs:** Quignard Alain

- 17:00-17:15 **INVESTIGATION ON METAL MODIFIED ZEOLITES: CATALYST SCREENING FOR PYROLYSIS OF PINE WOOD AND SUNFLOWER STALK**  
Gozde Duman, Ege University (Turkey)
- 17:15-17:30 **MICROPYROLYSIS COUPLED TO GC/MS AS A SET-UP TO INVESTIGATE FAST PYROLYSIS BEHAVIOR OF BIOMASS CONSTITUENTS AND THE EFFECT OF INTRINSIC CATALYSTS**  
Jop Vercruysse, Ghent University (Belgium)
- 17:30-17:45 **UNDERSTANDING THE EFFECTS OF CATALYST PROPERTIES ON BIOMASS PYROLYSIS OVER ZSM-5 TYPE ZEOLITES: COMPARISON OF MICRO AND PROCESS DEVELOPMENT SCALES**  
Charles Mullen, ARS-USDA Eastern Regional Research Center (United States)
- 17:45-18:00 **FAST PYROLYSIS OF BIOMASS AND IN-LINE STEAM REFORMING PROCESS FOR HYDROGEN PRODUCTION**  
Aitor Arregi, University of the Basque Country (Spain)
- 18:00-18:15 **THE MECHANISM OF CATALYTIC FAST PYROLYSIS**  
Victoria Custodis, Institute for Chemical and Bioengineering, ETH Zurich (Switzerland), Paul Scherrer Institut (Switzerland)
- 18:15 Farewell talk, by Anthony Dufour, chairman of PYRO2016

Gala Dinner - City Hall of Nancy - entrance Place Stanislas - 54000 Nancy

20:00 Gala Dinner at the City Hall of Nancy

## POSTER SESSION 1: Monday 9 May & Tuesday 10 May

### BIOMASS / FAST PYROLYSIS

- P1001 POTENTIAL OF VIRGINIA MALLOW AS AN ENERGY FEEDSTOCK FOR FAST PYROLYSIS PROCESSING**  
Banks Scott (1), Nowakowski Daniel (1), Snieg Malwina (2), Stolarski Mariusz (2), Bridgwater Tony  
1 - Bioenergy Research Group (United Kingdom), 2 - Department of Plant Breeding and Seed Production (Poland)
- P1002 CARBON-13 ISOTOPE SPECTROMETRY FOR FAST PYROLYSIS CHEMISTRY**  
Carrier Marion (1), Bridgwater Anthony (1)  
1 - European Bioenergy Research Institute, Aston University (United Kingdom)
- P1003 FAST PYROLYSIS OF DIFFERENTLY-TREATED OKRA (ABELMOSCHUS ESCULENTUS) STALKS BY PY-GC/MSD**  
Ghalibaf Maryam (1)  
1 - University of Jyväskylä (Finland)
- P1004 INHIBITION OF CHAR FORMATION FROM CELLULOSE IN FAST PYROLYSIS WITH AROMATIC SUBSTANCES**  
Kawamoto Haruo (1), Shoji Taeko, Saka Shiro  
1 - Kyoto University (Japan)
- P1005 BIOFUELS DEVELOPMENT BY FAST PYROLYSIS PROCESS FROM BIOMASS IN KOREA**  
Kim Jae-Kon (1), Park Jo Yong (1), Park Cheon-Kyu (1), Ha Jong Han (1), Oh Chang Ho (2)  
1 - Petroleum Quality & Distribution Authority(K-Petro) (South Korea), 2 - DAEKYUNG ESCO (South Korea)
- P1006 AMMONIA AS CARRIER GAS IN FLUIDIZED-BED FAST PYROLYSIS AND ITS EFFECTS ON BIO-OIL YIELD AND PROPERTIES**  
Liu Yunquan (1), Zhu Shenjia (1), Wang Duo (1)  
1 - Xiamen University (China)
- P1007 FAST PYROLYSIS PROCESSING OF MISCANTHUS X GIGANTEUS USED IN PHYTOREMEDIATION FOR PRODUCTION OF FUELS AND CHEMICALS**  
Nowakowski Daniel Jozef (1), Banks Scott, Mos Michal, Bridgwater Tony  
1 - European Bioenergy Research Institute, Aston University (United Kingdom)
- P1008 FAST PYROLYSIS OF BAGASSE AND GROUNDNUT BRIQUETTES USING PY-GC/MS AND PY-FT-IR**  
Ojha Deepak (1), Ravikrishnan Vinu  
1 - PhD Candidate (India)
- P1009 MIGRATION OF AAEMS AND CHLORIDE DURING BIOMASS PYROLYSIS IN AN ENTRAINED FLOW REACTOR**  
Yin Xin (1)  
1 - Ping LU (China)
- P1010 IMPACT OF HOT WATER PRETREATMENT ON THE PYROLYSIS OF BIRCH AND SPRUCE WOOD**  
Zhurinsh Aivars (1), Dobele Galina (2), Jurkjane Vilhelmine (2), Meile Kristine (2), Plavniece Ance (2)  
1 - Latvian State Institute of Wood Chemistry (Latvia), 2 - Latvian State Institute of Wood Chemistry (Latvia)
- ### BIOMASS /KINETICS
- P1011 KINETIC MODEL OF THE PYROLYSIS OF BIOMASS COAL BRIQUETTES**  
Barriocanal Carmen (1), Florentino Laura, Montiano Maria, Diaz-Faes Elvira  
1 - Instituto Nacional del Carbon - Consejo Superior de Investigaciones Cientificas (Spain)
- P1012 COMBUSTION CHARACTERISTICS AND KINETIC ANALYSIS OF HYDROTHERMALLY DERIVED AND PYROLYTIC CARBON MATERIALS**  
Bin Li (1), Min Zhao (1), Nan Deng (1), Ke Zhang (1)  
1 - Zhengzhou Tobacco Research Institute of CNTC (China)
- P1013 KINETIC MODELS FOR THE PYROLYSIS OF BIOMASS FUEL IN A DROP TUBE FURNACE.**  
Brilhac Jean-François (1)  
1 - Laboratoire Gestion des Risques et Environnement, Université de Haute Alsace (France)
- P1014 SIGNIFICANCE OF THE ACTIVATION ENERGY AND ITS IMPLICATIONS FOR BIOMASS PYROLYSIS KINETICS**  
Carrier Marion (1), Auret Lidia (2), Bridgwater Anthony (1), Knoetze Hansie (2)  
1 - European Bioenergy Research Institute, Aston University (United Kingdom), 2 - Université de Stellenbosch (South Africa)
- P1015 BIOMASS PYROLYTIC POLYGENERATION: EVOLUTION OF BAMBOO CHAR STRUCTURE**  
Chen Yingquan (1), Yang Haiping (2), Chen Hanping (2)  
1 - State Key Laboratory of Coal Combustion Huazhong University of Science and Technology (China), 2 - State Key Laboratory of Coal Combustion Huazhong University of Science and Technology (China)
- P1016 GAS-PHASE REACTION MECHANISMS OF LEVOGLUCOSAN AS THE INTERMEDIATE OF BIOMASS GASIFICATION**  
Fukutome Asuka, Kawamoto Haruo (1), Saka Shiro  
1 - Kyoto University (Japan)
- P1017 PYROLYSIS AND COMBUSTION KINETIC STUDY OF HYDROTHERMALLY CARBONIZED GLUCOSE-GRAPHENE OXIDE HYBRIDS**  
Ke Zhang (1), Bin Li (1), Min Zhao (1), Jiaxiao Cai (1)  
1 - Zhengzhou Tobacco Research Institute of CNTC (China)
- P1018 FIRST PRINCIPLES BASED KINETIC MODEL FOR BIOMASS FAST PYROLYSIS: CYCLIC MODEL COMPOUNDS**  
Khandavilli Muralikrishna (1)  
1 - Ghent University (Belgium)
- P1019 EXPERIMENTAL TESTS AND NUMERICAL MODELING OF BIOMASS PYROLYSIS IN A VERTICAL- TUBE REACTOR**  
Lorreyte Clarisse (1), Randrianalisoa Jaona (1), Pron Herve (1), Haussener Sophia (2)  
1 - Groupe en Recherche en Sciences pour l'Ingénieur (France), 2 - Laboratory of renewable energy science and engineering (Switzerland)
- P1020 EVALUATION OF THE BEHAVIOR OF COLOMBIAN BIOMASS UNDER CONDITIONS OF PYROLYSIS AND GASIFICATION OF BIOCHAR: A KINETIC APPROACH**  
Marrugo Escobar Gloria, Chejne Farid (1), Valdes Carlos (1)  
1 - Universidad Nacional de Colombia (COLOMBIA) (Colombia)
- P1021 LEVOGLUCOSAN FORMATION FROM CELLULOSE: PYROLYSIS MECHANISM IN THE PRESENCE OF RADICAL-FORMING SPECIES**  
Mattonai Marco, Ribechini Erika (1), Colombini Maria Perla  
1 - Dipartimento di chimica e chimica industriale, Università di Pisa (Italy)
- P1022 DENSIFIED MICROALGAE AS A PRECURSOR FOR SYN-GAS PRODUCTION**  
Roman Suero Silvia (1), Ledesma Cano Beatriz (1), Alvarez-Murillo Andres (1), Gonzalez Gonzalez Juan Félix (1)  
1 - Universidad de Extremadura - Uex (SPAIN) (Spain)

## POSTER SESSION 1: Monday 9 May & Tuesday 10 May

|                                 |   |
|---------------------------------|---|
| <b>P1023</b>                    | <b>COMPARATIVE KINEMATIC STUDY OF PRE AND NON-PRE-TREATED VINEYARD WOODY RESIDUES</b><br>Rosas Mayoral J. Guillermo (1), Suarez Sergio (1), Gomez Natalia (1), Martinez Olegario (1), Cara Jorge (1), Sanchez Marta (1)<br>1 - Institute of Natural Resources, Chemical and Environmental Engineering Group, University of Leon (Spain)   |
| <b>P1024</b>                    | <b>EXPERIMENTAL STUDY ON THE INITIAL THERMAL DECOMPOSITION OF RESORCINOL</b><br>Vargas Diana (1) (2), Toraman Hilal (2), Carstensen Hans-Heinrich (2), Almeida Streitwieser Daniela (1), Van Geem Kevin (2), Marin Guy (2)<br>1 - Departamento de Ingenieria Quimica, Universidad San Francisco de Quito (Ecuador), 2 - Laboratory for Chemical Technology, Ghent University (Belgium)  |
| <b>P1025</b>                    | <b>ENHANCED THERMAL SEGREGATION OF LIGNIN AND CELLULOSE DECOMPOSITION PRODUCTS: AN ANALYTICAL STUDY OF TIME AND TEMPERATURE EFFECTS</b><br>Waters Christopher (1), Crossley Steven (1), Resasco Daniel (1), Mallinson Richard (1), Lobban Lance (1)<br>1 - University of Oklahoma (United States)   |
| <b>P1026</b>                    | <b>UPGRADING OF RICE STRAW AND LEUCAENA BY DEGRADATIVE SOLVENT EXTRACTION USING 1-METHYLNAPHTHALENE AND KEROSENE AT 350 OC</b><br>Worasuwanarak Nakorn (1)<br>1 - King Mongkut's University of Technology Thonburi (Thailand)   |
| <b>P1027</b>                    | <b>CELLULOSE, XYLAN AND LIGNIN INTERACTIONS DURING PYROLYSIS OF LIGNOCELLULOSIC BIOMASS</b><br>Yu Jie (1), Paterson Nigel (1), Millan Marcos (1)<br>1 - Department of Chemical engineering [Imperial College London] (United Kingdom)   |
| <b>BIOMASS / SLOW PYROLYSIS</b> |   |
| <b>P1028</b>                    | <b>SLOW PYROLYSIS OF CHILEAN OAK: CHARACTERIZATION OF VOLATILE EMISSIONS AND BIO-OIL BY GC/MS</b><br>Alejandro Serguei (1), Cerda Cristian, Montecinos Adan<br>1 - Wood Engineering Department, Faculty of Engineering, University of Bio-Bio (Chile)   |
| <b>P1029</b>                    | <b>CHARACTERIZATION OF THE LIQUID BY-PRODUCTS OBTAINED DURING TORREFACTION OF TYPICAL HUNGARIAN BIOMASS WASTE MATERIALS</b><br>Barta-Rajnai Eszter (1), Sebestyan Zoltan (1), Czegeny Zsuzsanna > (1), Jakab Emma (1)<br>1 - Hungarian Academy of Sciences, Research Centre for Natural Sciences (Hungary)  |
| <b>P1030</b>                    | <b>EVALUATION OF LIGNIN HYDROUS PYROLYSIS RESIDUES TO PRODUCE BIOCOKES AFTER CARBONIZATION</b><br>Castro Diaz Miguel (1), Uguna Clement (2) (1), Stevens Lee (1), Diaz-Faes Elvira (3), Barriocanal Carmen (3), Snape Colin (1)<br>1 - University of Nottingham (United Kingdom), 2 - Centre for Environmental Geochemistry, British Geological Survey (United Kingdom), 3 - Instituto Nacional del Carbon - Consejo Superior de Investigaciones Cientificas (Spain)  |
| <b>P1031</b>                    | <b>THERMOGRAVIMETRIC ANALYSIS, COMPOSITION AND PORE DEVELOPMENT DURING PYROLYSIS OF COCONUT CORE</b><br>Duarte Shirley (1) (2), Lu Pin (1), Rolon Juan (3), Monteiro Gonçalo (4) (1), Perré Patrick (1)<br>1 - Laboratoire de Génie des procédés et matériaux, CentraleSupélec (French Southern and Antarctic Territories), 2 - Faculty of Chemicals Sciences - National University of Asuncion (Paraguay), 3 - Faculty of Engineering, National University of Asuncion (Paraguay), 4 - Faculty of Engineering, University of Porto (Portugal)    |
| <b>P1032</b>                    | <b>PREPARATION OF HIGH SURFACE AREA-ACTIVATED CHAR FROM BIO-CHAR BY KOH ACTIVATION AND ITS APPLICATION IN PHENOL ADSORPTION</b><br>Hwang Hyewon (1), Sahin Olga (2), Choi Joon Weon (3)<br>1 - Department of Forest Sciences, CALS, Seoul National University (SNU) (South Korea), 2 - Institut fuer Katalyseforschung und -technologie (IKFT), Karlsruhe Institute of Technology (Germany), 3 - Graduate School of International Agricultural Technology, Institute of Green-Bio Science and Technology, Seoul National University (South Korea) |
| <b>P1033</b>                    | <b>TORREFACTION AS A PRE-TREATMENT FOR FLASH PYROLYSIS: A CHAIN ANALYSIS</b><br>Louwes Alexander, Bramer Eddy (1), Brem Gerrit (1)<br>1 - Thermal Engineering - University of Twente (Netherlands)  |
| <b>P1034</b>                    | <b>EXOTHERMAL PHENOMENA DURING TORREFACTION OF WOOD CHIPS</b><br>Melkior Thierry (1)<br>1 - Commissariat à l'Energie Atomique et aux Energies Alternatives (France)   |
| <b>P1035</b>                    | <b>OPTIMISATION OF TORREFACTION AND PYROLYSIS OF INVASIVE ALIEN PLANTS FOR ENERGY APPLICATIONS</b><br>Mundike Jhonnah (1), Collard Francois-Xavier, Gorgens Johann<br>1 - Stellenbosch University (South Africa)  |
| <b>P1036</b>                    | <b>CHARACTERIZATION OF ACTIVATED CARBONS OBTAINED FROM DIFFERENT BAMBOO RESIDUE CARBONIZATES</b><br>Ngamyng Chatri (1), Rodriguez Correa Catalina (1), Kruse Andrea (1)<br>1 - University of Hohenheim (Germany)  |
| <b>P1037</b>                    | <b>ASSESSMENT OF THE TECHNICAL FEASIBILITY OF ACTIVATED CARBON PRODUCTION FROM HYDROCHAR</b><br>Rodriguez Correa Catalina (1), Suwelack Kay (2) (1), Kruse Andrea (1)<br>1 - University of Hohenheim (Germany), 2 - Fraunhofer Institute for Technological Trend Analysis (Germany)   |
| <b>P1038</b>                    | <b>TGA/DSC STUDY OF ENERGY FLOWS FROM BIOMASS SLOW PYROLYSIS</b><br>Roy-Poirier Audrey (1), Mignard Dimitri (2), Masek Ondrej (2), Pritchard Colin (2)<br>1 - National Research Council Canada (Canada), 2 - University of Edinburgh (United Kingdom)   |
| <b>P1039</b>                    | <b>IMPROVED CHARCOAL YIELD FROM PYROLYSIS OF BIOMASS FOR HEATING FUEL</b><br>Russell Scott (1), Snape Colin (1), Langston Paul (1), Turrion Juan (2)<br>1 - University of Nottingham (United Kingdom), 2 - CPL Industries (United Kingdom)  |
| <b>P1040</b>                    | <b>FINITE ELEMENT AND SPACE-TIME INTEGRAL MODELS FOR BIOMASS TORREFACTION</b><br>Shi Xiaogang (1), Ronsse Frederik (1), Pieters Jan (1)<br>1 - Ghent University (Belgium)   |
| <b>P1041</b>                    | <b>HYDROTHERMAL CARBONIZATION OF BIOMASS CONSTITUENTS</b><br>Sinag Ali (1), Donar Yusuf (1)<br>1 - Ankara University (Turkey)   |
| <b>P1042</b>                    | <b>BIOCHAR FROM MEDIUM PYROLYSIS TEMPERATURES FOR SMELTING PLANT APPLICATIONS</b><br>Surup Gerrit (1), Nielsen Henrik (1), Vehus Tore (1), Eidem Per (2)<br>1 - University of Agder (Norway), 2 - Eramet Norway AS (Norway)   |
| <b>P1043</b>                    | <b>EFFECT OF OXYGEN CONCENTRATIONS ON THE TORREFACTION OF BIOMASS AT TEMPERATURE BELOW 300OC</b><br>Worasuwanarak Nakorn (1)<br>1 - King Mongkut's University of Technology Thonburi (Thailand)   |

**POSTER SESSION 1: Monday 9 May & Tuesday 10 May****BIO-OIL**

- P1044 PRODUCTION OF BIO-OILS AND BIO-CHAR THROUGH MICROWAVE ASSISTED PYROLYSIS OF ARUNDO DONAX**  
Bartoli Mattia (1)  
1 - Department of Chemistry "Ugo Schiff", University of Florence (Italy)
- P1045 MILD UPGRADING OF FAST PYROLYSIS OIL TO LOW CORROSIVE AND STORAGE STABLE BIO-OIL**  
Brodin Fredrik (1), Celaya Javier (2), Toven Kai (1)  
1 - Paper and Fibre Research Institute (Norway), 2 - Norwegian University of Science and Technology - NTNU (NORWAY) (Norway)
- P1046 COMPARISON OF CATALYTIC ESTERIFICATION AND VACUUM-ASSISTED DEWATERING OF WOOD-BASED FAST PYROLYSIS OIL AND THEIR APPLICATION IN MARINE MULTI-COMPONENT FUELS**  
Brodin Fredrik (1), Celaya Javier (2), Toven Kai (1)  
1 - Paper and Fibre Research Institute (Norway), 2 - Norwegian University of Science and Technology - NTNU (NORWAY) (Norway)
- P1047 DEOXYGENATION OF USED COOKING OIL AND FATTY ACIDS VIA PYROLYSIS AND CATALYTIC VAPOURS UPGRADING FOR AVIATION BIOFUEL PRODUCTION**  
Buffi Marco (1), Rizzo Andrea Maria (1), Chiaramonti David (2), Prussi Matteo (2)  
1 - Department of Industrial Engineering, University of Florence (Italy), 2 - Renewable Energy Consortium for R&D (Italy)
- P1048 AN INVESTIGATION INTO MULTICOMPONENT FUEL BLENDS USING PYROLYSIS OIL, MARINE FUEL AND ALTERNATIVE BLEND COMPONENTS**  
Chong Katie (1), Bridgwater Tony  
1 - Aston University (United Kingdom)
- P1049 ESTERIFICATION WITH HIGHER ALCOHOLS TO IMPROVE THE QUALITY OF FAST PYROLYSIS CONDENSATES**  
Conrad Stefan (1), Van Loo Tom (1), Schulzke Tim (1), Kaluza Stefan (1)  
1 - Fraunhofer Institute for Environmental, Safety, and Energy Technology UMSICHT (Germany)
- P1050 TOWARDS A BETTER CHARACTERIZATION OF BIOMASS PYROLYSIS BIO-OIL BY ESI-FTICRMS**  
Hertzog Jasmine (1), Carré V. (1), Le Brech Y. (2), Aubriet F. (1)  
1 - Lorraine University, LCP-A2MC, ICPM (France), 2 - Laboratoire Réactions et Génie des Procédés (France)
- P1051 PREDICTING PYROLYSIS OIL COMPOSITION, HHV AND CATALYTIC ACTIVITY USING CUMULATIVE ATOMIC RATIOS FROM PY-GC/MS DATA**  
Merckel Ryan (1), Heydenrych Mike (1)  
1 - Department of Chemical Engineering (South Africa)
- P1052 PREDICTION OF PROPERTIES AND ELEMENTAL COMPOSITION OF BIOMASS PYROLYSIS OILS BY NMR AND PARTIAL LEAST SQUARES ANALYSIS**  
Mullen Charles (1), Strahan Gary (1), Boateng Akwasi (1)  
1 - ARS-USDA Eastern Regional Research Center (United States)
- P1053 UTILIZATION OF PROCUTS FROM THERMO-CATALYTIC REFORMING IN INTERNAL COMBUSTION ENGINES**  
Neumann Johannes (1), Jäger Nils (1), Apfelbacher Andreas (1), Daschner Robert (1), Hornung Andreas (2) (3) (4) (1)  
1 - Fraunhofer-Institute for Environment, Safety, and Energy Technology UMSICHT (Germany), 2 - Università di Bologna (Italy), 3 - University of Birmingham (United Kingdom), 4 - Friedrich-Alexander University Erlangen-Nürnberg (Germany)
- P1054 APPLICATION AND VALORISATION OF THERMO-CATALYTIC REFORMING LIQUIDS**  
Neumann Johannes (1), Schmitt Nina (1), Apfelbacher Andreas (1), Daschner Robert (1), Hornung Andreas (2) (3) (4) (1)  
1 - Fraunhofer-Institute for Environment, Safety, and Energy Technology UMSICHT (Germany), 2 - Università di Bologna (Italy), 3 - University of Birmingham (United Kingdom), 4 - Friedrich-Alexander University Erlangen-Nürnberg (Germany)
- P1055 FAST PYROLYSIS BIO-OIL UPGRADING BY CATALYTIC HYDRODEOXYGENATION**  
Nowakowski Daniel Jozef (1), Santosa Miki, Frye John, Zacher Alan, Bridgwater Tony  
1 - European Bioenergy Research Institute, Aston University (United Kingdom)
- P1056 UPGRADING OF BIO-OIL QUALITY VIA HYDRODEOXYGENATIVE PROCESS WITH METAL CATALYST IN A CONTINUOUS FLOW REACTOR**  
Oh Shinyoung (1), Choi In-Gyu, Choi Joon Weon  
1 - Seoul National University (South Korea)
- P1057 STABILITY ASSESSMENT OF FAST PYROLYSIS BIO-OILS: EVALUATION OF MICRO-CARBON RESIDUE INCREASE BASED TEST**  
Pala Mehmet (1), Leijenhorst Evert (2), Yildiz Guray (1), Ronsse Frederik (1), Prins Wolter (1)  
1 - Department of Biosystems Engineering, Ghent University (Belgium), 2 - Biomass Technology Group BV (Netherlands)
- P1058 CHARACTERIZATION OF THE LIQUID PRODUCTS OBTAINED FROM THE FAST PYROLYSIS IN A PILOT BFB PLANT**  
Park Jo Yong (1), Kim Jae-Kon (1), Kim Sin (1), Cheon-Kyu Park (1), Ha Jong Han (1), Oh Chang Ho (2)  
1 - Korea Petroleum Quality & Distribution Authority(K-Petro) (South Korea), 2 - DAEKYUNG ESCO (South Korea)

**ORGANIC GEOCHEMISTRY**

- P1059 MEASUREMENT FOR FIRE DAMAGE LEVEL IN FOLIAR BIOMASS USING PYROLYSIS COMPOUND SPECIFIC HYDROGEN ISOTOPIC ANALYSIS ( $\delta^2\text{D PY-CSIA}$ )**  
Almendros Gonzalo, Jimenez-Morillo Nicasio T., Gonzalez-Pérez José A. (1), Sanz Jesus, Ruiz-Matute Ana I., De La Rosa José M., Gonzalez-Vila Francisco J.  
1 - IRNAS-CSIC (Spain)
- P1060 A NEW, QUICK, CLEAN AND EASY WAY TO MEASURE PAH AVAILABILITY IN CONTAMINATED SOILS USING THERMODESORPTION COUPLED WITH MOLECULAR ANALYSES**  
Biache Coralie (1), Lorgeoux Catherine (2), Saada Alain (3), Colombano Stéfan (3), Faure Pierre (1)  
1 - Laboratoire Interdisciplinaire des Environnements Continentaux (France), 2 - GeoRessources (France), 3 - Bureau de recherches géologiques et minières (France)
- P1061 THERMOCHEMOLYSIS FOR AN ALL IN ONE ANALYSIS OF THE MAIN BIOMOLECULAR FAMILIES IN SOILS AND SEDIMENTS. COMPARISON WITH CLASSICAL CHEMICAL DEGRADATIONS FOR THE ANALYSIS OF LIPIDS, LIGNIN AND CARBOHYDRATES IN A PEAT BOG.**  
Grasset Laurent (1), Younes Khaled (1)  
1 - INSTITUT DE CHIMIE DES MILIEUX ET MATERIAUX DE POITIERS (France)
- P1062 LABORATORY MATURATION OF SEVERAL CONIFER RESINS IN AN ATTEMPT TO TRANSFORM PLANT RESIN INTO AMBER**  
Hauteville Yann (1)  
1 - UMR 7359 Georessources (France)
- P1063 ASSESSING THE DIAGENETIC PATHWAYS OF RESIN ACIDS OF THE ABIETANE & PIMARANE CLASSES BY CONFINED PYROLYSIS**  
Hauteville Yann (1), Michels Raymond (2), Burklé-Vitzthum Valérie, Randi Aurélien, Lorgeoux Catherine (3), Catteloin Delphine  
1 - UMR 7359 Georessources (France), 2 - Lorraine University-GeoRessources-CNRS-CREGU (France), 3 - Géorressources (France)

## POSTER SESSION 1: Monday 9 May & Tuesday 10 May

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| <b>P1064</b> | <b>SIGNATURE OF PYROLYTIC ALKANES FOR THE ASSESSMENT OF SOIL CARBON SEQUESTRATION</b><br>Jimenez-Gonzalez Marco A. , Almendros Gonzalo , Alvarez Ana M., Carral Pilar, Gonzalez-Pérez José A. (1), Jimenez-Morillo Nicasio T., Gonzalez-Vila Francisco J.<br>1 - IRNAS-CSIC (Spain)  |
| <b>P1065</b> | <b>SOIL ORGANIC MATTER ALTERATIONS RESULTING FROM POST-FIRE RESTORATION ACTIONS</b><br>Jimenez-Morillo Nicasio T., Jordan Antonio, Zavala Lorena M., Granged Arturo J. P., Gonzalez-Vila Francisco J., Gonzalez-Pérez José A. (1)<br>1 - IRNAS-CSIC (Spain)  |
| <b>P1066</b> | <b>ACCURACY OF THE ROCK-EVAL METHOD ISO 5725-1-5725-6</b><br>Kashapov Roman (1), Goncharov Ivan (1)<br>1 - JSC «TomskNIPIneft» (Russia)  |
| <b>P1067</b> | <b>PYROLYSIS PARAMETERS FEATURES OF THE RUSSIAN ARCTIC OUTCROPS</b><br>Kashapov Roman (1), Goncharov Ivan (1), Oblasov Nikolay (1), Samoilenko Vadim (1), Trushkov Pavel (1)<br>1 - JSC «TomskNIPIneft» (Russia)   |
| <b>P1068</b> | <b>SUSPENDED PARTICULATE MATTER FROM MOSELLE RIVER (LORRAINE, FRANCE) : ORGANIC CHARACTERIZATION USING PY-GCMS</b><br>Le Meur Mathieu (1), Mansuy-Huault Laurence (1), Bauer Alan (2), Gley Renaud (1), Lorgeoux Catherine (3), Montargès-Pelletier Emmanuelle (4)<br>1 - Laboratoire Interdisciplinaire des Environnements Continentaux - LIEC (Vandoeuvre-Les-Nancy, France) (France), 2 - Laboratoire Interdisciplinaire des Environnements Continentaux (France), 3 - Géoresources (France), 4 - Université de Lorraine, Laboratoire Interdisciplinaire des Environnements Continentaux (France) |
| <b>P1069</b> | <b>CONJUGATED KINETIC EFFECT OF ALKYL BENZENES AND H<sub>2</sub>S ON ALKANES CRACKING</b><br>Leguizamon Guerra Nestor Camilo (1), Burklé-Vitzthum Valérie , Michels Raymond (2), Lanuzel Frédéric, Bounaceur Roda (3), Marquaire Paul-Marie (3)<br>1 - Laboratoire Réactions et Génie des Procédés - Georesources (France), 2 - University of Lorraine / CNRS / CREGU, GeoResources Laboratory (France), 3 - Laboratoire Réactions et Génie des Procédés (France)  |
| <b>P1070</b> | <b>THE CP+TV WOOD DATA BASE (I): CAPABILITIES &amp; APPLICATION SCOPE</b><br>Mann Ulrich (1)<br>1 - Forschungszentrum Jülich GmbH (Germany)  |
| <b>P1071</b> | <b>THE CP+TV WOOD DATA BASE (II): SELECTED CASE HISTORIES</b><br>Mann Ulrich (1)<br>1 - Forschungszentrum Jülich GmbH (Germany)  |
| <b>P1072</b> | <b>PY-GC AS A USEFUL METHOD FOR GENERATED PRODUCT PREDICTION IN PALEOZOIC SHALE FORMATIONS IN POLAND</b><br>Matyasik Irena (1), Kierat Maria (1), Brzuszek Pawel (1)<br>1 - 1 Oil and Gas Institute -National Research Institute (Poland)  |
| <b>P1073</b> | <b>EVIDENCE FOR THE ROLE OF MINERALS ON THE GENERATION OF H<sub>2</sub>S AND CO<sub>2</sub> UPON AQUATHERMOLYSIS OF HEAVY OILS AND OIL SANDS IN CONFINED HYDROUS PYROLYSIS EXPERIMENTS: IMPLICATION FOR STEAM INJECTION PROCESSES FOR OIL RECOVERY</b><br>Michel Pauline (1)<br>1 - IFP Energies Nouvelles (France)  |
| <b>P1074</b> | <b>HONEY-LIKE SCENTED DEPOSITS IN A LAVA TUBE FROM LA PALMA ISLAND (SPAIN)</b><br>Miller Ana Zelia (1), De La Rosa José Maria (1), Pereira Manuel (2), Garcia-Sanchez Angela (1), Jurado Valme (1), Fernandez Octavio (3), Gonzalez-Pérez José (1), Saiz-Jimenez Cesareo (1)<br>1 - Instituto de Recursos Naturales y Agrobiología de Sevilla (Spain), 2 - CERENA, Instituto Superior Tecnico, Universidade de Lisboa (Portugal), 3 - Grupo de Espeleología Tebexcorade-La Palma (Spain)   |
| <b>P1075</b> | <b>PYROLYTIC PARAMETERS SECTION BAZHENOV FORMATION OF WESTERN SIBERIA (RUSSIA)</b><br>Trushkov Pavel (1), Goncharov Ivan (1), Samoilenko Vadim (1), Kashapov Roman (1)<br>1 - JSC «TomskNIPIneft» (Russia)   |
| <b>WASTE</b> |  |
| <b>P1076</b> | <b>PYROLYSIS-CATALYSIS OF WASTE PLASTICS TO METHANE FOR HIGH VALUE AROMATIC PRODUCTS</b><br>Akubo Kaltume (1), Nahil Mohamad (1), T. Williams Paul (1)<br>1 - School of Chemical & Process Engineering (United Kingdom)  |
| <b>P1077</b> | <b>CRACKING OF BIOMASS TAR MODEL COMPOUNDS USING TYRE PYROLYSIS CHAR</b><br>Al-Rahbi Amal (1), Williams Paul (2)<br>1 - University of Leeds (United Kingdom), 2 - University of Leeds (United Kingdom)   |
| <b>P1078</b> | <b>CHEMICAL CHARACTERIZATION OF ORANGE JUICE WASTES FOR APPLICATION IN PYROLYSIS PROCESS</b><br>Alvarez Jon (1), Amutio Maider (1), Lopez Gartzen (1), Artetxe Maite (1), Barbarias Itsaso (1), Arregi Aitor (1), Santamaria Laura (1), Freire Fabio, Olazar Martin (1)<br>1 - University of the Basque Country (Spain)  |
| <b>P1079</b> | <b>MODELLING THE COMPOSITION OF THE GAS OBTAINED BY GLYCERIN GASIFICATION</b><br>Alvarez-Murillo Andres (1), Ledesma Cano Beatriz (1), Roman Suero Silvia (1), Sabio Rey Eduardo (1), Gonzalez Gonzalez Juan Félix (1)<br>1 - Universidad de Extremadura - Uex (SPAIN) (Spain)   |
| <b>P1080</b> | <b>STRUCTURE AND ACTIVITY OF ZSM-5 AND FLY ASH-DERIVED ZSM-5 CATALYS FOR SELECTIVE FORMATION OF AROMATICS FROM PYROLYTIC VAPORS OF RUBBER WASTES</b><br>Atong Duangduen (1), Vichaphund Supawan (2), Sricharoenchaikul Viboon (3), Aht-Ong Duangdao (4)<br>1 - National Metal and Materials Technology Center (Thailand), 2 - National Metal and Materials Technology Center (Thailand), 3 - Department of Environmental Engineering, Faculty of Engineering, Chulalongkorn University (Thailand), 4 - Department of Materials Science, Faculty of Science, Chulalongkorn University (Thailand)      |
| <b>P1081</b> | <b>LEATHER CHARACTERISATION FROM DIFFERENT ANIMAL SPECIES AND TANNING PROCESS BY TGA AND PY-GC/MS</b><br>Banon Elena (1), Marcilla Antonio (2), Garcia Angela (2), Leon Milagros (2)<br>1 - Spanish Footwear Technology Institute (INESCOP) (Spain), 2 - Department of Chemical Engineering, University of Alicante (Spain)  |
| <b>P1082</b> | <b>PYROLYSIS-CATALYTIC STEAM REFORMING OF POLYSTYRENE IN A TWO-STAGE REACTION SYSTEM</b><br>Barbarias Itsaso (1), Lopez Gartzen (1), Amutio Maider (1), Artetxe Maite (1), Alvarez Jon (1), Arregi Aitor (1), Olazar Martin (1)<br>1 - University of the Basque Country (Spain)  |



## POSTER SESSION 1: Monday 9 May & Tuesday 10 May

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| <b>P1083</b> | <b>STEPWISE CITRUS WASTE PYROLYSIS. CARBON FOOTPRINT &amp; LCA.</b><br>Bustos-Martinez Diana (1)<br>1 - Universidad de Nuevo Leon (Mexico)   |
| <b>P1084</b> | <b>INFLUENCE OF CLASSIC AND INNOVATIVE DRYING PROCESSES ON THE MOLECULAR CHARACTERISTICS OF SEWAGE SLUDGE</b><br>Collard Marie (1), Laduranty Joelle (1), Allavena Audrey (1), Karpel Vel Leitner Nathalie (1), Teychene Benoit (1), Lemeé Laurent (1)<br>1 - INSTITUT DE CHIMIE DES MILIEUX ET MATERIAUX DE POITIERS (France)   |
| <b>P1085</b> | <b>KINETIC STUDY AND THERMAL DECOMPOSITION BEHAVIOR OF VISCOELASTIC MEMORY FOAM</b><br>Conesa Juan A. (1), Font Rafael, Garrido Maria, Soler Aurora<br>1 - University of Alicante (Spain)  |
| <b>P1086</b> | <b>DECOMPOSITION OF MATERIALS COMBINING BIOMASS AND WASTE FROM ELECTRICAL AND ELECTRONIC EQUIPMENT (WEEE)</b><br>Conesa Juan A. (1), Soler Aurora, Font Rafael, Garrido Maria<br>1 - University of Alicante (Spain)  |
| <b>P1087</b> | <b>REVEALING THE STRUCTURE AND MECHANISMS INVOLVED IN THE PRODUCTION OF SEWAGE SLUDGE CHARS</b><br>De La Rosa José M (1), Paneque Marina (1), Jimenez-Morillo Nicasio (1), Gonzalez-Pérez José (1), Kern Jürgen (2), Aragon Carlos (3), Knicker Heike (1)<br>1 - IRNAS-CSIC (Spain), 2 - Leibniz-Institut für Agrartechnik Potsdam-Bornim e.V. (Germany), 3 - CENTA (Spain)  |
| <b>P1088</b> | <b>TRANSFORMATION BEHAVIOR OF ARSENIC DURING THERMAL TREATMENT OF P.VITTATA, A ARSENIC HYPERACCUMULATOR</b><br>Duan Lunbo (1), Xiaole Li (1), Ying Jiang (2), Philip Longhurst (2), Mei Lei (3)<br>1 - Southeast University (China), 2 - Cranfield University (United Kingdom), 3 - Chinese Academy of Sciences (China)  |
| <b>P1089</b> | <b>THERMAL TREATMENT OF WOOD WASTE FOR PARTICLEBOARD PRODUCTION</b><br>Girods Pierre (1), Rogaume Yann (1), Lemonon Jérôme (1), Colin Baptiste (1)<br>1 - Laboratoire d'Etude et de Recherche sur le MATériau Bois (France)  |
| <b>P1090</b> | <b>EFFECT OF CARBON NANOTUBES ON THERMAL AND CATALYTIC PYROLYSIS OF POLYOLEFINS</b><br>Gutierrez Omar (1), Palza H.<br>1 - Facultad de Ciencias Exactas y Aplicadas, Instituto Tecnológico Metropolitano (Colombia)  |
| <b>P1091</b> | <b>CHARACTERIZATION OF PYROLYSIS REACTION OF WASTE PAPER LAMINATED PHENOLIC PRINTED CIRCUIT BOARD</b><br>Kim Young-Min (1) (2), Han Tae Uk (2), Hwang Byeonga (2), Lee Yunhee (2), Park Young-Kwon (3), Kim Seungdo (2)<br>1 - Frontier Laboratories Ltd. (Japan), 2 - Department of Environmental Sciences and Biotechnology, Hallym University (South Korea), 3 - School of Environmental engineering, University of Seoul (South Korea) |
| <b>P1092</b> | <b>AIR GASIFICATION STUDY IN FLUIDIZED BED REACTOR: COMPARISON OF WOOD AND WASTE FROM CITY OF ABOMEY-CALAVI</b><br>Kple Melhyas (1) (2), Girods Pierre (2), Anjorin Malahimi (1), Fagla Benoît (1), Debal Matthieu (2), Colin Baptiste (2), Rogaume Yann (2)<br>1 - Laboratoire d'Energétique et de Mécanique Appliquée (Benin), 2 - Laboratoire d'Etude et de Recherche sur le MATériau Bois (France)                                     |
| <b>P1093</b> | <b>CO-PYROLYSIS BEHAVIORS OF BEECH WOOD AND POLYETHYLENE MIXTURES</b><br>Kumagai Shogo (1), Fujita Kohei (1), Kameda Tomohito (1), Yoshioka Toshiaki (1)<br>1 - Graduate school of Environmental Studies, Tohoku University (Japan)  |
| <b>P1094</b> | <b>PRODUCING HYDROGEN AND HIGH VALUE CARBON NANOTUBES FROM PLASTICS WASTE USING NI- AND FE-BASED CATALYSTS</b><br>Liu Xiaotong (1), Zhang Yeshui (2), Nahil Mohamad (3), Williams Paul (2), Wu Chunfei (1)<br>1 - University of Hull (United Kingdom), 2 - School of chemical and process engineering (United Kingdom), 3 - MOHAMAD NAHIL (United Kingdom)   |
| <b>P1095</b> | <b>HYDROTHERMAL LIQUEFACTION OF ANIMAL BY-PRODUCTS: DIFFERENT EXTRACTION PROCESSES</b><br>Marcilla Antonio (1), Garcia Angela (1), Leon Milagros (1), Catala Lucia (1), Martinez Isabel (1), Navarro Rosa (1)<br>1 - Department of Chemical Engineering, University of Alicante (Spain)  |
| <b>P1096</b> | <b>EFFECT OF THE PROCESS TEMPERATURE ON THE PRODUCTS GENERATED BY HYDROTHERMAL LIQUEFACTION OF ANIMAL BY-PRODUCTS</b><br>Marcilla Antonio (1), Garcia Angela (1), Leon Milagros (1), Catala Lucia (1), Martinez Isabel (1), Navarro Rosa (1)<br>1 - Department of Chemical Engineering, University of Alicante (Spain)   |
| <b>P1097</b> | <b>NUMERICAL MODELLING OF THE PYROLYTIC DEGRADATION OF PLASTIC COMPOUNDS</b><br>Masmoudi Amal (1), Baccar Mounir (1), Naifar Fahmi (2)<br>1 - Computational Fluid Dynamic and Transfer Phenomena, National Engineering School of Sfax-Tunisia (Tunisia), 2 - National Engineering School of Sfax-Tunisia (Tunisia)   |
| <b>P1098</b> | <b>EPOXY RESIN FAST PYROLYSIS STUDIED IN MICRO-FLUIDISED BED</b><br>Masson Amandine (1), Lopez Rojas Luis, Mercy Michel (1), Dufour Anthony (1), Hu Guo-Hua (1), Mauviel Guillain (1), Burkle-Vitzthum Valerie (1)<br>1 - Laboratoire Réactions et Génie des Procédés (France)   |
| <b>P1099</b> | <b>ENHANCING SYNTHESIS GAS QUALITY FROM DRY REFORMING OF WASTE PLASTICS</b><br>Md Saad Juniza (1), Nahil Mohamad Anas (1), T. Williams Paul (1)<br>1 - School of Chemical & Process Engineering (United Kingdom)   |
| <b>P1100</b> | <b>EFFECT OF HIGH HEATING RATES ON THE PRODUCTION OF LIMONENE BY PYROLYSIS OF WASTE TYRES</b><br>Mkhize Ntandoyenkosi (1), Van Der Gryp Percy (1), Danon Bart (1), Gorgens Johann (1)<br>1 - Department of Process Engineering, University of Stellenbosch (South Africa)  |
| <b>P1101</b> | <b>FUELS BY RECYCLING OF WASTE PLASTICS FROM END OF LIFE VEHICLES</b><br>Norbert Miskolczi (1), Zsuzsanna Czégény (2), Janos Bozi (2), Janos Soja (1)<br>1 - MOL Department of Hydrocarbon and Coal Processing, University of Pannonia (Hungary), 2 - Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences (Hungary)  |
| <b>P1102</b> | <b>THERMO-CATALYTIC REFORMING OF MUNICIPAL SOLID WASTE</b><br>Ouali Miloud (1) (2), Conti Roberto (3) (2), Jäger Nils (1) (2), Gasson James (1) (2), Hornung Andreas (4) (3) (1) (2)<br>1 - Birmingham University School of Chemical Engineering (United Kingdom), 2 - Fraunhofer UMSICHT (Germany), 3 - Università di Bologna [Bologna] (Italy), 4 - Friedrich-Alexander University Erlangen-Nürnberg (Germany)                           |
| <b>P1103</b> | <b>ONLINE STUDY ON THE INFLUENCE OF THERMAL TREATMENT OF HUSY ON THE CATALYTIC PYROLYSIS OF POLYPROPYLENE WITH PHOTOIONIZATION MASS SPECTROMETRY</b><br>Pan Yang (1)<br>1 - University of Science and Technology of China (China)  |
| <b>P1104</b> | <b>RECYCLED POLYMERS FROM WEEE IN FOOD CONTACT ARTICLES ON THE EUROPEAN MARKET: COMPLETING THE STORY BY PYROLYSIS GC-MS</b><br>Puype Franky (1)<br>1 - Institute for Testing and Certification (Czech Republic)  |

## POSTER SESSION 1: Monday 9 May & Tuesday 10 May

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| <b>P1105</b> | <b>CATALYTIC PYROLYSIS OF WASTE PLASTICS USING STAGED CATALYST FOR PRODUCTION OF GASOLINE RANGE HYDROCARBONS</b><br>Ratnasari Devy (1), Nahil M.a., Williams P.t.<br>1 - Energy Research Institute (United Kingdom)   |
| <b>P1106</b> | <b>CATALYTIC PYROLYSIS OF REFUSED PLASTIC FUEL OVER ZEOLITES</b><br>Ro Donghoon, Hong Yeojin, Lee Yejin, Lee Heejin, Park Young-Kwon (1)<br>1 - School of Environmental engineering, University of Seoul (South Korea)  |
| <b>P1107</b> | <b>INFLUENCE OF DEMINERALIZATION ON PYROLYSIS OF SUGARCANE BAGASSE AND TRASH</b><br>Rodriguez-Machin Lizet (1), Prins W., Ronsse F.<br>1 - Ghent University (BELGIUM) (Belgium)   |
| <b>P1108</b> | <b>USE OF SEWAGE SLUDGE AND MANURE ASH FOR H<sub>2</sub>S REMOVAL FROM THE PYROLYSIS GAS</b><br>Ruiz-Gomez Nadia (1), Ceamanos Jesus (1), Calavia Alejandro (1), Gea Gloria (1), Fonts Isabel (2) (1), Atienza-Martinez Maria (1)<br>1 - Aragon Institute of Engineering Research (I3A) [Zaragoza] (Spain), 2 - Centro Universitario de la Defensa (CUD) [Zaragoza] (Spain) |
| <b>P1109</b> | <b>BTEX FRACTIONS FROM THE CATALYTIC PYROLYSIS OF WASTE POLYMERS</b><br>Sajdak Marcin (1), Nowakowski Daniel (2), Riasat Selma (3)<br>1 - Institute for Chemical Processing of Coal (Poland), 2 - European Bioenergy Research Institute (EBRI), Aston University (United Kingdom), 3 - School of Engineering and Applied Science, Aston University (United Kingdom)         |
| <b>P1110</b> | <b>IMPLEMENTATION OF A NEW PYROLYSIS REACTOR IN LINZ</b><br>Schwarzinger Clemens (1), Warchol Gerd<br>1 - Institute for Chemical Technology of Organic Materials, Johannes Kepler University (Austria)  |
| <b>P1111</b> | <b>VALORISATION OF LOW QUALITY BIOFUELS BY HYDROTHERMAL CARBONISATION</b><br>Smith Aidan (1), Ross Andrew (1)<br>1 - University of Leeds (United Kingdom)   |
| <b>P1112</b> | <b>CATALYTIC CRAKING OF NITROGEN CONTAINING PLASTICS USING SPENT FCC CATALYST</b><br>Tani Haruki (1), Hirasawa Masahiro (2), Gytoku Koji (3), Murakami Yayoi (3), Fujimoto Kaoru (3), Asami Kenji (3), Noda Shuji (4)<br>1 - Nagoya University (Japan), 2 - Nagoya University (Japan), 3 - The University of Kitakyushu (Japan), 4 - Environment Energy Co. Ltd. (Japan)    |
| <b>P1113</b> | <b>INDUSTRIAL WASTE DERIVED CAO-BASED CATALYSTS FOR UPGRADING OF VOLATILES DURING JATROPHA RESIDUES PYROLYSIS</b><br>Vichaphund Supawan (1), Atong Duangduen (1), Sricharoenchaikul Viboon (2)<br>1 - National Metal and Materials Technology Center (Thailand), 2 - Department of Environmental Engineering, Faculty of Engineering, Chulalongkorn University (Thailand)   |
| <b>P1114</b> | <b>CONVERSION OF EARTHWORM MANURE INTO ENVIRONMENTALLY-FRIENDLY ADSORBENTS THROUGH PYROLYSIS</b><br>Wang Zhanghong (1), Shen Dekui (1), Xiao Rui (1)<br>1 - Southeast University (China)  |
| <b>P1115</b> | <b>SLOW PYROLYSIS OF ORGANIC FRACTION OF MUNICIPAL SOLID WASTE AND USING THE AQUEOUS PHASE PRODUCT IN ANAEROBIC DIGESTION</b><br>Yang Yang (1), Venetsaneas Nikolaos (2), Bridgwater Tony (1), Banks Charles (2), Heaven Sonia (2)<br>1 - European Bioenergy Research Institute (United Kingdom), 2 - Faculty of Engineering and the Environment (United Kingdom)           |
| <b>P1116</b> | <b>CARBON NANOTUBES AS VALUE ADDED PRODUCTS ALONG WITH HYDROGEN PRODUCTION BY PYROLYSIS CATALYTIC-GASIFICATION OF WASTE TIRES</b><br>Zhang Yeshui (1), Williams Paul (1)<br>1 - School of chemical and process engineering (United Kingdom)   |

## POSTER SESSION 2: Wednesday 11 May & Thursday 12 May

### ANALYTICAL PYROLYSIS

- P2001 CHARACTERIZATION OF ACRYLONITRILE-1,3-BUTADIENE-STYRENE/ POLYAMIDE 6 (ABS/PA6) BLENDS BY PYROLYSIS-GAS CHROMATOGRAPHY (PY-GC) WITH DIFFERENT DETECTOR SYSTEMS**  
Alarcon Salinas Sebastian (1), Kuch Peter (1), Gerd Knupp (1), Johannes Steinhaus (1) and Dietrich Sülthaus (2)  
1 - Hochschule Bonn-Rhein-Sieg - University of Applied Sciences, Germany  
2 - AKRO-PLASTIC GmbH, Im Stiefelfeld 1, 56651 Niederzissen, Germany
- P2002 PYROLYSIS STUDY OF WOOD DEGRADATION CAUSED BY INORGANIC COMPOUNDS**  
Antuskova Vaclava (1), Tamburini Diego (2), Lucejko Jeannette (3) (2), Modugno Francesca (2), Kuc̄rova Irena (1)  
1 - Department of Chemical Technology of Monument Conservation, University of Chemistry and Technology Prague (Czech Republic), 2 - Department of Chemistry and Industrial Chemistry, University of Pisa (Italy), 3 - Institute for the Conservation and Valorization of Cultural Heritage, National Research Council (Italy)
- P2003 MICROSTRUCTURAL ANALYSIS OF PURE AND LI DOPED CD FERRITES (CDLIXFE(2-X)O4-Y) NANOFABRICATED BY CO-PRECIPIATION METHOD**  
Anu (1), Gupta Munish (2) (3), Mudsainiyan R.k. (4), Randhawa B.s. (5)  
1 - Department of Chemistry, Baring Union Christian College, Batala (India), 2 - Department of Chemistry, DAV College, Amritsar (India), 3 - Department of Chemistry, Centre for Advanced studies-II, Guru Nanak Dev University, Amritsar (India), 4 - Department of Chemistry, Guru Nanak Dev University (India), 5 - Department of Chemistry, Guru Nanak Dev University, Amritsar (India)
- P2004 PY/GC-MS TO EVALUATE THE ACTIVITY OF A THERMOSTABLE LACCASE PRODUCED BY STREPTOMYCES IPOMOEAE IN THE DEGRADATION OF LIGNIN FROM WHEAT STRAW**  
Arias M. Enriqueta , Blaquez Alba, Hernandez Manuel, Rodriguez Juana, Gonzalez-Pérez José A. <jag@irnase.csic.es> (1), Jiménez-Morillo Nicasio T., Gonzalez-Vila Francisco J.  
1 - IRNAS-CSIC (Spain)
- P2005 APPLICATION OF ANALYTICAL PYROLYSIS FOR SEARCH OF MECHANISMS OF BIOMASS COMPONENTS TRANSFORMATION INDUCED BY MICROWAVE TORREFACTION**  
Arshanitsa Alexandr (1), Dizhbite Tatiana, Bikovens Oskars, Jurkjane Vilhelmine, Lauberts Maris, Telysheva Galina  
1 - Latvian State Institute of Wood Chemistry (Latvia)
- P2006 ACID TREATMENT OF PHRAGMITES FOR SUGAR AND SUGAR DERIVATIVES PRODUCTION**  
Bartoli Mattia (1)  
1 - Department of Chemistry "Ugo Schiff", University of Florence (Italy)
- P2007 MULTI-ANALYTICAL APPROACH TO CHARACTERISE MODERN OIL PAINT FORMULATIONS**  
Bonaduce Ilaria (1), Colombini Maria Perla (2) (3), Degano Ilaria, Duce Celia (4), La Nasa Jacopo (4), Modugno Francesca (2), Tine Maria Rosaria (4)  
1 - Dipartimento di Chimica e Chimica Industriale Università di Pisa (Italy), 2 - Department of Chemistry and Industrial Chemistry, University of Pisa (Italy), 3 - Institute for the Conservation and Valorization of Cultural Heritage, National Research Council (Italy), 4 - Department of Chemistry and Industrial Chemistry, University of Pisa (Italy)
- P2008 THE DISCOVERING OF NEW MARKERS FOR ARCHAEOLOGICAL PURPOSES: EGA-MS, PY-GC/MS AND GC/MS INVESTIGATION ON WOOD AND BARK PITCH REPLICA**  
Bulfaro Maria, Ribechini Erika (1), Colombini Maria Perla  
1 - Dipartimento di chimica e chimica industriale, Università di Pisa (Italy)
- P2009 AN EXPERIMENTAL INVESTIGATION INTO THE ABSENCE OF COMBUSTION IN AN ELECTRICALLY HEATED TOBACCO SYSTEM**  
Cozzani Valerio (1), Mcgrath Thomas (2), Smith Maurice (2), Schaller Jean Pierre (2), Zuber Gerard (2)  
1 - University of Bologna [Bologna] (Italy), 2 - Philip Morris International Research and Development (Switzerland)
- P2010 CHARACTERIZATION OF TRADITIONAL EAST ASIAN PAPERS USING PY-GC/MS AND PY-GCXGC/MS**  
Daheur Ghizlene > (1), Han Bin (1), Sablier Michel (1), Vilmont Léon-Bavi (1)  
1 - Centre de recherche sur la Conservation USR 3224 du CNRS, Muséum National d'Histoire Naturelle (France)
- P2011 THE MECHANISM OF BIOMASS PYROLYSIS STUDIED BY VARIOUS ANALYTICAL METHODS**  
Dufour Anthony (1), Le Brech Yann (1)  
1 - CNRS Nancy (France)
- P2012 ON-LINE ANALYSIS OF BIOMASS PYROLYSIS TAR BY PHOTOIONIZATION MASS SPECTROMETRY**  
Dufour Anthony (1), Liangyuan Jia (1), Le Brech Yann (1), Mauviel Guillain (1), Qi Fei (2), Bente Von Frowein Matthias (3)  
1 - CNRS Nancy (France), 2 - Shanghai Jiao Tong University (China), 3 - Photonion (Germany)
- P2013 CHARACTERIZATION OF CHEMICAL COMPOSITION VARIATIONS IN DIFFERENT SPRUCE WOOD ZONES BY PY-GCMS**  
Dumarcay Stephane (1), Gérardin Philippe (2)  
1 - Laboratoire d'Etudes et de Recherche sur le Matériau Bois (France), 2 - Laboratoire d'Etudes et de Recherche sur le Matériau Bois (France)
- P2014 SPME-GC-MS TO TRACE THE DYNAMICS OF COMPOUNDS EVOLVED DURING STEPWISE PYROLYSIS**  
Ghidotti Michele (1)  
1 - Università di Bologna - Centro Interdipartimentale di Ricerca Industriale Energia e Ambiente - Unita operativa Biomasse (Italy)
- P2015 PYROLYSIS-COMPOUND SPECIFIC ISOTOPE ANALYSIS (PY-CSIA). TECHNIQUE AND APPLICATIONS**  
Gonzalez-Perez José A. (1), Jimenez-Morillo Nicasio T., De La Rosa José M., Knicker Heike, Gonzalez-Vila Francisco J.  
1 - IRNAS-CSIC (Spain)
- P2016 INVESTIGATIONS ON PHYSICO-CHEMICAL PARAMETERS OF PURE AND SM3+ DOPED CD FERRITES (CD1-XSMXFE2O4+0.5X ; X = 0.0-0.3) SYNTHESIZED BY SOLUTION COMBUSTION METHOD**  
Gupta Munish (1) (2), . Anu (3), Mudsainiyan R.k. (4), Randhawa B.s. (4)  
1 - DAV COLLEGE, AMRITSAR (India), 2 - Guru Nanak Dev University (India), 3 - BARING UNION CHRISTIAN COLLEGE (India), 4 - GURU NANAK DEV UNIVERSITY (India)
- P2017 NEW KINETIC APPROACH ON PYROLYSIS POLY-(METHYL METHACRYLATE) USING EGA-MS**  
Han Tae Uk (1), Kim Young-Min (2) (1), Hwang Byeonga (1), Park Young-Kwon (3), Kim Seungdo (1)  
1 - Department of Environmental Sciences and Biotechnology, Hallym University (South Korea), 2 - Frontier Laboratories Ltd. (Japan), 3 - School of Environmental engineering, University of Seoul (South Korea)
- P2018 DEVELOPMENT OF IDENTIFICATION METHODS OF DRYING OILS COMPOSED OF DIFFERENT MAIN COMPONENTS BY PY-GC/MS**  
Hayato Horii (1), Takayuki Honda (2)  
1 - Department of Applied Chemistry, Meiji Graduated (Japan), 2 - Department of Applied Chemistry, Meiji University (Japan)

## POSTER SESSION 2: Wednesday 11 May & Thursday 12 May

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| P2019 | <b>PY-GC/MS ANALYSIS OF THE COLORING MATERIALS OF A YOMEIMON GATE OF THE NIKKO TOSHOGU SHRINE</b><br>Honda Takayuki (1), Nobuhiko Kitano (2), Noritake Sato (3)<br>1 - Meiji University Science and Technology (Japan), 2 - Independent Administrative Institution National Research Institute for Cultural Properties (Japan), 3 - Association for the Preservation of the Nikko World Heritage Site Shrines and Temples (Japan)  |
| P2020 | <b>SCIENTIFIC ANALYSIS OF IMITATION LACQUERWARE USING "PAPIER-MACHE"</b><br>Idei Soichiro (1)<br>1 - Graduate School of Science and Technology, Meiji University (Japan)   |
| P2021 | <b>INFLUENCE OF THE TEMPERATURE RISE TIME ON PYROGRAMS IN ANALYTICAL PYROLYSIS</b><br>Jonsson Helena (1), Lars-Ove Jonsson (1)<br>1 - Pyrol AB (Sweden)  |
| P2022 | <b>HIGH PRESSURE TANDEM CATALYTIC REACTOR-GC/MS SYSTEM AND ITS APPLICATIONS</b><br>Kim Young-Min (1) (2), Michael Soll (3), Ito Koichi (1), Teramae Norio (1), Watanabe Atsushi (1), Hosaka Akihiko (1), Park Young-Kwon (4), Kim Seungdo (2)<br>1 - Frontier Laboratories Ltd. (Japan), 2 - Department of Environmental Sciences and Biotechnology, Hallym University (South Korea), 3 - Frontier Laboratories Ltd. (Germany), 4 - School of Environmental engineering, University of Seoul (South Korea)   |
| P2023 | <b>CHROMIDENT - TOWARDS A COMPREHENSIVE UTILIZATION OF PYROLYTIC FINGERPRINTS FOR SAMPLE COMPARISON AND QUALITY CONTROL</b><br>Klingberg Andreas (1), Wenig Philip (1), Binder Janos (1), Azeez Akeem (2), Fladung Matthias (3), Meier Dietrich (4)<br>1 - Lablicate UG (Germany), 2 - Ekiti State University, Department of Chemistry (Nigeria), 3 - Thünen Institute of Forest Genetics (Germany), 4 - Thünen Institute of Wood Research (Germany)   |
| P2024 | <b>STUDY ON CHINESE HISTORICAL LACQUER CULTURE AND TECHNOLOGY - ANALYSIS OF CHINESE QIN-HAN DYNASTY LACQUERWARE-</b><br>Lu Rong (1), Yamabuki Midori (1), Ando Daisuke (1), Miyakoshi Tetsuo (1)<br>1 - meiji university (Japan)   |
| P2025 | <b>THE DRAMATIC EFFECT OF THE ALUM TREATMENT ON THE OSEBERG WOOD COLLECTION: A PY-GC/MS AND ICP-OES STUDY</b><br>Lucejko Jeannette (1) (2), Tamburini Diego (2), Modugno Francesca > (2), Colombini Maria Perla (1) (2), Gambineri Francesca (3), Kutzke Hartmut (4)<br>1 - Institute for the Conservation and Valorization of Cultural Heritage, National Research Council (Italy), 2 - Department of Chemistry and Industrial Chemistry, University of Pisa (Italy), 3 - Laboratori ARCHA Srl (Italy), 4 - Museum of Cultural History, University of Oslo (Norway) |
| P2026 | <b>CHEMICAL CHANGES OF THERMO-HYDRO TREATED BIRCH VENEERS</b><br>Meija-Feldmane Anete (1) (2), Dobele Galina (2), Grinins Juris (2), Andersone Ingeborga (2), Cirule Dace (1) (2), Jurkjane Vilhelmine (2), Andersons Bruno (2)<br>1 - Latvia University of Agriculture (Latvia), 2 - Latvian State Institute of Wood Chemistry (Latvia)   |
| P2027 | <b>CHARACTERIZATION AND AGEING STUDIES OF AQUAZOL RETOUCHING PAINTS USING TECHNIQUES BASED ON PYROLYSIS</b><br>Modugno Francesca (1), La Nasa Jacopo (1), Orsini Sibilla (1), Duce Celia (1), Spepi Alessio (1), Tine Maria Rosaria (1), Ubaldi Vanessa (2), De Luca Daphne (2)<br>1 - Department of Chemistry and Industrial Chemistry, University of Pisa (Italy), 2 - Department of Basic Science and Foundations, University of Urbino (Italy)   |
| P2028 | <b>THE COMBINATION OF PYROLYSIS-BASED TECHNIQUES TO EVALUATE THE STATE OF PRESERVATION OF ARCHAEOLOGICAL WOOD IN THE PRESENCE OF CONSOLIDATING AGENTS</b><br>Modugno Francesca (1), Tamburini Diego (1), Lucejko Jeannette (2) (1), Colombini Maria Perla (2) (1)<br>1 - Department of Chemistry and Industrial Chemistry, University of Pisa (Italy), 2 - Institute for the Conservation and Valorization of Cultural Heritage, National Research Council (Italy)   |
| P2029 | <b>END GROUP ANALYSIS OF STYRENE-BUTYL ACRYLATE COPOLYMERS PREPARED USING BENZOYLPEROXIDE INITIATOR BY STEPWISE CHEMOLYSIS-PYROLYSIS GAS CHROMATOGRAPHY</b><br>Ohtani Hajime (1), Takeuchi Kaoru (1), Kaneko Asako (2), Kiura Masaaki (2), Momose Hikaru (2)<br>1 - Nagoya Institute of Technology (Japan), 2 - Mitsubishi Rayon Co., Ltd. (Japan)   |
| P2030 | <b>CHEMICAL ANALYSIS OF UV IRRADIATED B-72 BY PY-GC/MS AND EGA-MS</b><br>Okamoto Shun (1), Takayuki Honda (2)<br>1 - Graduate school of Science and Technology, Meiji univ. (Japan), 2 - School of Science and Technology, Meiji univ. (Japan)   |
| P2031 | <b>QUANTIFICATION OF POLYVINYLPIRROLIDONE (PVP) AND POLYVINYLALCOHOL (PVOH) IN POLYAMIDE FILMS BY PYROLYSIS GC-MS</b><br>Puype Franky (1)<br>1 - Institute for Testing and Certification (Czech Republic)  |
| P2032 | <b>FEASIBILITY OF PYROLYSIS GC-MS FOR THE CHARACTERIZATION OF CHEMICAL MODIFIED POLYMER SURFACES</b><br>Puype Franky (1)<br>1 - Institute for Testing and Certification (Czech Republic)   |
| P2033 | <b>ANALYTICAL PYROLYSIS OF PRETREATED HEMP SHIVES LIGNOCELLULOSE TO LEVOGLUCOSAN AND LEVOGLUCOSENONE</b><br>Rizhikovs Janis (1), Dobele Galina (1), Zhurinsh Aivars (1), Paze Aigars (1), Meile Kristine (1), Puke Maris (1), Brazdausks Prans (1)<br>1 - Latvian State Institute of Wood Chemistry (Latvia)   |
| P2034 | <b>CHEMICAL CHARACTERISATION OF TARS FROM THERMAL CONVERSION OF BIOMASS BY 1D GAS CHROMATOGRAPHY COMBINED WITH SILYLATION</b><br>Sajdak Marcin (1), Chrubasik Maciej (1), Muzyka Roksana (1)<br>1 - Institute for Chemical Processing of Coal (Poland)   |
| P2035 | <b>ANALYTICAL PYROLYSIS AS A METHOD TO QUANTITATIVE ANALYSIS OF FOSSIL FUELS CONTAMINANTS IN BIOCHAR</b><br>Sajdak Marcin (1), Nowakowski Daniel (2), Bridgwater Anthony (2)<br>1 - Institute for Chemical Processing of Coal (Poland), 2 - European Bioenergy Research Institute, Aston University (United Kingdom)   |
| P2036 | <b>THERMALLY ASSISTED CHEMOLYSIS USING HYDROGEN DONOR REAGENT FOR STRUCTURAL ANALYSIS OF INTRACTABLE CROSS-LINKING POLYMERS</b><br>Sakai Shun (1), Kano Ryota (1), Ohtani Hazime (1)<br>1 - Nagoya Institute of Technology (Japan)   |

## POSTER SESSION 2: Wednesday 11 May & Thursday 12 May

|                            |   |
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| P2037                      | <b>DETERMINATION OF FORMALDEHYDE AS A PYROLYSIS PRODUCT USING ANALYTICAL PYROLYSIS DERIVATIZATION-GC/MS</b><br>Sam Karen (1), Dowling Jennifer (1)<br>1 - CDS Analytical (United States)  |
| P2038                      | <b>ANALYTICAL PYROLYSIS IN THE INVESTIGATION OF TURQUOISE IMITATIONS AND TREATMENTS</b><br>Schwarzinger Clemens (1), Schwarzinger Bettina<br>1 - Institute for Chemical Technology of Organic Materials, Johannes Kepler University (Austria)   |
| P2039                      | <b>ANALYSIS OF THE AROMATIC COMPOSITION OF INTERNAL COMMON RAIL INJECTOR DEPOSITS VIA THERMAL DEGRADATION</b><br>Streibel Thorsten (1) (2), Lau Kornelia (2), Klingbeil Sophie (2), Junk Rene (2), Schümann Ulrike (2), Zimmermann Ralf (1) (2)<br>1 - Helmholtz Zentrum München (Germany), 2 - University of Rostock (Germany)   |
| P2040                      | <b>SCIENTIFIC ANALYSIS OF JÅCEMON RELIC EXCAVATED THE MINAMIKÅCENUMA RUINS</b><br>Takahashi Shinichi (1), Honda Takayuki (2)<br>1 - Graduate school of Science and Technology, Meiji univ. (Japan), 2 - Meiji University Graduate School of Science and Technology (Japan)  |
| P2041                      | <b>ANALYSIS AND IDENTIFICATION OF RYUKYU LACQUERWARES DECORATED WITH WISTERIA VINE BY PYROLYSIS-GAS CHROMATOGRAPHY/MASS SPECTROMETRY AND 87SR/86SR ISOTOPE RATIO MEASUREMENTS</b><br>Tetsuo Miyakoshi (1)<br>1 - Meiji University (Japan)   |
| P2042                      | <b>VERIFICATION OF THE ABSENCE OF COMBUSTION IN AN ELECTRICALLY HEATED TOBACCO SYSTEM</b><br>Yan Hui (1), Fujita Osamu (2)<br>1 - Graduate School of Engineering, Hokkaido University, N13W8, Kita-ku, Sapporo, 060-8628, Japan (Japan), 2 - Faculty of Engineering, Hokkaido University, N13W8, Kita-ku, Sapporo, 060-8628, Japan (Japan)  |
| P2043                      | <b>ODOR ANALYSIS OF PEROXIDE DEGRADED POLYPROPYLENE BY PYROLYSIS GAS CHROMATOGRAPHY-MASS SPECTROMETRY</b><br>Yang Rui (1), Wang Zhaocheng (1), Liu Ying (1), Wang Yanfang (2), Chen Shangtao (2), Zhang Fengbo (2)<br>1 - Department of Chemical Engineering, Tsinghua University (China), 2 - Synthetic Resin Laboratory, PetroChina Petrochemical Research Institute (China)  |
| <b>BIOMASS / CATALYSIS</b> |   |
| P2044                      | <b>EFFECT OF ALKALI AND ACID PRE-TREATMENT ON GRASS PYROLYSIS</b><br>Barbiero Chiara (1)<br>1 - Institute for Chemicals and Fuels from Alternative Resources (Canada)   |
| P2045                      | <b>A DETAILED QUALI-QUANTITATIVE ANALYSIS OF PRODUCTS FROM PYROLYSIS-ZEOLITE CRACKING OF THE MICROALGAE SPIRULINA</b><br>Daniele Fabbri (1) (2), Torri Cristian (1), Bianchini Emma (1), Pistocchi Rossella (1), Guerrini Franca (1), Rombola Alessandro (1), Massoli Patrizio (3)<br>1 - University of Bologna (Italy), 2 - University of Bologna (Italy), 3 - Istituto Motori CNR (Italy)   |
| P2046                      | <b>CATALYTIC PYROLYSIS OF WASTE LIGNIN FROM PULPING PROCESS FOR BIO-OIL PRODUCTION</b><br>Hawangchu Yotwadee (1), Atong Duangduen (2), Sricharoenchaikul Viboon (3) (4)<br>1 - International program on hazardous substance and environmental management Graduate School, Chulalongkorn University (Thailand), 2 - National Metal and Materials Technology Center, National Science and Technology Development Agency (Thailand), 3 - Energy Research Institute, Chulalongkorn University, Bangkok, Thailand (Thailand), 4 - Department of Environmental Engineering, Faculty of Engineering (Thailand) |
| P2047                      | <b>CATALYTIC PYROLYSIS OF BIOMASS USING AN INTEGRATED CONCEPT</b><br>Heeres H.j. (1)<br>1 - University of Groningen (Netherlands)   |
| P2048                      | <b>STUDYING CATALYZED BIOMASS PYROLYSIS AND CATALYST DEACTIVATION AND REGENERATION BY USING A TANDEM MICRO REACTOR GC-MS</b><br>John Mommers (1), Mengerink Ynze (1), Kramer Jurjen (1), Oevering Henk (1)<br>1 - DSM (Netherlands)   |
| P2049                      | <b>CATALYTIC PYROLYSIS OF EMPTY FRUIT BUNCH IN A BENCH-SCALE FIXED BED REACTOR</b><br>Kim Beom-Sik (1), Kim Young-Min (1), Jae Jungho (2), Suh Dong Jin (2), Yoo Kyung-Seun (3), Kim Seungdo (4), Jeon Jong-Ki (5), Jung Sang-Chul (6), Park Young-Kwon (1)<br>1 - University of Seoul (South Korea), 2 - Korea Institute of Science and Technology (South Korea), 3 - Kwangwoon University (South Korea), 4 - Hallym University (South Korea), 5 - Kongju National University (South Korea), 6 - Suncheon National University (South Korea)  |
| P2050                      | <b>EFFECTS OF SUPPORTS ON THE PRODUCTION OF FUEL-RANGE HYDROCARBONS IN THE HYDROTREATMENT OF SOYBEAN OIL WITH PLATINUM-BASED CATALYSTS</b><br>Kim Chul Ung (1), Hyung Ju Kim (1), Tae Wan Kim (1), Ho-Jeong Choi (1), Soon Yong Jeong (1), Jeong Rang Kim (1)<br>1 - Center for Convergent Chemical Process (South Korea)   |
| P2051                      | <b>SUPERCRITICAL ETHANOLYSIS OF LIGNIN IN THE PRESENCE OF RU-NI BIMETALLIC CATALYST</b><br>Kim Jae-Young (1), Park Shin Young (1), Shinyoung Oh (1), Hwang Hyewon (1), Lee Jae Hoon (1), Moon Jaegwan (1), Choi Joon Weon (1)<br>1 - Seoul National University (South Korea)  |
| P2052                      | <b>CATALYTIC DEPOLYMERIZATION OF LIGNIN IN SUPERCRITICAL ETHANOL/WATER MIXTURES</b><br>Kristianto Ivan (1) (2), Limarta Susan (1) (2), Suh Dong Jin (1) (2), Jae Jungho (1) (2)<br>1 - Korea University of Science and Technology (South Korea), 2 - Korea Institute of Science and Technology (South Korea)  |
| P2053                      | <b>CATALYTIC PYROLYSIS OF LIGNIN WITH SOLID ACID CATALYSTS</b><br>Lee Hyung Won (1), Lee Heejin (1), Kim Young-Min (1), Jae Jungho (2), Suh Dong Jin (2), Kim Seungdo (3), Park Young-Kwon (1)<br>1 - University of Seoul (South Korea), 2 - Korea Institute of Science and Technology (South Korea), 3 - Hallym University (South Korea)   |
| P2054                      | <b>INVESTIGATION OF THE CATALYTIC EFFECT OF TRANSITION METALS ON THE SUBCRITICAL HYDROTHERMAL LIQUEFACTION OF NON-WOODY BIOMASS</b><br>Lee Jae Hoon (1), Hwang Hyewon (1), Choi In-Gyu (1), Choi Joon Weon (2) (3)<br>1 - Department of Forest Sciences, CALS, Seoul National University (SNU) (South Korea), 2 - Graduate School of International Agricultural Technology, Seoul National University (SNU) (South Korea), 3 - Institute of Green-Bio Science and Technology, Seoul National University (SNU) (South Korea)   |

## POSTER SESSION 2: Wednesday 11 May & Thursday 12 May

|                           |  |
|---------------------------|--|
| <b>P2055</b>              | <b>PRODUCTION OF VALUABLE PRODUCTS BY CATALYTIC UPGRADING OF PYROLYTIC OIL FROM JATROPHA WASTE OVER METAL/ZEOLITE CATALYSTS</b><br>Lee Kyong-Hwan (1), Lee Jin-Hyuk (1), Hwang Kyung-Ran (1), Lee Jin-Suk (1), Han Jeong Sik (2)<br>1 - Climate Change Energy Research Division, KIER (South Korea), 2 - R&D, Agency for Defense Development (South Korea)   |
| <b>P2056</b>              | <b>CATALYTIC PYROLYSIS OF BIOMASS IN NH<sub>3</sub> GAS WITH FLUIDIZED BED</b><br>Ma Hao (1), Zhou Zhongyue, Qi Fei<br>1 - MOE Key Laboratory for Power Machinery and Engineering, Shanghai Jiao Tong University (China)   |
| <b>P2057</b>              | <b>CATALYTIC CONVERSION OF PYROLYTIC VAPORS OF WOODY BIOMASS</b><br>Margeriat Alexandre (1), Schuurman Yves, Laurenti Dorothée, Geantet Christophe, Guilhaume Nolgen, Mirodatos Claude<br>1 - IRCELYON, UMR 5256, CNRS - Université Lyon 1 (France)  |
| <b>P2058</b>              | <b>PY-GC/MS AND EGA-MS INVESTIGATION ON FRUCTOSE, INULIN AND TOPINAMBOUR: THE PYROLYSIS PRODUCTS AND THE EFFECTS OF CATALYSTS</b><br>Massaro Arianna, Ribechini Erika (1), Colombini Maria Perla<br>1 - Dipartimento di chimica e chimica industriale, Università di Pisa (Italy)  |
| <b>P2059</b>              | <b>EFFECT OF ZEOLITE PORE SIZE ON CATALYTIC CONVERSION OF LIGNIN MODEL COMPOUNDS DURING PYROLYSIS</b><br>Moon Jaegwan (1), Park Shin Young (1), Lee Jae Hoon (1), Choi Joon Weon (2) (3)<br>1 - Department of Forest Sciences, CALS, Seoul National University, Seoul (South Korea), 2 - Graduate School of International Agricultural Technology, Seoul National University, Pyeongchang (South Korea), 3 - Institute of Green-Bio Science and Technology, Seoul National University, Pyeongchang (South Korea) |
| <b>P2060</b>              | <b>CATALYTIC PYROLYSIS OF LIGNIN USING CO- AND NI-DOPED ZEOLITE CATALYSTS</b><br>Nowakowski Daniel Jozef (1), Sajdak Marcin, Bridgewater Tony<br>1 - European Bioenergy Research Institute, Aston University (United Kingdom)  |
| <b>P2061</b>              | <b>EFFECT OF CALCIUM OXIDE ON YIELD AND COMPOSITION OF BIO-OIL OBTAINED FROM SUGARCANE BAGASSE FAST PYROLYSIS</b><br>Osorio Velasco Jessi (1), Chejne Farid (2)<br>1 - Universidad Nacional de Colombia (COLOMBIA) (Colombia), 2 - Universidad Nacional de Colombia (COLOMBIA) (Colombia)  |
| <b>P2062</b>              | <b>CATALYTIC FAST PYROLYSIS OF PONGAMIA PINNATA WASTE USING ZEOLITE Y PREPARED FROM COAL FLY ASH</b><br>Soongprasit Kanit (1), Sricharoenchaikul Viboon (2), Atong Duangduen (1)<br>1 - National Metal and Materials Technology Center, National Science and Technology Development Agency (Thailand), 2 - Department of Environmental Engineering, Faculty of Engineering (Thailand)  |
| <b>P2063</b>              | <b>NI-, FE-, CO- AND CU-BASED CATALYSTS FOR HYDROGEN PRODUCTION FROM CATALYTIC GASIFICATION OF BIOMASS</b><br>Wu Chunfei (1), Liu Xiaotong (1), Nahil Mohamad (2), Williams Paul (3)<br>1 - University of Hull (United Kingdom), 2 - MOHAMAD NAHIL (United Kingdom), 3 - School of chemical and process engineering (United Kingdom)   |
| <b>P2064</b>              | <b>STEAM REFORMING OF PYROLYSIS VAPORS OVER CHAR BASED CATALYST</b><br>Yanik Jale (1), Duman Gozde<br>1 - Ege University (Turkey)  |
| <b>P2065</b>              | <b>CATALYTIC PYROLYSIS OF OLIVE POMACE</b><br>Yanik Jale (1), Duman Gozde<br>1 - Ege University (Turkey)   |
| <b>BIOMASS / REACTORS</b> |  |
| <b>P2066</b>              | <b>FLUIDIZED BED PYROLYSIS OF OLIVE KERNEL BIOMASS IN A THERMOGRAVIMETRIC REACTOR</b><br>Al-Farraj Abbas (1)<br>1 - Cardiff University School of Engineering (United Kingdom)  |
| <b>P2067</b>              | <b>GUAYULE (PARTHENIUM ARGENTATUM) PYROLYSIS BIOREFINING - PRODUCTION OF HYDROCARBONS FROM GUAYULE VIA TAIL-GAS REACTIVE PYROLYSIS</b><br>Boateng Akwasi (1), Mullen Charles (1), Elkasabi Yaseen (1)<br>1 - ARS-USDA Eastern Regional Research Center (United States)   |
| <b>P2068</b>              | <b>EXPERIMENTAL COMPARISON OF FAST AND INTERMEDIATE PYROLYSIS AT PILOT SCALE</b><br>Funke Axel (1), Tomasi-Morgano Marco (1), Dahmen Nicolaus (1), Leibold Hans (1)<br>1 - Karlsruhe Institute of Technology (Germany)   |
| <b>P2069</b>              | <b>PROCESS SIMULATION OF THE CHEMICAL LOOPING PROCESS FOR HYDROGEN PRODUCTION USING HEAVY FRACTION OF BIO-OIL AND CARBON EMISSION ANALYSIS</b><br>Heng Lijun (1), Zhang Huiyan, Zhou Mengmeng, Xiao Rui<br>1 - Southeast University (China)  |
| <b>P2070</b>              | <b>PLASMA/CATALYST DEVELOPMENT TO PRODUCE HIGH QUALITY SYNGAS FROM BIOMASS</b><br>Nahil Mohamad (1), Williams P.t.<br>1 - MOHAMAD NAHIL (United Kingdom)   |
| <b>P2071</b>              | <b>CATALYTIC AND NON-CATALYTIC BIOMASS PYROLYSIS PROCESS IN A CONTINUOUS SCREW REACTOR</b><br>Solar Jon (1), De Marco Isabel, Caballero Blanca Maria, Lopez-Uriónabarrenechea Alex, Adrados Aitziber, Rodriguez Nélida, Gastelu Naia<br>1 - Chemical and Environmental Engineering Depart. (UPV/EHU) (Spain)   |
| <b>P2072</b>              | <b>PRODUCTION OF PYROLYSIS OILS FROM BROWN ALGAE USING AN AUGER-TYPE CONTINUOUS PYROLYSIS REACTOR</b><br>Suh Dong Jin (1), Choi Jae-Wook (1), Ha Jeong-Myeong (1), Jae Jungho (1)<br>1 - Korea Institute of Science and Technology (South Korea)   |

## POSTER SESSION 2: Wednesday 11 May & Thursday 12 May

|                                |   |
|--------------------------------|---|
| P2073                          | <b>TECHNO-ECONOMIC ANALYSIS OF DECENTRAL CHP CONCEPTS BASED ON PYROLYSIS</b><br>Tomasi Morgano Marco (1), Konath Tim (1), Leibold Hans (1), Richter Frank (1), Stapf Dieter (1)<br>1 - Karlsruhe Institute of Technology (Germany)  |
| P2074                          | <b>STUDY OF THE IMPACT OF BIOMASS COMPOSITION ON SYNGAS QUALITY IN A BUBBLING FLUIDIZED BED REACTOR THROUGH MODELING AND SIMULATION</b><br>Wang Meihong (1), Aneke Mathew (1)<br>1 - Process and Energy Systems Engineering, School of Engineering, University of Hull (United Kingdom)   |
| P2075                          | <b>STOCHASTIC REACTOR MODELLING FOR BIOMASS PYROLYSIS</b><br>Weber Kathrin (1), Li Tian (1), Lovas Terese (1), Seidel Lars (2), Perlman Cathleen (2), Mauss Fabian (2)<br>1 - Norwegian University of Science and Technology (Norway), 2 - LOGE AB (Sweden)   |
| P2076                          | <b>PYROLYSIS-GASIFICATION OF SAWDUST FOR HIGH H<sub>2</sub>/CO-RATIO SYNGAS THROUGH CHEMICAL LOOPING PROCESS IN A DUAL FLUIDIZED BED SYSTEM</b><br>Zeng Jimin (1), Xiao Rui (1), Zeng Dewang (1), Fang Yan (1), Shao Shanshan (1)<br>1 - Southeast University (China)   |
| <b>FOSSIL FUELS</b>            |   |
| P2077                          | <b>BIOMASS/COAL CONTAINING BRIQUETTES</b><br>Barriocanal Carmen (1), Florentino Laura, Diaz-Faes Elvira<br>1 - Instituto Nacional del Carbon - Consejo Superior de Investigaciones Cientificas (Spain)  |
| P2078                          | <b>USE OF ADDITIVES TO AVOID OXIDATION AND TO RECOVER THE COKING PROPERTIES OF BITUMINOUS COALS</b><br>Barriocanal Carmen (1), Vega Maria, Fernandez Ana, Casal M, Diaz-Faex Elvira<br>1 - Instituto Nacional del Carbon - Consejo Superior de Investigaciones Cientificas (Spain)  |
| P2079                          | <b>N AND S CONVERSION DURING PRESSURIZED PYROLYSIS UNDER CO<sub>2</sub> ATMOSPHERE IN FLUIDIZED BED</b><br>Duan Lunbo (1), Duan Yuanqiang, Cai Liang, Changsui Zhao<br>1 - Southeast University (China)   |
| P2080                          | <b>STUDY OF THE FORMATION OF AROMATICS IN THE PYROLYSIS OF CYCLOPENTENE</b><br>Herbinet Olivier (1), Rodriguez Anne (1), Husson Benoit (1), Battin-Leclerc Frédérique (1), Wang Zhandong (2), Cheng Zhanjun (2), Qi Fei (2)<br>1 - Laboratoire Réactions et Génie des Procédés (France), 2 - National Synchrotron Radiation Laboratory (China)  |
| P2081                          | <b>PYROLYSIS AND GASIFICATION OF HIGH ASH COAL IN STEAM AND CO<sub>2</sub></b><br>Jayaraman Kandasamy (1), Belandria Veronica (2) (1), Bostyn Stéphane (2) (1), Gokalp Iskender (1)<br>1 - Institut de Combustion Aérothermique Réactivité et Environnement (France), 2 - IUT d'Orléans (France)  |
| P2082                          | <b>APPLYING IONIC LIQUID TO INHIBIT COAL SPONTANEOUS COMBUSTION VIA GREEN ANALYTICAL METHODS AND KINETIC MODELS BY TG/FTIR</b><br>Laiwang Bin (1)<br>1 - Doctoral Program, Graduate School of Engineering Science and Technology, National Yunlin University of Science and Technology, Yunlin (China)  |
| P2083                          | <b>INFLUENCE OF PRESSURE (1 MBAR -1 000 BAR) ON THE PYROLYSIS OF ALKANES: EXPERIMENTS AND KINETIC MODELING</b><br>Lannuzel Frédéric, Bounaceur Roda (1), Burkle-Vitzthum Valerie (1), Michels Raymond (2), Scacchi Gerard, Marquaire Paul-Marie (1)<br>1 - Laboratoire Réactions et Génie des Procédés (France), 2 - University of Lorraine / CNRS / CREGU, GeoRessources Laboratory (France) |
| P2084                          | <b>HIGH PRESSURE PYROLYSIS OF HIGH-DENSITY HYDROCARBON FUEL</b><br>Liu Guozhu (1)<br>1 - Tianjin University (China)   |
| P2085                          | <b>CATALYTIC PYROLYSIS MECHANISM OF N-PENTANE TO PRODUCE LIGHT OLEFINS</b><br>Liu Guozhu (1), Hou Xu (2)<br>1 - Tianjin University (China), 2 - Tianjin University (China)  |
| P2086                          | <b>KINETIC ANALYSIS OF NON-ISOTHERMAL PYROLYSIS OF OIL SAND BITUMEN USING MULTIPLE GAUSSIAN-DISTRIBUTED ACTIVATION ENERGY MODEL</b><br>Shin Sangcheol (1), Im Soo Ik (1), Rho Nam Sun (2), Lee Ki Bong (1)<br>1 - Korea University (South Korea), 2 - Korea Institute of Energy Research (South Korea)  |
| P2087                          | <b>EFFECT OF ATMOSPHERE REACTION, COAL RANK AND HEATING RATE ON THE DEVOLATILIZATION OF COLOMBIAN COALS</b><br>Valdes Carlos (1), Chejne Farid (1), Roman Juan (1), Marrugo Gloria (1), Montoya Jorge (1)<br>1 - Universidad Nacional de Colombia (COLOMBIA) (Colombia)   |
| P2088                          | <b>USE OF A MECHANICALLY FLUIDIZED BED PYROLYSER FOR BITUMEN AND ASPHALTS APPLICATIONS</b><br>Villemont Clément (1), Briens Cedric (2), Berruti Franco (2), Mangin Patrice (3)<br>1 - Université du Québec à Trois Rivières (Canada), 2 - University of Western Ontario (Canada), 3 - Université du Québec à Trois Rivières (France)  |
| <b>HYDROCARBONS / KINETICS</b> |   |
| P2089                          | <b>CLOSED-SYSTEM PYROLYSIS OF ALIPHATIC ETHERS AT ELEVATED PRESSURE</b><br>Alpermann Theodor (1)<br>1 - Federal Institute for Geosciences and Natural Resources (Germany)   |
| P2090                          | <b>STUDY OF THE FORMATION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) FROM HYDROCARBON PYROLYSIS IN LOW-PRESSURE GAS CARBURIZING CONDITIONS</b><br>Bensabath Tsilla (1) (2), Monnier Hubert (1), Glaude Pierre-Alexandre (2)<br>1 - Institut national de recherche et de sécurité (France), 2 - Laboratoire Réactions et Génie des Procédés (France)   |
| P2091                          | <b>PYROLYSIS OF N-BUTYLCYCLOHEXANE AT HIGH PRESSURE (100 BAR). STABILITY OF NAPHTHENES IN PETROLEUM RESERVOIRS</b><br>Bounaceur Roda (1), Béhar Françoise (2), Rakotoalimanana Darwin (1), Burklé-Vitzthum Valérie (1), Marquaire Paul-Marie (1)<br>1 - Laboratoire Réactions et Génie des Procédés (France), 2 - Total E&P (France)  |
| P2092                          | <b>AROMATIC FORMATION DURING THE PYROLYSIS OF TETRAHYDROFURAN IN A JET-STIRRED REACTOR</b><br>Herbinet Olivier (1), Frottier Ophélie (1), Battin-Leclerc Frédérique (1)<br>1 - Laboratoire Réactions et Génie des Procédés (France)   |
| P2093                          | <b>KINETIC MODELING OF TRIS(3-CHLOROETHYL)AMINE PYROLYSIS</b><br>Lizardo Huerta Juan Carlos (1), Sirjean Baptiste (1), Verdier Laurent (2), Fournet René (1), Glaude Pierre-Alexandre (1)<br>1 - Laboratoire Réactions et Génie des Procédés (France), 2 - DGA Maîtrise NRBC (France)   |
| P2094                          | <b>MECHANISM OF DIBENZOFURAN PYROLYSIS AND OXIDATION</b><br>Marquaire Paul-Marie (1), Tritz Audrey, Ziegler-Devin Isabelle, Bounaceur Roda (1), Simon Yves<br>1 - Laboratoire Réactions et Génie des Procédés (France)  |
| P2095                          | <b>FUNCTIONALIZED CARBON-BASED SUPPORT MATERIALS FROM BENCH-SCALE BATCH PYROLYSIS FOR PHOTOCATALYTIC OXIDATION OF VOLATILE ORGANIC COMPOUNDS (VOCS)</b><br>Masek Ondrej (1), Colmenares Juan, Lisowski Pawel<br>1 - University of Edinburgh (United Kingdom)  |

## POSTER SESSION 2: Wednesday 11 May & Thursday 12 May

- P2096 KINETIC STUDY OF METHYLCYCLOHEXANE PYROLYSIS**  
Simon Yves (1)  
1 - Laboratoire Réactions et Génie des Procédés (France)
- P2097 MICROKINETIC MODELING OF HYDROGEN PRODUCTION BY CATALYTIC PARTIAL OXIDATION OF PROPANE OVER CeO<sub>2</sub>**  
Simon Yves (1)  
1 - Laboratoire Réactions et Génie des Procédés (France)
- P2098 PYROLYSIS OF DIETHYL ETHER IN A JET STIRRED REACTOR**  
Vin Nicolas (1), Battin-Lelerc Fr d rique (1), Herbinet Olivier (1)  
1 - Laboratoire R actions et G nie des Proc d s (France)
- P2099 EXPERIMENTAL AND AB INITIO STUDIES ON PYROLYSIS MECHANISM OF THREE ISOMERIC DIHYDROXYBENZENES**  
Yuki Furutani (1), Huamei Yang (1), Shinji Kudo (2), Jun-Ichiro Hayashi (2), Koyo Norinaga (2)  
1 - Interdisciplinary Graduate School of Engineering Sciences, Kyushu University (Japan), 2 - Institute for Materials Chemistry and Engineering, Kyushu University (Japan)

### INSTRUMENTATION

- P2100 BIOMASS PYROLYSIS REACTIONS AND PRODUCTS AS STUDIED BY THERMAL ANALYSIS TECHNIQUES**  
Andr  R. (1), Lebourleuxa G. (1), Mayoux C. (1), Wirth E. (1)  
1 - SETARAM Instrumentation (France)
- P2101 DEVELOPMENT OF A NOVEL SILICA-BASED MICROWAVE RECEPTOR FOR MICROWAVE PYROLYSIS APPLICATIONS**  
Hamzehlouia Sepehr (1), Latifi Mohammad (1), Legros Robert (1), Chaouki Jamal (1)  
1 - Polytechnique Montr al (Canada)
- P2102 DEVELOPMENT OF A NEW SAMPLING METHOD BY CARBON NANOTUBE BASED GECKO TAPE FOR PY-GC/MS**  
Nagai Yoshitaka (1), Kamiya Yoshimi (2), Honda Takayuki (3)  
1 - Graduate School of Science and Technology, Meiji Univ. (Japan), 2 - Tokyo Metropolitan Industrial Technology Research Institute (Japan), 3 - School of Science and Technology, Meiji Univ. (Japan)
- P2103 EXPANSION OF THERMAL ANALYSIS TECHNIQUE BY USING A PYROLYZER**  
Ozaki Ryo (1), Takayuki Honda (2)  
1 - Meiji University Graduate School of Science and Technology (Japan), 2 - Meiji University School of Science and Technology (Japan)
- P2104 MODIFIED PYROPROBE FOR STUDYING THERMOCHEMICAL REACTIONS: DESIGN, CHARACTERIZATION, AND EXPERIMENTATION**  
Pecha Brennan (1), Montoya Jorge (1), Howe Dan (2), Chejne Farid (3), Garcia-Perez Manuel (1)  
1 - Washington State University (United States), 2 - Pacific Northwest National Laboratory (United States), 3 - Universidad Nacional de Colombia (Colombia)
- P2105 NEW FURNACE-TYPE PYROLYZER FEASIBLE FOR HIGH-PERFORMANCE ANALYTICAL PYROLYSIS MEASUREMENTS WITH EASY INSTALLATION, OPERATION, AND MAINTENANCE**  
Watanabe Atsushi (1), Ito Koichi (1), Soll Michael (1), Terame Norio (2) (1), Ohtani Hajime (3)  
1 - Frontier Laboratories Ltd (Japan), 2 - Tohoku University [Sendai] (Japan), 3 - Nagoya Institute of Technology (Japan)



# ABSTRACTS

The following sections include abstracts of all papers presented during the symposium.

Abstracts are divided into topics, then type of presentation (oral, poster), and listed in alphabetic order by surname of the presenter or first author (as submitted in the platform).

**Abstracts topics are displayed in the following order:**

- Keynote lecture abstracts
- Special session abstract
  
- Analytical pyrolysis – oral presentations
- Analytical pyrolysis – poster presentations
  
- Biomass / Catalysis – oral presentations
- Biomass / Catalysis – poster presentations
  
- Biomass / Fast pyrolysis – oral presentations
- Biomass / Fast pyrolysis – poster presentations
  
- Biomass / Kinetics – oral presentations
- Biomass / Kinetics – poster presentations
  
- Biomass / Reactors – oral presentations
- Biomass / Reactors – poster presentations
  
- Biomass / Slow pyrolysis – oral presentations
- Biomass / Slow pyrolysis – poster presentations
  
- Bio-oil – oral presentations
- Bio-oil – poster presentations
  
- Fossil fuels – oral presentations
- Fossil fuels – poster presentations
  
- Hydrocarbon / Kinetics – oral presentations
- Hydrocarbon / Kinetics – poster presentations
  
- Instrumentation – oral presentations
- Instrumentation – poster presentations
  
- Organic geochemistry – oral presentations
- Organic geochemistry – poster presentations
  
- Waste / Reactors – oral presentations
- Waste – poster presentations



ABSTRACTS

# Keynote lectures

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## ANALYTICAL PYROLYSIS AS A TOOL FOR THE CHARACTERISATION OF ORGANIC MATERIALS IN CULTURAL HERITAGE

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Natural organic materials are common constituents of objects with artistic and historical value. Most paintings, artisanal artifacts of historical relevance and archaeological findings are made or contain organic materials of various origin and chemical nature, including plant and animal lipids, proteins and fibres, natural resins, waxes, polysaccharides, dyes and wood. In addition to natural materials, since the end of the 19<sup>th</sup> century, synthetic polymers have been produced and used in the field of cultural heritage, to restore works of art, but also as main constituents. Most of these materials are characterised by a macromolecular nature: in some cases they are polymers, others undergo oligomerisation or cross-linking reactions as an effect of time, exposure to light and air, and human processing.

Due to the macromolecular nature of all those materials, analytical pyrolysis coupled with gas chromatography mass spectrometry (Py/GC/MS) can be a fast and efficient approach for identifying such organic materials in samples from cultural heritage. Moreover, some of these organic materials cannot be chemically processed for GC/MS analysis and analytical pyrolysis is thus the only possible approach. The chemical composition of a sample is reconstructed on the basis of a detailed interpretation of the fragments produced, both in terms of molecular pattern recognition and presence of specific markers. Pyrolysis products of organic materials found in cultural heritage are often polar molecules with low volatility. In order to improve their chromatographic separation and analytical response, specific reagents are most commonly added to the sample prior pyrolysis, achieving the in situ thermally-assisted hydrolysis of specific bonds and the derivatisation of polar groups present in the pyrolysis products. Transmethylation (i.e. tetramethylammonium hydroxide), and silylation (i.e. hexamethyldisilazane) are the most common approaches adopted.

Analytical pyrolysis in the analysis of samples from cultural heritage objects, is not only an analytical methodology to be used for the identification of organic materials. It is also a fundamental tool of multi-analytical strategies aimed at understanding the chemical composition of the organic materials, and how this changes as an effect of their history and ageing environment. When studying objects of artistic and historical value, understanding the chemical changes undergone by their constituting materials as an effect of age, burial conditions, interaction with other organic and inorganic materials, photo-oxidative degradation, as well as the effect of physico-chemical processing adopted by men in order to obtain the wanted characteristics of the materials, is of fundamental importance. This knowledge is at the basis of a reliable identification of the source of organic materials found in samples of unknown composition, and is necessary to improve restoration methodologies and conservation strategies. In this context, analytical pyrolysis - intended as the chemical degradation of a material induced by heat - can not only be interfaced with GC/MS systems, but also be used in a variety of other instrumental configurations, for example in thermal gravimetric analysis (TGA), or coupled directly with a mass spectrometer (i.e. direct exposure mass spectrometry-DEMS, evolved gas analysis-mass spectrometry - EGA/MS), or infrared spectrophotometer (i.e. and thermogravimetric analysis coupled with Fourier transform infrared spectroscopy TGA/FTIR), giving insight into different aspects of the chemical composition of the investigated materials.

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## Kinetic modeling of pyrolysis reactions: from light gas to solids

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Pyrolysis is an important process, which has been extensively used since many years for the production of several products. Steam Cracking or Fluid Catalytic Cracking are examples of very common and recognized chemical processes. More recently it is worth considering the pyrolysis of biomass to produce bio-oils. Moreover, pyrolysis is a fundamental step in other phenomena. The combustion of gas, liquid and solid fuels is generally preceded by their pyrolysis.

Unfortunately, the chemical modeling of pyrolysis can be a very challenging problem, especially when considering liquid heavy feedstocks or solids. The dimensions and complexity of the mechanisms describing these processes justify the adoption of analogy rules and other simplifying assumptions within the different chemical reaction classes. The levels of simplification have to be carefully evaluated to make them coherent with the final aim of the model.

One of the most successful technique in the field is lumping, which groups together a large number of real components into a properly selected reduced number of equivalent components. The corresponding reactions need to be grouped in lumped reactions too.

This work aims at presenting the activity that the CRECK-modeling group at Politecnico di Milano has carried out during the years in modeling the pyrolysis of gas and liquid fuels first, of polymers after, and finally of biomasses. The main features and general rules will be presented and some examples will illustrate the results.

## GEOCHEMICAL TRANSFORMATION AND TRANSPORT PROCESSES AS REVEALED BY KINETIC DETERMINATIONS AND MOLECULAR INDICATORS

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Pyrolysis is widely used to examine the biological and diagenetic origins of complex, naturally-occurring geopolymeric materials by breaking them down into more readily analysable, volatile fragments. Geopolymers or macromolecules make up the biggest proportion of the global carbon budget (>95%), with the mass amounting to 10<sup>16</sup> tons, mainly in a dispersed form. Kerogen, the fraction of sedimentary organic matter that is insoluble in common organic solvents, is the major macromolecular component of sedimentary organic matter in rocks and precursor of petroleum. Relating the structure and composition of macromolecules to their precursor organisms and the diagenetic modification undergone since death, as well as modelling their progressive thermal degradation during progressive subsidence, are the fundamental lines of research being undertaken today in upstream (exploration and production) petroleum science.

The pyrolysis methods used for studying petroleum systems can be divided into two basic categories, one being dynamic and open (anhydrous) - used for evaluating present-day composition, - and the other static and closed (hydrous or anhydrous) - for simulating thermal degradation over geological timescales. Here we outline how, when used together, these methods enable the bulk composition of petroleum generated in source rocks to be assessed, and therefore PVT properties, to be predicted. In that regard, it is important to note that phase behaviour is the major control of gas versus oil occurrence in petroliferous basins.

Our methodology begins with the organofacies concept, which states that kerogen abundance and composition are relatable to depositional settings. Our facies, five in all, are based on potential petroleum type and are determined by the open system pyrolysis of kerogens or asphaltenes using programmed temperature heating. The results are essentially insensitive to temperature rise time because the macromolecules involved are depleted in heteroelements. Having used that method as a secondary screening tool, a smaller number of samples is usually selected for calculating the bulk kinetic parameters of petroleum generation. To do so, four heating rates are employed to measure pyrolysis rate curves, from which a single frequency factor and a distribution of activation energies are calculated in a first order kinetic model. Petroleum compositions are then assigned to the activation energy potentials using low pressure Microscale Sealed Vessel Pyrolysis (Horsfield et al., 2015), a method employing 40ul reaction vessels for online analysis of C<sub>1+</sub> components with high precision. The utility of this so-called PhaseKinetics approach (di Primio and Horsfield, 2006) has been proven by regional calibrations from petroleum systems worldwide.

In this presentation the pyrolysis systems themselves will be outlined, addressing reproducibility and linearity, speed and degree of sophistication. The results of PhaseKinetics modelling will be illustrated. Lastly, we will illustrate how the presence of tetralin and a catalyst in MSSV vessels releases biological markers from the macromolecular matrices, thereby enabling the biological origins and precursors of the released species to be ascertained..

### References

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## SOME STEPS IN THE DEVELOPMENT OF COKE MANUFACTURE IN EUROPE

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Today, the world coke production is about 700 million tons (Mt) per year. This production is growing with the industrial development of China. China alone produces now 480-500 Mt of coke per year. In 2000, its production was 120 Mt and the world production was around 350 Mt. The European Union produced about 39 Mt in 2014. It was producing 52 Mt in 2000 and 90 Mt in the 1980s, considering the same perimeter as present European Union.

Coke plants were constructed when coke started to be used in the blast furnace. The first who operated a blast furnace with coke was Abraham Darby in UK in 1709, more than 300 years ago. The number of blast furnaces operated with coke increased gradually in the 18<sup>th</sup> and 19<sup>th</sup> century. At the beginning of the 20<sup>th</sup> century nearly all blast furnaces used coke as fuel and reducing agent. In the 18<sup>th</sup> century coke was mainly produced in coke piles or beehive ovens without volatile matter recovery. The by-product recovery ovens technology developed in the middle of the 19<sup>th</sup> century. Various types of ovens were constructed in UK, Germany, Belgium, France. Many coking plants were erected near the coal mines in all countries, especially in Europe. Integrated coking plants in steel works were also constructed.

In the 20<sup>th</sup> century major changes in the coke oven technology appeared. Coke ovens became bigger, mechanized and environmental issues were reduced. In the first half of the 20<sup>th</sup> century coke ovens were 3 to 4 meter high. In the 1970s, tall ovens (up to 7.5 m high) were constructed. Fos-sur-Mer coking plant is one of the first examples in Europe. Then tall ovens (> 6 m) became the standard size. The average oven width was between 350 and 450 mm. In the 1980s wider ovens were proposed by German constructors, with oven chamber average width around 500 and 600 mm. The Kaiserstuhl III coking plant in the Ruhr (Germany) erected at the beginning of the 1990s went one step further with very big oven chambers: 7.63 m high, 18 m long and 610 mm wide. In Germany Ruhrkohle and German coke oven constructors proposed the so-called Jumbo Coking Reactor (h x l x w: 10 m x 20 m x 850 mm) charged with preheated coal and the concept of Single Chamber reactors with 2-product technology: coke and reduction gas production by cracking of the raw gas.

At the same time the demand for blast furnace was high. So various techniques were implemented to increase the productivity of coke oven batteries. A significant development was coal blend drying or preheating (250-260°C). Three technologies were industrially applied in several coke plants in Europe and in the rest of the world. The performance of preheating charging was very high but operation of the batteries was problematic: high pressure in the ovens, dust emissions, very high coking rate... Coal preheating was abandoned in most plants in the 1980s. Coke demand was lower than before so batteries came back to wet gravity charging or stamp charging.

Stamp charging is another significant development in coking plants. It started in Europe in the 19<sup>th</sup> century to produce coke from high volatile poor coking coals. Stamping allows to significantly increase the bulk density of the coal charge (from about 750 kg/m<sup>3</sup> to more than 1000 kg/m<sup>3</sup> on dry basis, with modern stamping machines) and to improve coke cohesion. Typical blends must be used to get high coke quality and avoid high swelling pressure resulting from the high bulk density. New 6.3 m high batteries at ZKS Dillingen (Germany) are State-of-the Art stamp charging batteries. These batteries are equipped with a pressure regulation system called SOPRECO to avoid door emissions. State-of-the-Art top charging batteries are the 2 batteries of 70 ovens of KBS Schwelgern coking plant in Germany. Ovens are 8.4 m high, 20 m long and 590 mm wide. Annual coke production is 2.75 million tons. Batteries are equipped with PROven pressure regulation system to avoid emissions during the carbonisation cycle.

When coal injection in the blast furnaces increased coke strength after partial gasification by CO<sub>2</sub> (measured by the CSR Nippon Steel Corp. standardized test) became more important. A lot of research work was carried out to find the way to increase coke CSR by action on the coal blend design, the blend preparation and carbonisation conditions. If in the 1980s a CSR value of 55-56% was considered as good, today target CSR values are around 70%.

## BIOMASS PYROLYSIS VAPOR AS AN INTERMEDIATE TO FUELS AND CHEMICALS

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Meeting greenhouse gas reductions will require renewable energy technologies for the transportation sectors (about 30% of the total energy use in the US and Europe) and fast pyrolysis of biomass presents a range of high throughput, low cost approaches to reach carbon reduction goals. Pyrolysis allows one to deconstruct the complex, heterogeneous mixtures of biopolymers present in plant matter in roughly one second and produce carbonaceous vapor at yields up to 70%. This presentation will discuss producing these vapors and catalytically converting them to produce liquid transportation fuels that can compete with existing fossil-based fuels.

The biomass pyrolysis step is quite complicated involving important unimolecular and biomolecular chemistry coupled with equally important heat and mass transport restrictions that arise from the structure of the biomass and the reactors that are necessary to volatilize solid materials. At a molecular level, depolymerisation and cracking of the biopolymers determine the product suite that is observed in pyrolysis vapors [1], but this chemistry occurs in heterogeneous mixtures within plant cell walls and is influenced by cell and plant anatomical structures (lumen, pits, vascular bundles, etc). Accurate heat and mass transport in particles of biomass requires detail accounting of these structures[2]. Finally, multiphase modelling of reactors provides an understanding of the effects of bulk heat and mass transport upon product composition.

Catalytic upgrading of pyrolysis vapors to produce fuels and chemicals can be accomplished using acidic catalysts, such as zeolites, at moderate temperatures, 500 °C. These catalysts facilitate coupling and dehydration reactions that result in the formation of primarily aromatic molecules, olefins and light gases. Rapid deactivation of the catalysts due to the build up of coke requires that short residence times and high biomass to catalyst ratios be used[3]. As a result, upgrading is best accomplished in circulating fluidized bed riser reactors[4], where short residence times are possible and the catalyst is regenerated by burning off the coke.

In order to improve the economics of vapour phase upgrading, it is necessary to increase the yields of hydrocarbons. Producing higher value co-products can also help and we are exploring both of these options. Optimizing reactor conditions[5] (steam composition, temperature, catalyst to biomass ratio, etc), adding reductants (H<sub>2</sub>, CO, etc) and modifying the catalyst can improve carbon yields and partially oxygenated intermediates are valuable precursors for polymer formation.

In addition to using zeolites, pyrolysis vapors can be upgraded using metals catalysts in the presence of molecular hydrogen. Hydrodeoxygenation and hydrogenation reduce the oxygenates in pyrolysis vapors and readily forms hydrocarbons.

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## **SUPPORTING THE INDUSTRY IN SCALING UP BIOMASS FAST PYROLYSIS TECHNOLOGY BY BUILDING ON PIONEERING WORK**

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Fundamental research related to fast pyrolysis of biomass dates back to the 60's and the 70's, when laboratory scale studies were carried out among others by F. Shafizadeh, A. Bradbury, A. Roberts, T. Nunn, W. Peters, J. Howard, M. Antal, T. Milne, E. Soltes, H. Stiles, and several others. Industrially driven efforts to produce liquid fuels employing fast pyrolysis were started after the first oil price crises. Occidental Petroleum built the first pilot scale pyrolysis unit in the 70's. After this work, pioneering process development work especially by D. Scott (at the University of Waterloo), J. Diebold (at SERI and later NREL), and J. Lede (CNRS) are important milestones. In the 90's, three pilot plants employing fluidized-bed (FB) technology were built in Europe, one based on UoW work in Spain (by Union Fenosa), and one based on the Ensyn technology in Italy (by ENEL). The third FB pilot plant in Europe was built in Finland by Fortum, based on its own technology. However, none of these developments were continued further, the low price of mineral oil being the major challenge at the time. While FB technologies were indebted to the work of Scott, the Dutch company BTG has developed and extended the ablative concept pioneered by Diebold and Lede. Interest in fast pyrolysis fuels was revived after the oil price increase starting around 2002, and three demonstration plants were built, commissioned and taken into operation: those of Fortum, Joensuu, in Finland by Valmet (planned capacity 50 000 t/a bio-oil), Empyro, Hengelo, in the Netherlands by BTG (22 000 t/a), and Renfrew, Ontario, in Canada by Ensyn (15 000 t/a).

Already during the 80's, first patents on the production of transportation fuels using hydroprocessing of pyrolysis bio-oil were published (D. Elliott at PNNL). Numerous fundamental studies using various pyrolysis technologies have since been initiated for the production of higher value products. During the 90's there was a rush of activities to (in-situ) catalytic pyrolysis: several European universities and institutes (BFH/TI, CERTH, University of Bilbao), UoW (collaborating with most groups on the field), C. Wang in Japan, and NREL. This technology has gained recently much new interest, and has been further developed among other by F. Agblevor (U of Utah), M. Olazar (UoB), I. Vasalos, and A. Lappas (CERTH). Employing zeolite catalyst to upgrade pyrolysis vapour (ex-situ) was developed by Diebold at NREL in the 90's. Later more alternatives have been developed, both based on both in-situ and ex-situ upgrading approaches. Co-processing of pyrolysis bio-oil in mineral oil refinery was first suggested by W. Baldauf (Veba Oel) in the early 1990's. Later this alternative has gained more interest. Co-processing of hydroprocessed (F. Mercader, University of Twente) and catalytic pyrolysis oils (F. Agblevor at Virginia Tech/USU) with vacuum gas oil in a refinery fluid catalytic cracking (FCC) unit has been proposed. Recently even thermal fast pyrolysis oil has been reported to be a potentially suitable co-feed in the FCC (A. Pinho, Petrobras). Also related to fast pyrolysis, in 2013 A. Boon at Shell has proposed an even simpler alternative by introducing wood co-fed directly to a FCC riser. This alternative should be a relatively low cost technology, provided overall carbon efficiency from biomass to bio-fuel components, a significant CO<sub>2</sub> emission reduction, and the remaining technical challenges are solved.



# MONTE-CARLO MODELLING OF THERMAL CRACKING OF RESIDUE FRACTIONS

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Over the last decades, the world demand for high-quality low-boiling products such as gasoline and diesel has continually increased. This trend stresses the importance of refining processes that convert heavy petroleum fractions, as residues, into lighter and more valuable clean products. Such petroleum residue conversion processes are generally based on the degradation of the largest molecules by thermal and/or catalytic cracking reactions at high temperature.

To accurately predict process performances, a reliable and accurate kinetic model is needed. Classic kinetic models for complex hydrocarbon mixtures use a lumped kinetics strategy, grouping molecules into chemical families, based on global properties. However, such models assume that similar physical properties result in similar chemical reactivities. Moreover, for heavy hydrocarbon mixtures, the number of families and reactions turns out to be so vast that this lumping approach is no longer manageable. These limitations lead to the development of more detailed kinetic models containing molecule-based reaction pathways, but these require a molecular description of the feed. Unfortunately, even the most advanced analytical techniques do not allow to identify the molecular detail of heavy petroleum feeds.

The present work focuses on the development of a two-step kinetic modelling strategy for heavy oil conversion processes. In this approach, the lack of molecular detail of the petroleum fractions is overcome by using a set of molecules that are carefully selected based on available analyses. The effect of conversion reactions is simulated by transforming each molecule, event by event, by means of Monte Carlo methods.

## Methodology

In a first step, the available analytical information is transformed into a set of molecules that has the same properties as the petroleum fraction. This "transformation" is carried out through a stochastic reconstruction (SR) algorithm. The petroleum fraction is represented by a series of probability distribution functions (pdf) for molecular structural attributes. These pdf's are sampled via a Monte Carlo procedure to determine the type and the number of structural blocks (cores, aromatic rings, alkyl chains, etc.) of a molecule. The construction of a molecule is repeated N times to obtain a mixture of molecules. The properties of the mixture are then compared to the available analyses, and an objective function is minimized by a genetic algorithm that modifies the parameters of the pdf's for structural attributes. In a second step, the effect of cracking is simulated on the generated set of molecules using a variable time step kinetic Monte Carlo simulation method. For each molecule, all potential reactions are identified and their associated rate constants are determined. These rate constants are calculated using appropriate Linear Free Energy Relationships (LFER) and represent the probability that a reaction occurs. After constructing cumulative probability distribution function, the next reaction and the time increment between the previous and the next reaction are randomly selected and executed. This procedure is repeated until the final simulation time is reached.

## Results

The above-described methodology was applied to thermal degradation of an Athabasca vacuum residue (VR). Elemental analysis (C, H, S, N, O), average molecular weight, specific gravity, simulated distillation, SARA separation and <sup>13</sup>C NMR were used to characterize the VR feed analytically. The vacuum residue was represented by a set of 5000 molecules in order to ensure an optimal balance between the required CPU time and the accuracy of the feedstock representation. The mixture properties obtained after the SR step show a good agreement with most of the analytical data. The kMC simulation then allowed to predict the conversion of the residue fractions. For each molecule, an algorithm makes an inventory of the possible reactions of the molecule, and calculates the corresponding rate coefficients by means of appropriate Linear Free Energy Relationships (LFER).

## Conclusions

A two-step modelling strategy for heavy oil conversion processes has been presented, consisting of a composition modelling step and a reaction modelling step. In this work, the methodology was applied to the conversion of an Athabasca vacuum residue. The simulation results were compared to the experimental data, illustrating that the combined "molecular reconstruction – stochastic simulation" approach accurately simulates the process performances. The proposed approach has several advantages: the complex feedstock is represented by means of a set of molecules. This representation allows to retain a molecular description of the reaction system throughout the entire reactor simulation. Moreover, the simulation of the reactions can be performed without a pre-defined kinetic network. In the kMC method, the kinetic network is generated "on-the-fly" as the reactions proceed.

# KEYS TO COMMERCIALY SUCCESSFUL COAL PYROLYSIS FOR PRODUCTION OF COAL TAR

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Pyrolysis provides the core technology for cascade utilization of coal, and research and development of coal pyrolysis technology can be dated back to 60 years ago. Although many different technologies have been tested in plants of pilot and industrial scales, there has not any coal pyrolysis plant in commercial running. After highlighting the necessity and current status of coal pyrolysis technology development, this report summarizes the critical challenges existing for establishing the commercially successful pyrolysis technology, and further analyzes the key techniques required to overcome such challenges. The presentation is then extended to our detailed work regarding an innovative pyrolysis reactor, the moving bed with internals, devised from such technical ideas. This covers fundamental studies at laboratory and process verification in a 1000 t/d pilot pyrolysis plant. Now, the technology is the way of building and running a 200 kt/a demonstration plant.

The obtained results from both laboratory and pilot tests show that the developed new pyrolysis technology enables high-yields production of both coal tar and pyrolysis gas. While the tar yield can reach 90% of the Gray-King Assay yield, the yield of pyrolysis gas containing about 70 vol.% H<sub>2</sub> and CH<sub>4</sub> is equivalent to that of coking oven. Especially, the new technology allows high production yield of coal tar at high temperatures such as around 1200 °C. The coal tar produced from the pyrolysis reactor has dust content low as 0.2 wt.%, remarkably lower than the dust contents above 10 wt.% for many other pyrolysis technologies. Meanwhile, the produced coal tar by the new technology has its density about 50 kg/m<sup>3</sup> lower than the tar from other pyrolysis plants such as coking oven, and its content of light fractions with boiling points below 360 °C is high as 70 wt.% in comparison with about 40 wt.% of the coal tar from coking oven. These parameters show that the new pyrolysis technology using the moving bed with internals has advanced technical performance, making its great potential to overcome the existing challenges of coal pyrolysis and successfully develop the commercial technology.

# CHEMICAL PROCESSING FOR FEEDSTOCK RECYCLING OF WASTE PLASTICS

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Recycling of materials such as waste plastics packaging, WEEE (Waste Electrical and Electronic Equipment) and waste vehicles and is one of the important issues from the viewpoint of the environmental problem and resource cycles. There are three categories such as mechanical recycling, feedstock recycling and energy recovery for the recycling of waste plastics. In any category, the processing is accompanied by some kinds of chemical reactions such as ionic and radical reactions. In particular, Polyethylene terephthalate (PET) and Polyvinyl chloride (PVC) are materials which are difficult to recycle due to chemical properties. In this presentation, I would like to focus on PET and PVC, and introduce some processing of the material recycling using their chemical reaction.

## 1. Selective Benzene Production from PET with alkali-compounds and Steam

It is a well known fact that sublimation substances, such as benzoic acid and terephthalic acid, are produced in the thermal decomposition of PET, and this causes problems in plastic recycling plants. However, it is clear that the addition of alkali oxide and hydroxide affect the high selectivity of benzene without producing sublimation substances [1]. First, PET was hydrolyzed in a steam atmosphere, and the resulting terephthalic acid was decarboxylized in the presence of alkali oxide. It was found that the best results were obtained at a decarboxylation temperature. The highest benzene yield of 80.7% and a purity of 90.2 wt% were achieved in the presence of  $\text{Ca}(\text{OH})_2$  and  $\text{Ba}(\text{OH})_2$ , respectively [2, 3]. Moreover, the selectivities for pyrolysis and hydrolysis during the steam decomposition of polyethers were quantified using  $^{18}\text{O}$ -labeled steam at different steam concentrations and decomposition temperatures. These results revealed that the selectivities for both pyrolysis and hydrolysis were significantly affected by the structure of the polyester. In addition, the thermogravimetric kinetic analysis of steam decomposition was consistent with the results of the  $^{18}\text{O}$ -labeling experiments [4].

## 2. Up-grade recycling of PVC using substitution reaction [5]

Polyvinylchloride (PVC) is one of the most common plastics in the municipal waste stream. In opposite to the other common plastics, it owns a high chlorine content of about 56 wt%. This makes it necessary to treat PVC separately from other plastics or, if not possible, to dechlorinate the entire plastic waste. In this review, we will describe the possibilities for the wet treatment of PVC. There are already processes applying aqueous sodium hydroxide solutions ( $\text{NaOH}(\text{aq})$ ) at temperatures between 200 and 250 °C at high pressure. The chlorine is removed mainly by the elimination of HCl, which is directly neutralized by NaOH, and NaCl is obtained. The dehydrochlorinated residue is a black solid material, which can be converted by thermolysis into char and oil. By replacing water by ethylene glycol (EG), high pressure can be avoided, making the whole process less expensive. The reaction can be carried out at a temperature just below the boiling point of EG at 196 °C. The lower polarity of the organic solvent offers also the advantage of a better contact between the solution and the solid PVC, leading to a more effective and faster dehydrochlorination of the PVC. The efficiency can be further improved by applying a ball mill or phase-transfer catalysts. Besides the elimination of HCl, the substitution of chlorine by hydroxyl groups takes place in a minor extent. More than 20% of the chlorine groups can be substituted at 190 °C, while more than 70% of the chlorine is eliminated in a NaOH solution. Other nucleophiles, such as azide and thiocyanate, have a similar effect on the elimination and substitution of chlorine. The reduction of the temperature increases the ratio between substitution and elimination, making it possible to obtain modified PVC from waste PVC with new properties.

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ABSTRACTS

# Special session

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# TOWARDS A REALISTIC KINETICS IN THE NON-ISOTHERMAL STUDIES. 30 YEARS OF A US-HUNGARIAN COOPERATION IN BIOMASS RESEARCH

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This presentation is a sort of commemoration of Michael J. Antal, Jr., who was an outstanding figure of the biomass community. It describes his cooperation with the author in the field of non-isothermal reaction kinetics in biomass studies. The consequences of this work for the future studies of complicated materials are also considered.

Biomasses and biomass products are rather complex materials. Their pyrolysis, gasification and combustion can rarely be described by single kinetic equations. Accordingly models based on more than one reaction should be assumed. The number of unknown model parameters obviously increases in this way. Such evaluation methods and strategies are needed that can provide dependable values for these parameters. The traditional linearization methods of the non-isothermal kinetics are not applicable here. The start of the work was the implementation of the (true, non-linear) method of least squares for non-isothermal experiments with models based on more than one reaction [1]. Reference [1] appears to be the first of its kind in the literature. As the work progressed, the simultaneous evaluation of experimental series became necessary [2], because the one-by-one evaluation of the experiments becomes mathematically undefined at the higher number of unknowns of a complex kinetic model. In a further step the information content of the experiments was increased by combining isothermal and non-isothermal sections in the temperature programs [3,4]. The last work of this cooperation was based on the simultaneous evaluation of linear, modulated and CRR (“constant reaction rate”) experiments<sup>1</sup> [5]. Besides the standard models of biomass pyrolysis and gasification, more complex cases were also examined. The thermal decomposition of cellulose in a confined environment was described by a multi-step reaction scheme combined with a hydrolysis reaction [2]. In another attempt more than one DAEM (distributed activation energy model) was employed so, that the differential and integral equations of the DAEM were solved numerically, without any artificial simplifications, and the curve fitting was based on the (true, non-linear) method of least squares [4]. When this cooperation reached its 10th anniversary, the results were summarized in a publication [6]. According to the Web of Sciences™, this special review has become the third article by the number of citations in the Journal of Analytical and Applied Pyrolysis.<sup>2</sup>

In my opinion, this road of development should be followed in the future; now without the wise advice of Michael J. Antal, Jr. The size and variety of the evaluated experimental series should be increased further and, on this basis, the complexity of the employed models could also be augmented. The aim is to find realistic models that could cope with the complex chemistry of the various biomasses and biomass products. The considerations outlined are hoped to be applicable outside of the biomass research, too.

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<sup>1</sup> The adding of a modulation (sine wave) to a linear T(t) is a well-known way to increase the kinetic information of the linear T(t) experiments. The CRR heating programs are irregular T(t) functions which results in a limited overall reaction rate.

<sup>2</sup> When the articles of this journal are listed with the “Times Cited – highest to lowest” sorting criterion in Web of Sciences™.



ABSTRACTS

# **Analytical pyrolysis**

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**Oral presentations**

## PYROLYSIS OF TIRE TRACES TO HELP RECONSTRUCT TRAFFIC ACCIDENTS: STUDY OF THE VARIATION OF TIRE CHEMICAL PROFILES

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Traffic accidents happen every day and represent the 8th cause of death in the world according to the World Health Organization [1]. Some of these accidents can lead to a forensic investigation in order to help the establishment of the sequence of events [2]. This is done by a reconstruction of the accident with the help of all traces collected on the scene and/or the involved objects (e.g. car, traffic sign, motorcycle's helmet).

Among the different traces used to reconstruct a traffic accident, tire traces are very useful (e.g. estimation of the trajectories, points of impact). One key step is the assessment of which vehicle is the source of the tire traces observed on the scene. The authors proved that chemical analysis by Py-GC/MS of the particles of tire traces is relevant to address this issue [3,4]. The Py-GC/MS method was developed and optimized with experimental designs in order to obtain the most repeatable results (i.e. low variation between replicates). Braking tests were then conducted on a racetrack to produce tire traces. Ten tires of different brands and models were used for these braking tests. The optimized Py-GC/MS method was applied on particles collected from the traces and on specimens of the ten tire treads at the origin of these traces. The abundance of 86 selected pyrolysates was integrated, normalised and pre-treated for each analysis to compare the pyrograms. A complete study of the variability within each specimen (i.e. trace or tire) and the variability between specimens was conducted on these data. This was done with the help of several multivariate statistics methods. The within variation was found lower than the between variation and full differentiation of the ten tires was achieved. Finally, the results demonstrated that the traces could be correctly linked to their tire source.

The next important step was to study whether the chemical profile varies between different tire treads in a given population. We have evaluated this variability on a random sample set of 60 tires divided into 11 brands and 22 models, with the developed Py-GC/MS method. Each tire was analysed three times and the chemical profile of each analysis was represented by the relative abundances of the 86 pyrolysates. Several reference materials included in tread formulation were also analysed and this led to the identification of around the half of the 86 pyrolysates of the tires. The data of tires (180 replicates of 86 variables) were treated with the help of multivariate statistics methods (e.g. Principal Component Analysis - PCA). The majority of the 60 tires are well separated according to the *model of tire*. In other words, chemical profiles of tires of different models are mainly discriminated between them supporting that tread formulations vary between models of tires. The study of the PCA loadings highlighted the most influent pyrolysates for the discrimination (e.g. isoprene and dipentene coming from natural rubber or synthetic polyisoprene).

This study on the between variation was finally combined with the data of traces to create a decision model to determine if two chemical profiles are differentiated or non-differentiated. This decision model was tested with blind tests and correct results were obtained. As a final point the developed methodology has been already used on real cases to help determine which vehicle was the source of a particular tire trace in a traffic accident involving several vehicles.

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## Value-added nitrogenous chemicals evolution from the pyrolysis of chitin and chitosan

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Chitin and chitosan (the deacetyl chitin) were the renewable and sustainable natural nitrogenous compounds, which can be transferred into value-added nitrogenous chemicals. This conversion can be achieved by the promising pyrolysis rapidly. In this study, the isothermal and non-isothermal pyrolysis processes and the nitrogenous chemicals evolution from chitin and chitosan were investigated. During the non-isothermal pyrolysis, the thermogravimetric characteristics, the kinetics, and the char residue evolution from chitin and chitosan were contrasted. The results showed that the two feedstocks both have only one major weight loss stage. In this stage, volatiles, including H<sub>2</sub>O, CO<sub>2</sub>, acetyl carbonyls and hydroxyls, were released. Wherein, the maximum weight loss temperature of chitin pyrolysis (397 °C) was higher than that of chitosan pyrolysis (298 °C). Meanwhile, the first-order kinetic model was established with the Coats–Redfern method, and the activation energy of chitin pyrolysis was 114.05 kJ·mol<sup>-1</sup>, which was slightly higher than that of chitosan pyrolysis (106.87 kJ·mol<sup>-1</sup>). Furthermore, the char residue evolution suggested that both carbonization and aromatization of the two feedstocks were aggravated after the maximum weight loss temperature. During the isothermal fast pyrolysis, the acetamido groups in chitin and chitosan were removed and transferred into acetic acid or acetamide. At the same time, the pyrolysis degradation contributed to the formation of some small molecule compounds (acetaldehyde, acetone, 1-hydroxy-2-propanone, and so on). Moreover, many acetamido chemicals, such as acetamido acetaldehyde (17.92%) and N-ethenyl-N-methyl acetamide (4.60%), were produced from the fast pyrolysis of chitin. The formations of these acetamido chemicals mainly benefited from the ring-opening depolymerization with the acetamido groups retaining. Different from the fast pyrolysis of chitin, chitosan was mainly pyrolyzed into pyridine, pyrazine, pyrrole, and their derivatives, which relative contents were up to 50.50% at 600 °C. The formations of these aza-heterocyclic chemicals came from the condensation reactions of primary amines and carbonyls, which profited from the free amino groups in chitosan. These differences in pyrolysis properties and formation routes of end products between chitin and chitosan were mainly because of their acetamido groups and amino groups. In summary, chitin can be used to produce acetamido chemicals through pyrolysis, and chitosan to aza-heterocyclic chemicals.

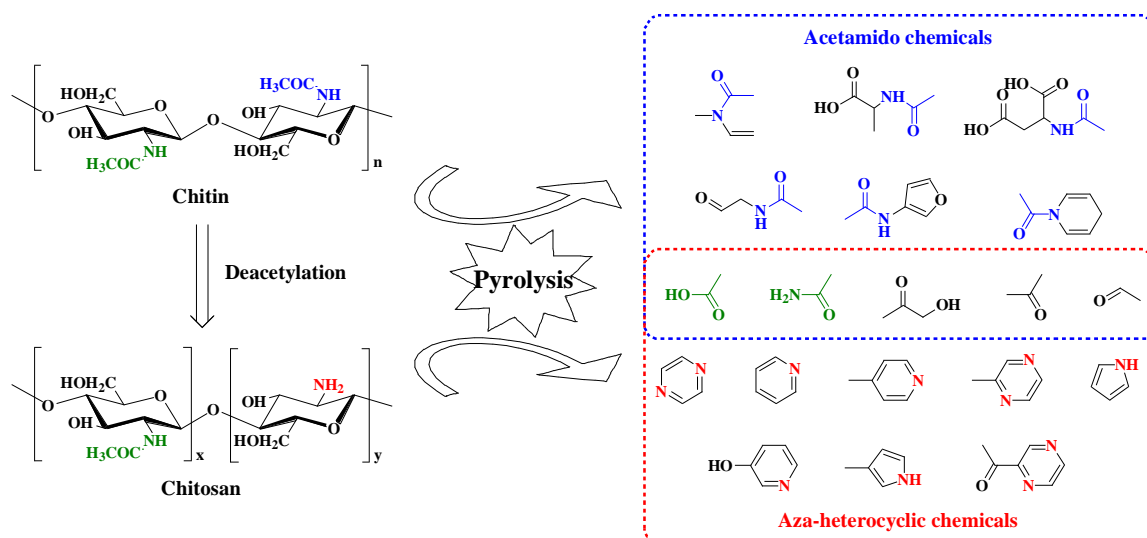


Figure 1 Value-added nitrogenous chemicals evolution from the pyrolysis of chitin and chitosan



## DETAILED ANALYSIS OF LESS VOLATILE PRODUCTS FORMED DURING THERMALLY ASSISTED HYDROLYSIS AND METHYLATION OF POLYMER SAMPLES

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Pyrolysis products formed during pyrolysis gas chromatographic (Py-GC) measurements of polymer samples are generally categorized into three fractions; 1) highly volatile pyrolyzates, 2) less volatile products, and 3) solid residues. Among these, only the volatile pyrolyzates can be observed in the pyrograms. However, the less volatile products are usually excluded from the analysis due to the use of GC separation, even if they possess useful information for the structural characterization of the polymer samples. Recently, we developed a pyrolysis device suitable for the measurements of the less volatile pyrolyzates [1]. This device is comprised of a pyrolysis unit based on the vertical microfurnace pyrolyzer and a movable pyrolysis tube made of stainless steel. The upper side of the pyrolysis tube is first set at the heated center of the pyrolysis unit. A polymer sample in a sample cup is introduced into the heated center and pyrolyzed under the flow of nitrogen carrier gas. The pyrolyzates are then transferred to the bottom side of the pyrolysis tube which is cooled down by air blow and the less volatile pyrolyzates are condensed. After that the pyrolysis tube is moved down out of the pyrolysis unit and blocked from the hot zone by moving the three port valve. Finally the trapped pyrolyzates are flushed by an appropriate solvent into a collection vial. The recovered pyrolyzates in the solution can be then subjected to the measurements suitable for less volatile products such as matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) and electrospray ionization (ESI)-MS combined with liquid chromatographic separation. The usefulness of this device was demonstrated by the recovery and observation of less volatile oligomeric pyrolyzates from some polymer samples.

In addition to ordinary Py-GC, thermally assisted hydrolysis and methylation (THM)-GC using tetramethylammonium hydroxide (TMAH) has been widely utilized for the characterization of intractable condensation polymers such as polyesters and polycarbonates. Even during the THM reaction of polymer samples, less volatile products are occasionally formed, and should be able to be analyzed by using the developed pyrolysis device. We have already reported that methyl acrylate oligomers formed by THM of a photocured acrylic resin sample are detected up to 18-mers in MALDI mass spectrum of the recovered products by this technique [1].

In this work, this method was applied to evaluate the efficiency of THM reaction of poly(butylene terephthalate) (PBT). Through the selective THM reaction at the ester linkages, PBT should be decomposed exclusively into 1,4-butane diol and its methyl derivatives, and dimethyl terephthalate. The observed yields of these products, however, are usually less than those expected in the THM chromatogram of PBT. This fact suggests that THM of PBT does not proceed quantitatively. However, direct evidence of insufficient THM reaction of PBT is hardly obtained by THM-GC measurement alone although minor peaks of products containing an ester linkage are sometimes observed in the THM chromatogram of PBT. In order to observe the larger products formed during THM of PBT, powdered PBT sample mixed with TMAH solution in a sample cup was introduced into the developed pyrolysis device at around 300 - 400 °C, and then the recovered products were subjected to MALDI-MS measurements. In the resultant MALDI mass spectra, various larger products from PBT, containing several ester linkages, were observed, indicating insufficient hydrolysis of ester bonds during THM reaction. Furthermore, the products with vinyl and/or carboxyl terminals were also detected in the mass spectra, which indicate that not only hydrolysis but also ordinary pyrolysis contribute to some extent to THM procedure of PBT. The formation yields and the distributions of the larger products varied depending on THM temperature and/or the amount and concentration of added TMAH solution. This information should be helpful to optimize THM-GC conditions of polymer samples.

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## BENEFITS OF THE USE OF PY-GCxGC/MS COMPARED TO PY-GC/MS: AN ILLUSTRATION THROUGH TWO EXAMPLES TAKEN FROM CULTURAL HERITAGE STUDIES

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The identification of molecular constituents within complex organic mixtures is typically achieved after a chromatographic separation. The most common technique for volatile analysis is gas chromatography (GC) coupled to mass spectrometry (MS), in order to make possible the separation and identification of individual molecular components in complex mixtures. However, many analytical applications still require a resolution power much higher than that provided by a single dimension. The introduction and development of comprehensive two-dimensional gas chromatography (GCxGC) offers greatly enhanced resolution and identification of organic analytes in complex mixtures compared to any one-dimensional separation technique. Initially promoted by the need to resolve highly complex petroleum samples, the technique's enormous separation power and enhanced ability to gather information has rapidly attracted the attention of analysts from all scientific fields. The revolutionary aspect of comprehensive GCxGC is that the entire sample is resolved on two distinct capillary columns of complementary selectivity, which results in enhanced peak resolution and peak detection. The increased resolution in combination with a third selective detection dimension (mass spectrometry) currently makes the comprehensive GCxGC/MS methodology the most powerful analytical device for the analysis of volatile and semi-volatile organic compounds [1].

In the past, the introduction of pyrolysis for the analysis of polymer samples permitted to enlarge the scope of analysis of polymers and natural materials through Py-GC/MS experiments [2]. Logically, coupling of Py with comprehensive GCxGC has found applications in the field of petrochemical analysis [3] but, direct on-line applications of Py-GCxGC/MS are not so commonly reported. To our knowledge, vertical furnace Py-GCxGC/MS has not been developed for Cultural Heritage applications.

We are proposing here an illustration of the benefits provided by Py-GCxGC/MS compared to Py-GC/MS for applications in the field of Cultural Heritage through the analysis of archaeological samples.

Two examples will be presented: (i) the analysis of collagens extracted from archaeological bones potentially contaminated by soil organic matters, (ii) the analysis of ancient East Asian papers samples, for which the identification of markers of origin allows the recovery of ancient manufacturing techniques.

These examples clearly demonstrate the great potential of Py-GCxGC/MS which provides (i) an increased sensitivity in comparison with Py-GC/MS due to focusing of the peak in the modulator resulting in narrow peaks with width at half height of 0.1 s or less, and increased separation from chemical background, (ii) an immediate and exhaustive fingerprint of the samples allowing differentiation of samples of slightly similar composition but, for which, changes are bearing high value information (e.g. ageing processes).

They illustrate how the selectivity of GCxGC increases the potential of pyrolysis coupled to gas chromatography for the distinction of collagen markers and contaminants in a one shot analysis through the analysis of the two-dimensional pyrograms. They also convincingly demonstrate the added-value of Py-GCxGC/MS in sample profiling for e.g. establishing composition-origin relationships as exemplified for traditional East Asian papers.

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## AMDIS & EXCEL: A POWERFUL COMBINATION FOR EVALUATING PY-GC/MS RESULTS

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Pyrolysis-gas chromatography/mass spectrometry using tetramethylammonium hydroxide for thermally-assisted hydrolysis and methylation (THM-Py-GC/MS) is presently the best analytical technique for comprehensive characterization of organic materials in Asian and European lacquers. A daunting challenge, though, is systematically sorting through the vast number of chromatographic peaks in order to accurately locate marker compounds that are characteristic of lacquer artists' materials.

AMDIS (Automated Mass spectral Deconvolution and Identification System) software, developed by NIST, is proven to be capable of extracting and locating library marker compounds in highly complex GC/MS data files. An AMDIS marker compound library of more than 700 compounds representing Asian and European lacquer and a number of other artists' materials has been compiled from information in various publications and private communications. A customized Excel workbook was developed to semi-automatically analyse and interpret the marker compound information in the AMDIS search report, using interpretation guides based upon knowledge shared by experts in material characterization that aid in accurate identification.

These software tools have been used in training workshops, organized by the Getty Conservation Institute, by scientists with varying levels of GC/MS experience to successfully identify artists' materials in complex samples from lacquered works of art. Based upon positive feedback from the workshop participants and successful application in their laboratories, we have concluded that the tools may be considered as an Expert System for Characterization with AMDIS Plus Excel (ESCAPE). Examples will be shown for using ESCAPE to identify a wide range of natural products in samples from lacquered objects and easel paintings.

## PYROLYSIS/GC-MS PROFILING AS A FAST PROCEDURE TO IDENTIFY THE INFLUENCE OF EXCESS CARBON AND LIMITED NITROGEN ON POLYHYDROXYALKANOATE MONOMER BIOSYNTHESIS BY *Bacillus thuringiensis*

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There is strong interest in research of biologically-derived polymers for the production of bioplastics. Polyhydroxyalkanoates (PHAs) are naturally-occurring polymers utilised in bioplastics. Microorganisms can produce the PHA plastic building components as a by-product of their cellular processes. It was found that bacterial strains are capable of PHA-production when grown in environments rich in excess carbon but limited in nitrogen, phosphorus, oxygen or magnesium contents. The current study used pyrolysis/GC-MS (Py/GC-MS) to investigate and compare PHA-monomer production by *Bacillus thuringiensis* when grown in a 30:1 ratio of carbon:nitrogen source. Thirty-six different nutrient combinations were used, each consisting of an excess of mannose, glucose, sucrose, cellulose, fructose, carboxymethylcellulose (CMC), starch, lactose or glycerol as carbon source and a shortage of NH<sub>4</sub>Cl, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, yeast extract or tryptone as inorganic and organic nitrogen sources, respectively. The fermentation conditions of the reaction vessels were, 14 d; 30 °C; 90 rpm with samples being taken after 24 h and 14 d for Py/GC-MS analysis (where tetramethylammonium hydroxide was used as a derivatising agent) and for making smears which were subjected to the Sudan Black B staining assay. The inorganic nitrogen sources proved to have no or little influence on PHA-production. PHA monomers were not detected when *B. thuringiensis* was grown in (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> in combination with any of the carbon sources. Whereas growth in NH<sub>4</sub>Cl in combination with cellulose or fructose resulted in only 9-Octadecenoic acid and 2-butenic acid 4,4-dimethoxy being synthesized, respectively. A general trend noted when yeast extract was used in combination with glucose, sucrose, cellulose, fructose, CMC, lactose or glycerol, was that either short chain length monomers consisting of 2, 4, or 5 carbons or long chain length monomers consisting of 16, 17, 18 or 19 carbons were observed after 24 h and 14 d. Of particular note was production of both 2-Butenoic acid and 2-Pentenoic acid in the cellulose and tryptone media combination, which according to literature are the monomeric units of poly(3-hydroxybutanoate-co-3-hydroxyvalerate) also known as the PHB-HV copolymer. Tryptone in combination with either sucrose or glucose, produced the short chain length 2-Butenoic acid. Only the tryptone and cellulose combination produced two medium length monomers, 2-Undecenoic acid and 2-Hexenoic acid, only after 24 h and 14 d, respectively. Tryptone in combination with glucose, sucrose, cellulose, fructose, CMC, starch or lactose produced long chain monomer consisting of either 16, 17, 18 or 19 carbons. Other general overall trends observed were that monomers found at 24h were absent after 14d with noticeably different, longer chain monomers being observed after 14d. Monomers that were present at 24h increased and/or decreased after 14. Lastly, monomers were present after 14d which weren't initially present after 24h. The staining effect was differ amongst the various nutrient combinations. Results from the Sudan Black B staining assay revealed that the intensity and number of black-stained cells increased after from 24 h to 14 d.

The current study demonstrated that Py/GC-MS was effective for the rapid characterisation of PHA-monomer production by nutrient stressed *B. thuringiensis* due to alteration of carbon and nitrogen sources. Organic nitrogen sources had a greater impact on PHA-monomer production in comparison to the inorganic nitrogen sources Previous studies report that the Sudan Black D staining assay is specific for intracellular polyhydroxybutyrate detection. However, the current study demonstrates the Sudan Black B staining assay can also be used for the detection of other types of intracellular PHAs and PHA co-polymers.

# DIRECT ANALYSIS OF RESIDUAL CHROMOPHORES ON PULP FIBRES USING PY-GC/MS

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## Abstract:

Brightness reversion is an unwanted phenomenon that frequently occurs in bleached wood pulps and products. A solution to this problem requires analysis and characterisation of the compounds (chromophores) that are the cause of the reversion. Currently, such characterisation and analysis methods are long and tedious as they entails extraction of the compounds followed by their analysis – a tall order considering that these compounds occur at very low concentrations. A typical analysis can take up to a week. We have explored using Py-GC/MS for direct analysis of chromophores on fibres in wood pulps – thus negating the need for prior extraction of the chromophores. Chromophores were identified in fully bleached chemical pulps and their concentrations were higher in the pulps that had experienced brightness reversion. The technique was then used to study the impact of cooking and bleaching conditions on the formation of chromophores. The results show that the main contributing factors to brightness reversion are furans and conjugated ketones. It was observed that the bleaching chemicals also have a significant impact on the formation of chromophores. This study revealed Py-GC/MS as a promising tool for direct analysis of residual chromophores in fully bleached chemical and in-process pulps. Thus we have developed a rapid and accurate method for analysis of chromophores directly on wood fibres.

**Keywords:** Chromophores, dissolving wood pulp, furans, ketones, Py-GC/MS, brightness, reversion

## IMPROVEMENT OF AROMATICS COMPOUNDS PRODUCTION FROM PYROLYSIS OF SCRAPS TYRES RUBBER USING HETEROPOLYACIDS BASED CATALYSTS

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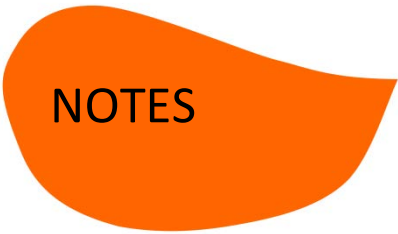
This research study presents the results of the improvement of aromatics compounds production produced by rubber of scrap tyres pyrolysis using heteropolyacids based catalysts.

For the catalyst synthesis were used four heteropolyacids as active phase:  $H_3PW_{12}O_{40}$ ,  $H_3PMO_{12}O_{40}$  and  $H_3PMO_{11}VO_{40}$ . The active phases were impregnated by the method of wet impregnation on commercial silica CARICT Q-10 (Fuji Silysia Chemical LTD). The catalysts were characterized by  $N_2$  adsorption - desorption, TPD  $NH_3$  desorption and pyridine adsorption-FTIR. These analysis allow the determination of the textural properties, total acidity, types of acid sites and the number of acid sites to each catalyst.

Initially, the experimental tests were carried out in a laboratory fixed bed reactor with two independent thermal zones. Two experimental set of tests were performed; the first constituted only by a thermal pyrolysis step in which the rubber of scrap tyres is transformed in vapours and gas compounds and the second constituted by a thermal pyrolysis step, exactly the same to the first test, and a catalytic step to reforming the vapours produced in the first step. For thermal pyrolysis, the reactor was charged with glass wool at the low zone and 9,7 g of tyre rubber at the high zone. The tests were performed at 466 °C, nitrogen flow of 155 Nml/min, pressure of 1 bar(g) and reaction time of 1 h. For the thermal pyrolysis with an additional catalytic step, the reactor was charged at the high zone with catalyst supported in glass wool and at low zone with tyre rubber (9,7 g), the mass catalyst/tyre rubber ratio was 0,2. The tests were performed at 466 °C for the low zone and 350 °C for the high zone, the pressure, nitrogen flow and reaction time were the same to thermal pyrolysis tests.

For all tests, the oil, char and gas yields are determined. The oil obtained in each test was recollected and characterized by GC-MS and GC-FID to identified and quantified the aromatics compounds. The aromatics concentration and yields obtained by two different tests were compared. The results show an increasing in the mass fraction of aromatics compounds when a catalytic step is added; increasing of 12.98, 20.55 and 20.99 wt% to  $H_3PW_{12}O_{40}$ ,  $H_4PMO_{11}VO_{40}$  and  $H_3PMO_{12}O_{40}$ , respectively, were observed experimentally. The results allow to confirm that the use of acid catalysts favours the aromatics production to a certain extent, as they also decrease the oil yield. In conclusion, it is possible to affirm that the concentration of aromatics compounds could be increased significantly using acid catalysts as heteropolyacid, in the pyrolysis process and according with analysis this can to be due to decomposition of dipentene (D, L limonene) and the secondary reactions of alkenes.

Finally, catalytic stability on the time was determined for each catalyst, the same operating conditions of second set of tests were used except that the catalytic step were charged with reused catalyst. Each one of them was reused one or two time for a total of 2 and 3h of reaction time for each catalyst. For all tests, the oil, char and gases yields were determined. The aromatics concentration in oil was calculate at end of each and compared with the results for the fresh catalysts. The activation time of  $H_3PMO_{12}O_{40}$  is the shortest compared with the other two, in the first hour of operation has the highest concentration of aromatics, however, deactivation is very quick and after the second hour of operation, the concentration of aromatic decreased. For determine the coke adhered during the catalyst test, a thermogravimetric analysis was performed for each reused catalyst. The test was performed in a thermogravimetric balance of TA-Instrument brand, model 2050 under the ASTM-D7582-12 standard. The results showed that the coke deposited on the catalysts is approximately 10%, this amount remained steady after 2 and 3 hours of reaction time.



NOTES

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ABSTRACTS

# **Analytical pyrolysis**

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**Poster presentations**



# CHARACTERIZATION OF ACRYLONITRILE-1,3-BUTADIENE-STYRENE/POLYAMIDE 6 (ABS/PA6) BLENDS BY PYROLYSIS-GAS CHROMATOGRAPHY (PY-GC) WITH DIFFERENT DETECTOR SYSTEMS

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Blends of acrylonitrile-1,3-butadiene-styrene (ABS) copolymer and polyamide 6 (PA 6) were characterized by analytical pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) and analytical pyrolysis-gas chromatography with flame ionization detector (Py-GC/FID) at 700 °C, respectively. The separated compounds were identified by using the mass spectral library and by calculation of the relative retentions. These blends have been chosen, since they play an important role in the automotive industry.[1]

Fivefold determinations of the polymer blends were carried out respectively with both methods. The peak area ratios of five major degradation products like acrylonitrile, toluene, styrene,  $\alpha$ -methylstyrene and caprolactam, were determined. The obtained analytical results were then used to compare the reproducibility of both GC/MS and GC/FID methods. With the aid of these results the relative standard deviation (RSD) of the determined peak area ratios was calculated. The performed statistical tests lead to the conclusion that the GC/FID method is more suitable for the quantification purposes than the GC/MS method.[2]. Current work is aimed now at quantification of blends composition.

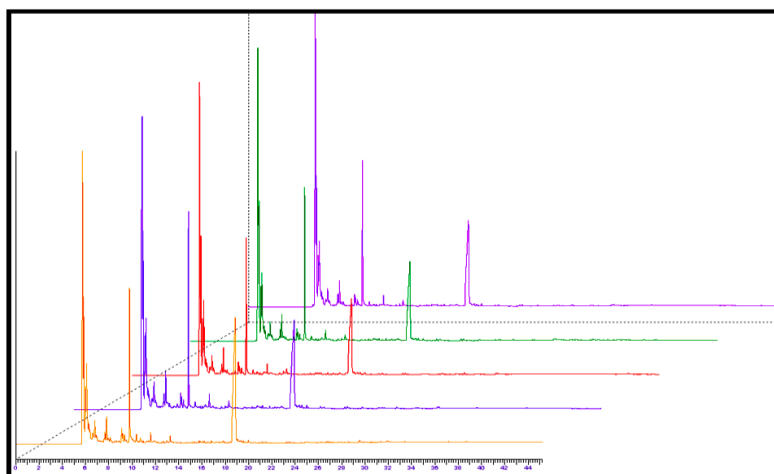


Figure 1 : GC/FID chromatograms of pyrolysates of a ABS/PA 6 blend at 700°C (fivefold determination)

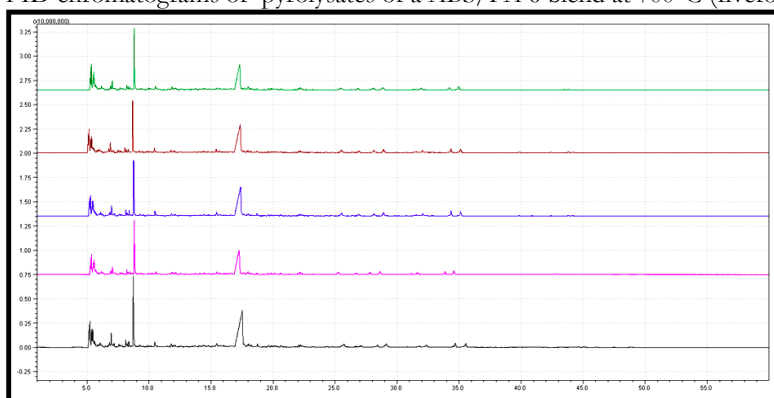


Figure 2 : TIC of pyrolysates of a ABS/PA 6 blend at 700°C (fivefold determination)

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## PYROLYSIS STUDY OF WOOD DEGRADATION CAUSED BY INORGANIC COMPOUNDS

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Wood is often treated with inorganic preservatives or fire retardants to prolong its service life. Protection against wood boring fungi and/or insects provides metal ions (arsenic, chromium, copper, zinc or mercury), some boron and fluorine compounds or sodium chloride. Ammonium salts and boron compounds are frequently used as fire retardants [1, 2]. But long-term exposure to inorganic compounds could accelerate degradation reactions and damage wood structure. Treating with inorganic compounds may lower pH value thus accelerating hydrolytic reactions. Transition metal ions may act as catalyst of oxidation. During treatment undesirable swelling may occur, causing decrease of mechanical strength. Recrystallization of inorganic compounds may cause mechanical damage of wood structure [2, 3]. Defibrillation of wood is a usual consequence of presence of higher amount of inorganic compounds [4].

The purpose of this study was to investigate the degradation of wood caused by the exposure to inorganic compounds. An analytical strategy mainly based on analytical pyrolysis techniques (EGA-MS and Py(HMDS)-GC/MS) was adopted to investigate a set of samples prepared by treating fir (*Abies Alba*) sawdust with solutions of chosen inorganic compounds (ammonium dihydrogen phosphate, ammonium chloride, ammonium sulphate, sodium chloride, sodium tetraborate decahydrate, copper sulphate pentahydrate, boric acid, zinc sulphate heptahydrate and hydrated iron (III) sulphate). After treatment, the samples were exposed to two different artificial ageing conditions: 60°C and combination of 60 °C and 80 % RH. All the results were compared to those obtained for an untreated unaged reference sample.

The difficulty for this kind of analysis regards the influence of inorganic compounds on pyrolysis reactions [5]. Generally, the changes observed in the results could be attributed to wood degradation and/or different yields of pyrolytic reaction pathways. To separate these two contributions, the samples were analysed before and after washing them with bidistilled water, in an attempt to remove or partially remove the inorganic salts.

By this way, information on the effects of inorganic compounds on both wood degradation and pyrolysis reactions were obtained, proving that some salts can alter the chemical structure of wood components (holocellulose and lignin) and should be avoided for any kind of wood long-term treatment.

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# MICROSTRUCTURAL ANALYSIS OF PURE AND Li DOPED Cd FERRITES ( $\text{CdLi}_x\text{Fe}_{(2-x)}\text{O}_{4-y}$ ) NANOFABRICATED BY CO-PRECIPITATION METHOD

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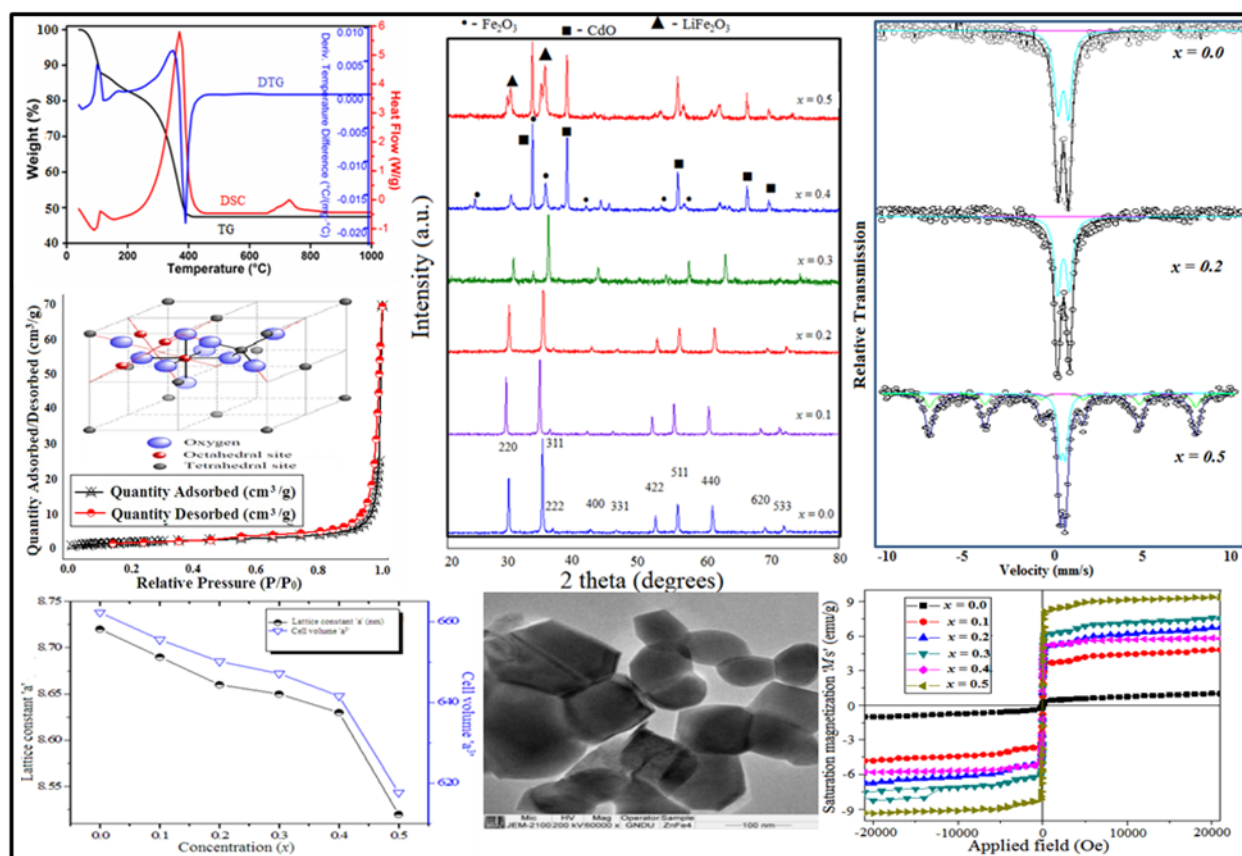
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## Abstract

Ammonium hydroxide as a precipitating reagent has been used for nanofabrication of pure and Li doped Cd ferrite particles ( $\text{CdLi}_x\text{Fe}_{(2-x)}\text{O}_{(4-y)}$ ;  $x = y = 0.0 - 0.3$ ) by co-precipitation method. Various spectroscopic techniques employed demonstrate the effect of Li ion (dopant) concentrations on the microstructural parameters of Cd ferrite nanoparticles obtained and justify the formation of single phasic, soft magnetic, nanocrystalline materials with novel physico-chemical properties. An increase in  $\text{Li}^+$  substitution inculcates a relative decrease in formation temperature as well as crystallite size thereby leading to an increase in magnetic parameters ( $M_s$ ,  $\mu\text{B}$ ) and relative surface area ( $S_{\text{BET}}$ ) of the as-synthesized ferrites. Mössbauer and magnetic studies demonstrate that the concentration as well as nature of dopant both control the site preference in the crystal lattices[1-3].



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## Py/GC-MS TO EVALUATE THE ACTIVITY OF A THERMOSTABLE LACCASE PRODUCED BY *Streptomyces ipomoeae* IN THE DEGRADATION OF LIGNIN FROM WHEAT STRAW

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Streptomyces are mycelial microorganisms with a high growth rate on solid substrate that have been studied for their potential to degrade lignocellulosic grass residues in solid-state fermentation and therefore with interest for biopulping purposes. In these studies, it has been demonstrated the ability of selected *Streptomyces* strains to solubilise lignin from wheat straw and produce a high depolymerization of this polymer. Among the enzymes involved in lignin degradation, oxidoreductases such as peroxidases and laccases have been involved.

In recent studies a thermostable laccase (SilA) produced by *Streptomyces ipomoeae* CECT 3341 presenting both physico-chemical and structural characteristics usually uncommon among microbial laccases was isolated. Thus, its high resistance to alkaline conditions and to high concentrations of sodium chloride opened up the biotechnological interest of this enzyme [1]. Moreover, the presence of two cupredoxin domains in its structure in contrast with most of fungal laccases drive us to elucidate the possible biological role of this laccase in lignin degradation of wheat straw.

For this study, the wild strain (SilA) and a deficient laccase mutant (SilA<sup>-</sup>) obtained through gene disruption were grown on wheat straw as substrate under solid-state fermentation (SSF) conditions. In addition, a non-inoculated substrate was used as control. After 7 days of incubation the alkali-lignin was extracted from fermented substrates, quantified and analyzed through analytical Py-GC/MS at 350 °C.

The alkali-lignin extracted was 12 times and 6 times higher for the wild-type strain than for the control and SilA<sup>-</sup> mutant strain, respectively. The analytical pyrolysis of the alkali-lignin extracts revealed conspicuous differences in their composition which is evident at a first sight of the pyrograms normalized to the polysaccharides-derived pyrolysis compound furfural (Fig. 1). The chromatogram obtained can be divided in three parts where main biogenic compounds elute; a first part from min 2-5 is dominated by polysaccharides-derived compounds, from min 5-14 are lignin-derived compounds including those from G, S and H units and from min 14 to the end of the chromatogram lipids-derived

compounds including high fatty acid peaks (FA14, 16 & 18), plant derived long chain alkanes with odd homologous dominance (C<sub>27</sub>-C<sub>33</sub>) and sterols could be identified.

From the results obtained, both from the qualitative alkali-lignin extracted from the fermented substrates and from the qualitative information provided by the analytical pyrolysis, it could be inferred that SilA laccase seems to be the main enzyme responsible for the lignin degradation activity of *Streptomyces ipomoeae* in wheat straw.

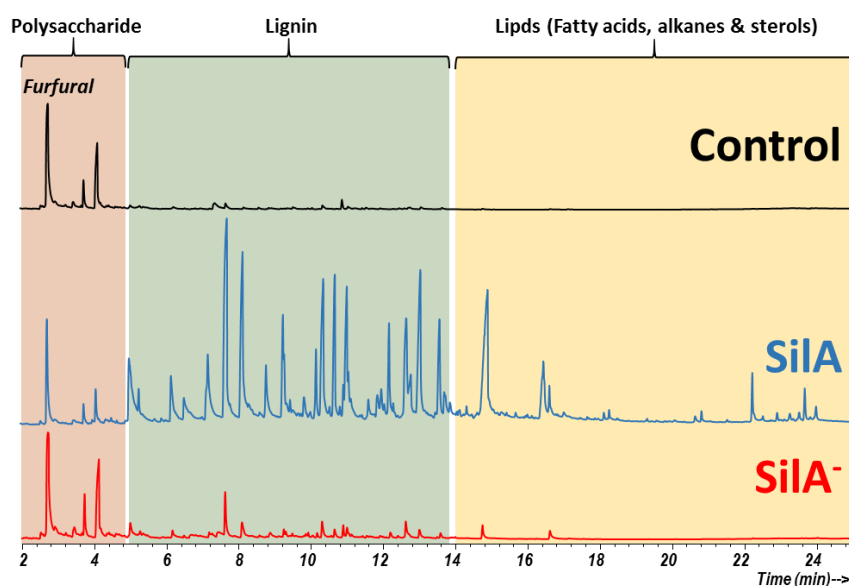


Figure 1 Pyrograms (350 °C) of alkali-lignin yields.

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## APPLICATION OF ANALYTICAL PYROLYSIS FOR SEARCH OF MECHANISMS OF BIOMASS COMPONENTS TRANSFORMATION INDUCED BY MICROWAVE TORREFACTION

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The mild thermal treatment of plant biomass in the temperature range of 200-300°C in the absence of air, so called torrefaction, is recognized as a high efficient method for improving of their fuel characteristics. The presence of polar groups in the constituents of lignocellulosic biomass makes them suitable substrates for microwave (MW) heating. The main advantages of MW-based technologies versus conventional heating include the selectivity and high rate volumetric heating of substrate, the ability to start and stop the process, instantaneously, improving the control processing [1]. In the present work, Py/GC-MS/FID, FTIR spectroscopy and wet chemical analysis were used to characterize the biomass components transformation under MW treatment aimed at the obtaining of biofuel and extractives. The treatment of pelletized plant biomass (debarked hardwood, softwood, and wheat straw) by MW was realized using the Latvian State Institute of Wood Chemistry originally designed MW laboratory reactor [2]. The input of microwave energy was regulated to provide the dynamic heating of biomass sample in interval 150 – 300 °C.

The development of condensation and carbonization processes in biomatrix polymers (hemicelluloses, cellulose, lignin) was described using Py/GC-MS/FID and FTIR results. In relation of carbohydrate complex of biomass samples the Py-GC/MS/FID results indicated the promoting levoglucosan formation during analytical pyrolysis that can be explained by increasing of ordered cellulose portion after MW treatment. The comparison of Py-GC/MS/FID results for softwood samples thermally treated using MW and convective heating revealed activation effect of MW irradiation on this process in the case of softwood and wheat straw, but not of hardwood.

The comparison of the Py-GC/MS/FID results obtained for softwood treated by microwave radiation with those after convective heating gave an evidence of higher rates of condensation reactions and increasing of lignin matrix aromaticity under MW treatment at temperatures 150-280 °C. In the case of hardwood lignin, the condensation reactions and increasing of matrix aromaticity occurred in less extent as compared with softwood and wheat straw.

Formation of extractable compounds as the result of MW treatment of both wood species and wheat straw was monitored and the significant increase in formation of hydrophilic extractable compounds enriched by polyphenolics was found. It seems to be of high importance for the application of microwave treatment in various biorefinery schemes because these extractives can become value source for development of additional technological links and production of novel commodities.

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## ACID TREATMENT OF PHRAGMITES FOR SUGAR AND SUGAR DERIVATIVES PRODUCTION

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Demand of sugars and sugars derivatives for chemical and biochemical manufacturing has grown year by year[1]. Nowadays, the research has been focussing on the search for new cheap feedstocks and conversion methods. For this reasons, Phragmites genera is very attractive. Phragmites is a perennial grass diffuse in all world. Over the last decades it has been introduced in the southwest of North America and has diffused rapidly and without any control. Its uncontrolled diffusion has exposed numerous areas to fire and landslide risk and damaged a great number of ecosystem with its high reproductive rate[2]. The most common way to dispose of it is combustion, but various biological and thermochemical treatments are currently under development to contribute to its management[3]. Among the thermal treatments, pyrolysis is very attractive in order to produce bio-oil rich in anhydrosugars. The main drawback in the use of Phragmites is the high inorganic content of up to 8.8 %. It is well known that the inorganic component can be promote the sugar decomposition during pyrolytic processes [4]. For this reason, in order to enhance the sugar and anhydrosugar concentrations, we have investigated the pre-treatment of the phragmites feedstock through acid washes using acetic acid solutions at different concentrations ( 2%, 10% and 17%). Similarly, the effect of using the acidic bio-oil watery phase from pyrolysis of a digestate has been studied. Untreated and treated feedstocks were then pyrolyzed in a mechanical fluidized bed batch reactor at two different temperatures (450°C and 550°C). Bio-oils were analysed with different techniques, like GC-MS/FID[5], HPLC-MS/MS[6], ATR FT-IR and NMR with qualitative and quantitative methodologies to investigate their composition. Yields of bio-oil increased after acid wash up to 53 %wt and interesting anhydrosugars, such as 1,4:3,6-Dianhydro- $\alpha$ -D-glucopyranose and Levoglucosan were detected in concentrations up to 3.4 and 33.7 mg/g after acid wash, respectively.

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## MULTI-ANALYTICAL APPROACH TO CHARACTERISE MODERN OIL PAINT FORMULATIONS

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The paint production was at the basis of the activities in artists' workshops up the 18th century: pure raw materials were purchased and then paint media were prepared according to traditional, and sometimes secret, recipes. When paint tubes became commercial products in the 19th century, the paint formulations have been adapted to meet new requirements, as the paint had to be stable during packaging, transport and storage, keeping the pigments in suspension, and had to exhibit uniform handling properties. Paintings made with these new formulations exhibit nowadays degradation patterns that are different to those seen in older works, presenting new phenomena, such as the formation of vulnerable 'medium skins' on paint surfaces, efflorescence, changes in surface gloss due to degradation and previous conservation treatments. The Cleaning Modern Oil Paintings (CMOP) project aims at making essential progress in the safeguarding of modern unvarnished oil paintings, by investigating the causes of their degradation phenomena, and to use this knowledge as the basis for developing methods for safe and effective surface cleaning.

In this context, understanding the formulation of the paint medium is of fundamental importance. In the modern oil formulations, metal soaps were commonly introduced as surfactants, to facilitate the dispersion of pigments into the medium. Among these, aluminum and zinc stearates were patented as dispersion agents and widely used after 1920. Moreover, in order to obtain the desired chemical/physical properties, oil mixtures and purified fraction of unsaturated fatty acids obtained from different natural or industrial sources were used. Stabilizers were also common additives, and can be divided into three classes: waxes or wax-like materials, which form a colloidal suspension in oil-pigment systems, water solutions, which allow the formation of a gelatinous emulsion water-oil, and inert pigments, such as alumina hydrate. Other common additives were the anti-skinning agents that allowed to maintain the dispersion of the pigments in the oil media during the curing process: these agents included volatile antioxidant materials, such as butylaloxime and tetrabutylphenol.

The complete characterisation of the different constituents of the paint formulations requires the development of a multi-analytical strategy, in which analytical pyrolysis plays a fundamental role. In this work we present how analytical techniques entailing the thermal degradation of the sample (thermal gravimetric analysis coupled with Fourier transform infrared spectroscopy TGA/FTIR, direct exposure mass spectrometry-DEMS, evolved gas analysis-mass spectrometry - EGA/MS) can be used for the characterisation of the different fractions of a modern oil formulation, in combination with other molecular techniques, including Gas Chromatography-Mass Spectrometry - GC/MS and High Pressure Liquid Chromatography Electrospray Ionisation MS (HPLC-ESI-MS).

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## THE DISCOVERING OF NEW MARKERS FOR ARCHAEOMETRIC PURPOSES: EGA-MS, Py-GC/MS AND GC/MS INVESTIGATION ON WOOD AND BARK PITCH REPLICA

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The chemical characterization of reference materials is an essential tool to achieve a proper scenario on the biomolecular markers, which allow us to identify archaeological organic remains and to know how ancient people created daily life objects. In this view, a collection of more than 30 tar and pitch was prepared from wood and barks of various deciduous trees (mainly from genus *Betula*) and conifers (mainly from genus *Pinus*) following traditional procedures. Reference pitch and tar were obtained after two days of pyrolysis of the various wood and barks according to the “Pile (autothermal)” process (carried out by Andreas Kurzweil, Arbeitsgruppe Teerschwele in Museumsdorf Düppel, Berlin, Germany). The pitch and tar were produced using an autothermal method where wood/barks are piled in a wide pit covered in the centre with clay. The firewood heats the wood/barks from the upper part of the pile and inside the pile the temperature ranges from 400 to 700°C.

Chemical investigation on such a collection was performed using evolved gas analysis–mass spectrometry (EGA-MS), analytical pyrolysis coupled with gas chromatography/mass spectrometry with *in situ* silylation using hexamethyldisilazane (Py(HMDS)-GC/MS) and gas chromatography/mass spectrometry (GC/MS) following alkaline hydrolysis, solvent extraction and derivatisation with a silylating agent.

EGA-MS provided information on the thermo-chemistry of pitch and tar along with in-depth compositional data thanks to the use of MS. Analytical pyrolysis and the analytical procedure based on GC/MS were used to assess the molecular composition of the replica and to identify a series of species acting as markers of botanical origin, of technological manipulation and eventually of degradation.



## AN EXPERIMENTAL INVESTIGATION INTO THE ABSENCE OF COMBUSTION IN AN ELECTRICALLY HEATED TOBACCO SYSTEM<sup>‡</sup>

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## AN EXPERIMENTAL INVESTIGATION INTO THE ABSENCE OF COMBUSTION IN AN ELECTRICALLY HEATED TOBACCO SYSTEM (EHTS)<sup>‡</sup>

Combustion occurs when biomass such as tobacco is ignited by a heat source in the presence of an oxidant (oxygen in air). The tobacco in a lit cigarette undergoes smoldering combustion at temperatures in excess of 600 °C[1]. A self-sustaining combustion process is established that consumes the tobacco forming ash and smoke containing more than 7,000 chemicals[2]. Regulatory bodies have classified a number of constituents of cigarette smoke as harmful and potential harmful[3].

One approach to reduce the levels of harmful and potentially harmful smoke constituents associated with combustible cigarettes has been to generate an aerosol by heating, rather than burning, tobacco. Some of the earlier tobacco products developed using this approach have been briefly reviewed by Baker [1] and Schorp et al.[4].

A series of experiments were performed to investigate if combustion occurs in a newly developed and patented electrically heated tobacco system<sup>‡</sup> that heats a specifically designed tobacco substrate. Experiments performed included a detailed temperature mapping of the heating system, mass balance and elemental analyses, and compositional analysis of the aerosol formed under an oxygen(air) and inert atmosphere.

Contrary to the increase in the temperature of tobacco that occurs when air is drawn through a lit cigarette, there is significant drop in the temperature of the tobacco substrate in the EHTS. The highest average temperature of the tobacco in the EHTS measured in close proximity to the heating element reaches approximately 300 °C, well below the temperature required for combustion of the tobacco substrate to occur[5]. Torrefaction of the tobacco substrate occurs close to the heating element. Operation of the EHTS in an atmosphere of nitrogen (where combustion cannot occur) yields an aerosol that is substantially equivalent to that produced in air.

The results of the experiments conducted confirm the absence of combustion in the EHTS. Due to the controlled operating temperature of the system, the aerosol generated is formed principally by the evaporation of water, nicotine and glycerin from the tobacco substrate and contains substantially lower levels of harmful and potentially harmful compounds when compared to cigarette smoke.

<sup>‡</sup> The Electrically Heated Tobacco System (EHTS) was developed by Philip Morris International

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## CHARACTERIZATION OF TRADITIONAL EAST ASIAN PAPERS USING PY-GC/MS AND PY-GCxGC/MS

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Paper is one of the great inventions of China dated approximately from 2,000 years [1]. The traditional East Asian handmade papers are manufactured by passing a fiber suspension through a screen resulting in forming a mat of intertwining fibers. The fibers selected for the manufacturing of East Asian paper vary chronologically and geographically in the past, and mucilaginous additives were specifically used in the process of papermaking [2]. The particularities of this papermaking process may help for the identification of ancient paper artefacts, and to pave way for new understandings of the techniques developed in hand paper making.

The present study has been initiated with the aim to tackle the problem of defining a micro-destructive method of analysis for the characterization of objects of museum collections. As assumed, the characterization of specific chemical markers will provide a protocol to define the chrono-geographical area of unknown paper artefacts, and will complete efficiently the identification of fibers by microscopy.

The fibres in papers are usually identified under the microscope by examination of characteristic morphological features. Because identification can be difficult, it is proposed to introduce the use of pyrolysis coupled to gas chromatography and mass spectrometry detection for exploring the chemical signature of materials used in traditional East Asian handmade papermaking. A new method is then developed to characterize chemical markers of these papers. The novelty of the approach lies in the targeting of fibres and mucilaginous compounds that come specifically in the final composition of the papers.

Analysis was conducted on reference papers samples made from different types of plants (koko, mitsumata, gampi and bamboo) traditionally prepared, varying the fibre cooking processes and the mucilaginous additives origin. It was demonstrated that the presence of specific triterpenoid and phytosterol chemicals can be correlated to the composition of the fibres. The method was successfully applied for the identification of museum artefacts in the course of their restoration.

Moreover, more detailed fingerprints of the samples were obtained using vertical furnace pyrolysis-GCxGC/MS, a new experiment developed in our laboratory for Cultural Heritage applications. Analysis conducted on the same samples (reference samples and museum artefacts) will be presented as a further development of our method which introduces new criteria for the characterization of traditional East Asian papers.

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## THE MECHANISM OF BIOMASS PYROLYSIS STUDIED BY VARIOUS ANALYTICAL METHODS

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Numerous analytical methods are commonly used to study the mechanism of biomass pyrolysis, namely: NMR, FTIR, GC/MS, etc. But all these methods are seldom combined for same biomass and same heating conditions. Here, we propose to combine the main cutting-edge methods for a comprehensive analysis of biomass pyrolysis products under well defined pyrolysis conditions.

Miscanthus pyrolysis has been conducted under slow pyrolysis conditions in U-shape fixed bed reactor. [1] The U-shape fixed bed reactor allows controlling mass transfers, temperature of the bed, quenching char at targeted temperatures and quantifying mass balances.

The mass yields in solid, condensable products and gas have been studied between 200°C and 500°C.

For the analysis of volatile products, the fixed bed is combined to (1) on-line analysis of the vapours (primary tar) by soft photoionisation mass spectrometry (single photoionisation time-of-flight mass spectrometer, SPI-TOFMS), (2) quantitative off-line analysis of condensed vapours by GC\*GC/MS-FID and (3) permanent gas analysis.

The soft on-line photoionisation analysis leads to a more interpretable mass spectra with few fragment ions [2] and gives the evolution of the main markers of volatiles produced in real-time as a function of the temperature. The chemical structure of the markers analyzed on-line by SPI-TOFMS is assigned by GC\*GC/FID-MS analysis.

The char as-produced in the fixed bed reactor was quenched at various targeted temperatures between 200°C and 500°C. The chemical moieties formed in the chars have been studied by solid state <sup>13</sup>C NMR [3,4]. A specific Cross Polarization method at the Magic Angle Spinning (CP/MAS) has been found to give similar spectra than the Direct Polarization quantitative method in much shorter acquisition times. A detailed molar balance on the evolution of carbon moieties was conducted on the various biochars. It is shown that below 300 °C xylan is the main source of aromatic formation while above this temperature the aromatization of cellulose occurs.

Finally, thermogravimetry, calorimetry, high temperature <sup>1</sup>H NMR (in-situ and real time analysis of the fluid phase formed during pyrolysis) and water extraction of the quenched char followed by size exclusion chromatography coupled with mass spectrometry (SEC/MS) have been combined in order to understand notably the effect of potassium on the mechanisms of biomass primary pyrolysis [5]. Calorimetry and in-situ <sup>1</sup>H NMR were also conducted in a fixed bed configuration therefore under similar mass transfer conditions than in the U-shape fixed bed reactor.

During the talk, we will show how all these analytical methods are complementary and interesting to assess the mechanism of biomass pyrolysis. This methodology can be applied to all other organic materials.

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## ON-LINE ANALYSIS OF BIOMASS PYROLYSIS TAR BY PHOTOIONIZATION MASS SPECTROMETRY

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Biomass pyrolysis generates volatile products which can be analyzed on-line by direct mass spectrometry or off-line after their condensation. The on-line analysis of volatiles is an interesting method because it has the ability to sample directly the volatiles from their reactive environment. Furthermore, the condensation of volatiles followed by the evaporation of the liquid in a GC injector could modify the composition of pyrolysis products. Mass spectra from direct on-line mass spectrometry can give interesting “fingerprints” of volatiles composition but the ionization method should be as soft as possible to obtain more easily interpretable mass spectra with few fragment ions. The photoionization (PI) is an efficient and soft ionization method for on-line analysis of biomass pyrolysis volatiles [1]. In this poster, we will present recent developments on PI-Mass Spectrometry (MS) analysis of biomass pyrolysis volatiles (1) in USTC-Hefei by synchrotron light PI-MS, (2) in CNRS-Nancy by PI-MS combined with various pyrolysis reactors.

(1) The synchrotron light offers an accurate, tunable and soft vacuum ultra violet (VUV) source for ionising the labile oxygenated tar. A unique device has been developed by Prof. F. Qi's group which combines a furnace for biomass pyrolysis, a sampling train for volatiles (through skimmers), an ionisation region where the synchrotron VUV light is focused, and a Q-TOF-MS (a triple quadrupole and a time-of-flight). The effect of photon energy on mass spectra has been studied. A potential new intermediate compound from cellulose pyrolysis has been revealed [2].

(2) In Nancy, a differential fixed bed reactor has been combined with a VUV lamp Single PI TOF-MS (SPI, 9.8eV) developed by the Photonion company. The fixed bed allows a good control of temperature and mass transfers under slow heating conditions (5K/min) [3]. The evolution of chemical markers from lignin, cellulose and hemicelluloses has been studied as functions of biomass types and temperature of pyrolysis. The chemical structure of markers has been assigned by GC/MS. The SPI-TOF-MS has been also combined to a micro-fluidised bed reactor to study the fast pyrolysis of different sizes and shapes of biomass particles [4]. Principal component analysis of the various MS “fingerprints” reveals interesting markers of some primary pyrolysis regimes which depend on biomass composition (e.g. ash content) or mass and heat transfer effects. Laser SPI (10.6eV) and laser Resonance Enhanced Multiphoton Ionisation (REMPI) were also tested [5].

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## CHARACTERIZATION OF CHEMICAL COMPOSITION VARIATIONS IN DIFFERENT SPRUCE WOOD ZONES BY PY-GCMS

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Wood durability versus weathering or biotic decay is basically attributed to extractives contained in its solid matrix but it could be interesting to focus on the macromolecular content to explain some unexpected behaviours. However, usual wood biopolymers chemical analyses are time consuming, involve numerous steps with hazardous chemicals and lead to the degradation of either holocellulose or lignin, depending on which is under scrutiny. Generally, the studied macromolecule is also slightly degraded and the results reliability is not excellent since it is difficult to multiply enough the experiments, mainly because of the quite high amount of wood material needed. The Py-GCMS technique appeared to be a convenient solution to these issues with a very fast sampling step, well-controlled analyses conditions and with an integrated data processing design.

After a validation step, this approach has been applied to determine the compositional differences between several regions of a spruce trunk, namely the pith, heartwood, sapwood and bark. Performed for three different heights of the tree, the measurements have shown interesting differences on the lignin monomeric composition according to the sampling height when the interpretation dealing with the polysaccharides derivatives is less obvious.

These results have been compared to those obtained on the residual parts of a spruce decayed by *Heterobasidion annosum* (or *Fomes*) in order to understand why this fungus, which is the most effective against spruce forest, is able to degrade the inner part of the tree without attacking the sapwood although heartwood is usually considered as the most durable tree zone. Very important variations between the healthy and the diseased trees have been observed but, in such a high amplitude, that it was impossible to conclude with a clear relationship between the chemical composition and the fungal decay resistance.

## SPME-GC-MS to trace the dynamics of compounds evolved during stepwise pyrolysis

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At-line monitoring of gases evolved during biomass pyrolysis could be an advantageous tool to understand process development. Molecular characterisation of pyrolysis vapours could also be useful to predict the composition of the resulting liquid fraction and the presence of valuable compounds could be directly assessed without time consuming wet chemical methods. Solid-phase microextraction (SPME) is a solventless technique able to pre-concentrate analytes onto polymer coated fibres applied for the determination of low molecular weight compounds in a variety of matrices. Its use in the analysis of bio-oil samples was reported as one of the most relevant advances in head space sampling techniques [1]. Carboxen-PDMS fibre was able to detect a wide range of polar and non-polar compounds in pyrolysis vapours at the bench scale level [2]. In this study SPME coupled with gas chromatography-mass spectrometry (GC-MS) was used to characterise the nature of volatile and semivolatile compounds evolved from the pyrolysis of biomass residues (e.g. seaweeds, coffee grounds) during different steps of thermal degradation. Stepwise pyrolysis was performed with a fixed bed vertical quartz reactor in the temperature range of 350-650°C. Four thermal steps were programmed, every 100°C with a heating rate of 5°C/min. A relatively simple and inexpensive sampling device was developed for online monitoring, avoiding the use of toxic solvents (Figure 1). Differences in patterns of compounds detected could explain the formation of pyrolysis products at different temperatures. The information acquired is important considering that volatile compounds produced during pyrolysis could be retained on the biochar affecting its environmental performance [3]. SPME was also used to study the catalytic conversion of the brown algae *Macrocystis pyrifera* (seaweed) with zeolites and to estimate the quality of the resulting pyrolysis vapours.

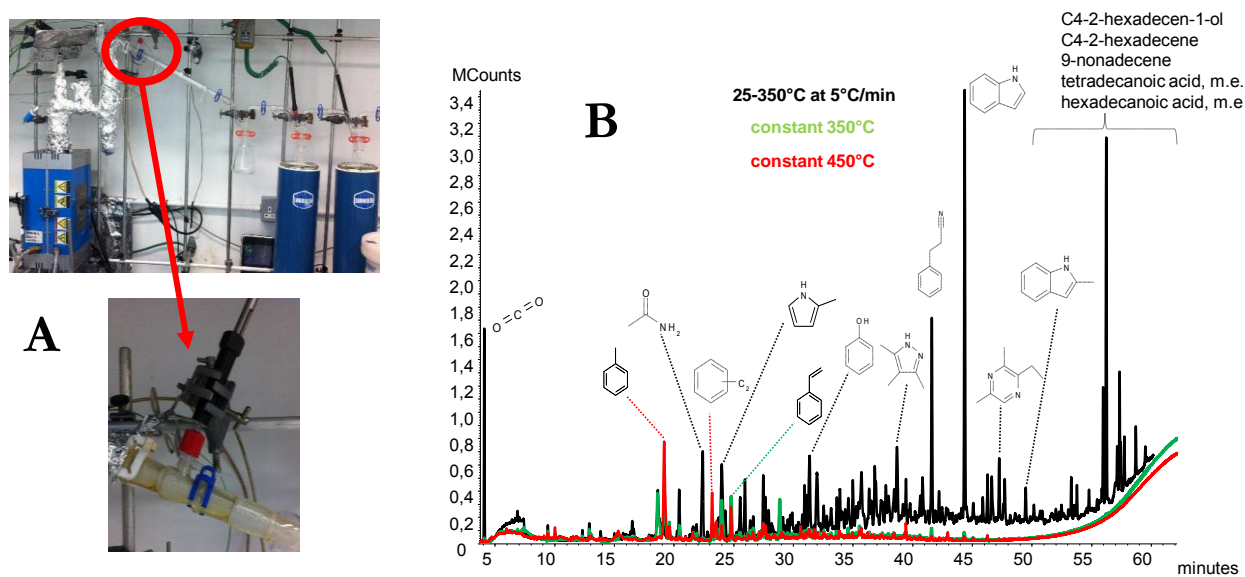


Figure 1A: Vertical pyrolyser modified with a sampling port for SPME. Sampling with Carboxen-PDMS fibre (exposure time: 20 minutes) was performed after the tar condensation step in a gas stream kept at 160°C by a heating tape. Figure 1B: total ion current chromatograms from SPME of *Macrocystis pyrifera* at different thermal steps. 112 compounds were tentatively identified, representative of the protein, lipid, polysaccharide and polyphenol fractions of the brown algae. The increase of carbonization inside the reactor with the pyrolysis temperature is evidenced by the presence of proxies of the charred biomass fraction in the gas stream (aromatic hydrocarbons).

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## PYROLYSIS-COMPOUND SPECIFIC ISOTOPE ANALYSIS (Py-CSIA). TECHNIQUE AND APPLICATIONS

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Pyrolysis-compound specific isotopic analysis (Py-CSIA) is a relatively novel technique to measure stable isotope proportions i.e.,  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$  and  $\delta^2\text{H}$ ,  $\delta^{18}\text{O}$  in individual compounds released by pyrolysis. This technique can provide valuable information on materials that are not soluble and therefore not amenable by conventional GC/MS techniques. The technique provides not only a molecular fingerprinting, but also allows the traceability of their formation processes and origin.

At the MOSS Group Stable Isotope Laboratories (LIE-MOSS), direct pyrolysis compound specific isotopic analysis (Py-CSIA) is conducted using a double-shot pyrolyzer (Frontier Laboratories, model 3030D) attached to a Trace Ultra GC system. The flux is conducted to a GC-Isolink System equipped with micro-furnaces for combustion (carbon and nitrogen) and for pyrolysis (hydrogen or oxygen). The system is coupled to a Delta V Advantage IRMS via a ConFlo IV universal interface unit (Py-GC-C/TC-IRMS) (Fig. 1a). The identification of specific peaks (structural information) are inferred by comparing the mass spectra from a conventional Py-GC/MS system with the Py-GC/FID and Py-GC/IRMS chromatograms obtained using same chromatographic conditions (Fig. 1b).

In this communication the general technical aspects and fundamentals of Py-CSIA will be presented as well as some recent examples of applications developed in our laboratories at the LIE-MOSS in different fields, including food industries [2] and synthetic polymer industries [1], research on fire/heat affected soil organic matter [3] and biomass and paleoclimate studies using fossil plant materials [4].

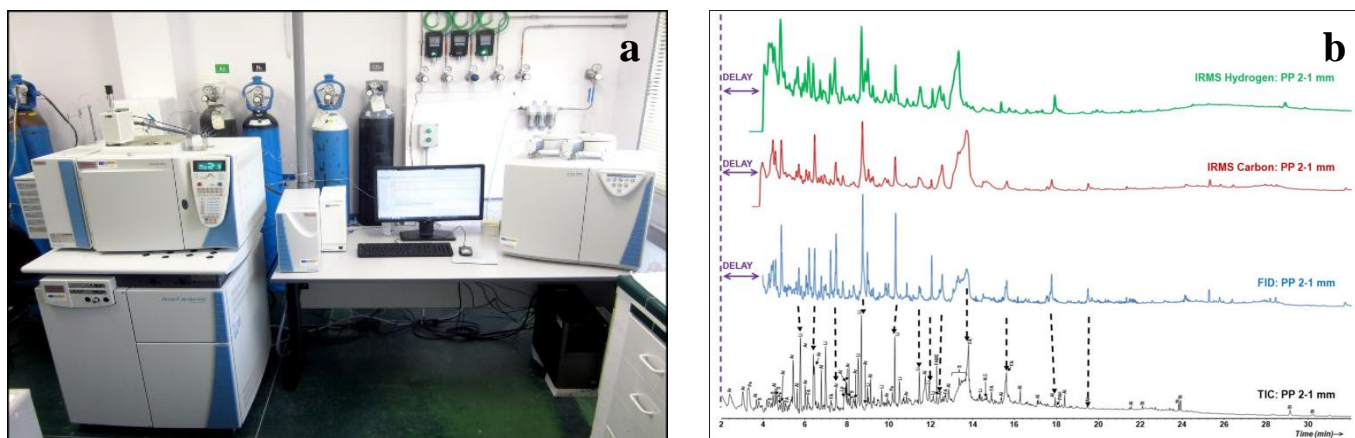


Figure 1: a) Py-GC-C/TC-IRMS (Thermo Scientific) at the LIE-MOSS; b): An example of Py-CSIA chromatograms ( $\delta^{13}\text{C}$  and  $\delta^2\text{H}$ ) of soil organic matter

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## INVESTIGATIONS ON PHYSICO-CHEMICAL PARAMETERS OF PURE AND Sm<sup>3+</sup> DOPED Cd FERRITES (Cd<sub>1-x</sub>Sm<sub>x</sub>Fe<sub>2</sub>O<sub>4+0.5x</sub>; x = 0.0-0.3) SYNTHESIZED BY SOLUTION COMBUSTION METHOD

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### Abstract

Herein, an attempt has been made to investigate the correlation between distributions of magnetic/nonmagnetic cations (Fe<sup>3+</sup>, Cd<sup>2+</sup> and Sm<sup>3+</sup>) over different crystallographic positions (octahedral; *Ob* or tetrahedral; *Td*) and the method employed for synthesis of pure and Sm<sup>3+</sup> substituted spinel Cd ferrites (Cd<sub>1-x</sub>Sm<sub>x</sub>Fe<sub>2</sub>O<sub>4+0.5x</sub>; x = 0.0-0.3) using solution combustion method. Powder X-ray diffraction study reveals that aqueous ammonia used as a combustion process chemical additive (CPCA) in self combustion process helps in nanofabrication of monophasic, pure and doped Cd ferrite particles up to x = 0.3 (afterwards a new phase of Sm<sup>3+</sup> orthoferrite starts arising) at a relatively lower temperature. Lattice constant 'a' derived for pure Cd ferrites has been found close to the reported value. Thermogravimetric analysis (TG-DTG-DSC) specifies the effect of doping Sm<sup>3+</sup> in Cd ferrite with decrease in formation temperature with respect to pure Cd ferrite obtained. Fourier transform infrared (FT-IR) spectra show the typical peaks in the region of 600–400 cm<sup>-1</sup> indicating metal oxide structure of Cd ferrite alloys. Electron microscopy techniques (SEM and TEM) used for determining the average size and shape of as-obtained ferrites depict fine particles as indicated by X-ray studies. Brunauer–Emmett–Teller surface area (S<sub>BET</sub>) and pore diameter of samples (by Barrett–Joyner–Halenda (BJH) method) (x = 0.0 and 0.3) reveal increase in surface area of mesoporous ferrite oxides with doping. Room temperature magnetization measurements using vibratory sample magnetometer (VSM) demonstrate the soft nature of pure Cd ferrite formed. With increase in dopant concentration, an increase in net magnetization value of doped ferrites with transition from soft to slightly hard spinel magnetic particles (having high coercivity value) have been observed. Room temperature Mössbauer spectra suggest that doped ferrite with fine particles prefer inverted or mixed spinel structure formation leading to increased magnetic parameters as per Neel's theory of magnetism. Large magnetic parameters (M<sub>s</sub> and low H<sub>c</sub>) of our materials make them particularly suitable for many electrical devices. Solution combustion technique employed for the ferrite under study has some advantages over other conventional methods that monophasic, fine particles with high surface area and large magnetic parameters are obtained at a relatively lower temperature [1-3].

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## New kinetic approach on pyrolysis poly-(methyl methacrylate) using by EGA-MS

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In the pyrolysis research, thermogravimetric analysis (TGA) and analytical pyrolyzer-gas chromatography/mass spectrometry (Py-GC/MS) were normally used for the study of pyrolysis kinetic and product characterization, respectively. Recently, various kinds of new technologies such as TG-MS, TG-IR and EGA-MS were newly introduced to make the easier understanding of pyrolysis behaviour of polymer. By these technologies, combined interpretation of kinetics and product characterization became possible in one instrument system.

EGA-MS is an analytical technology using a temperature programmable Py-GC/MS and can monitor evolved gases produced during the pyrolysis of polymer. To send the gas phase pyrolysis products to MS in a very short time, a short deactivated capillary tube is used together with enough high oven temperature to avoid any condensation in this tube. The thermal profile of specific pyrolysis product also can be monitored by extracting the target ion of specific pyrolysis product. Although EGA is being considered as possible tool for the kinetic analysis of polymer, it was not applied on the kinetic analysis of polymer yet.

In this study, EGA-MS using a Py-GC/MS system was attempted on the pyrolysis kinetic approach for polymer for the first time. Apparent activation energy ( $E_a$ ) values of poly-methyl methacrylate (PMMA) pyrolysis were obtained by a model-free (Ozawa method) and model-fitting (peak property method) kinetic analysis method from the total ion thermogram of PMMA pyrolysis using EGA-MS measurement. The activation energy values obtained by EGA/MS datum were quite comparable with those reported in other literatures using TGA datum. The other kinetic parameters such as pre-exponential factor ( $A$ ) and reaction order ( $n$ ) were able to be concluded by model fitting analysis method. The pyrolysis reaction model of PMMA was also verified as the reaction order function by comparing master plot obtained from our kinetic parameters ( $E_a$ ,  $A$ ,  $n$ ) to those of theoretical plots reported in the literatures.

## Development of identification methods of drying oils composed of different main components by Py-GC/MS

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In this study, analyzing the kind of film-coated drying oils. Recently, the ration of P/S (P: Palmitic acid, S: Stearic acid) was used as indicator for distinguishing the drying oils individually. Liquid perilla, tung and sunflower oil were treated at a constant temperature of 80 degrees for 24 h in oil bath. After this treatment, coating thin films thickness 90 μm of these oils added 25 wt% iron oxide (Fe<sub>2</sub>O<sub>3</sub>) to room temperature for 3 months. These samples were degraded by ultraviolet irradiation with wavelengths of 185 nm for 0–7 days, respectively. Difference between perilla and tung oil or sunflower and tung oil were characterized by Py-GC/MS (Table). P/S changed according to deterioration progress resulted from Py-GC/MS. Its index was unsuitable, consequently [1]. So by this research, Using the ration of C5/C6 (C5 :Pentanoic acid, C6 : Hexanoic acid) instead of this indicator. The value of new ration made a difference between these oils. Furthermore, perilla and sunflower oil were distinguished by another ration of C6/C7 (C7 :Heptanoic acid). Thus both C5/C6 and C6/C7 were useful for identifying perilla, tung and sunflower oil forming the thin film.

Table Changing ratio of ultraviolet irradiated perilla, tung and sunflower oil forming the thin film

| Entry | Sample        | Irradiation time | Pentanoic acid (C5) | Hexanoic acid (C6) | Heptanoic acid (C7) | C5/C6 | C6/C7 | Palmitic acid (P) | Stearic acid (S) | P/S  |
|-------|---------------|------------------|---------------------|--------------------|---------------------|-------|-------|-------------------|------------------|------|
| 1     | Perilla oil   | 0 day            | 4.2                 | 14.9               | 15.7                | 0.28  | 0.95  | 29.4              | 5.5              | 5.3  |
| 2     |               | 3 day            | 9.2                 | 11.2               | 11.3                | 0.82  | 0.99  | 24.5              | 2.1              | 11.7 |
| 3     |               | 7 day            | 9.5                 | 11.3               | 11.7                | 0.84  | 0.97  | 3.8               | N.D              | N.D  |
| 4     | Tung oil      | 0 day            | 26.3                | 9.7                | 10.0                | 2.71  | 0.97  | 7.9               | 4.8              | 1.6  |
| 5     |               | 3 day            | 26.6                | 9.7                | 10.9                | 2.74  | 0.89  | 4.7               | 2.5              | 1.9  |
| 6     |               | 7 day            | 27.2                | 9.9                | 11.5                | 2.75  | 0.86  | 4.5               | 1.8              | 2.5  |
| 7     | Sunflower oil | 0 day            | 3.2                 | 15.2               | 10.7                | 0.21  | 1.42  | 29.9              | 12.3             | 2.4  |
| 8     |               | 3 day            | 4.7                 | 18.7               | 10.3                | 0.25  | 1.82  | 22.0              | 3.2              | 6.9  |
| 9     |               | 7 day            | 7.7                 | 18.6               | 10.8                | 0.41  | 1.72  | 14.3              | 2.6              | 5.5  |

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## Py-GC/MS analysis of the coloring materials of a Yomeimon Gate of the Nikko Toshogu Shrine

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### Abstract

A Nikko Toshogu Shrine is one of the buildings designated as the national treasure. Furthermore, this temple is registered also into world heritage and is one of the worldwide important buildings. It is recorded as 1636 that the Nikko Toshogu Shrine became a mode of the presently. The Yomeimon Gate which has been this analysis target is one of the buildings where the study was conducted by "Major Repair of Heisei." When carrying out the radioparency analysis to the Yomeimon Gate, it turned out that there is an old painting also in the backside of the lamina of a surface painting (Figure 1).

The Japanese lacquer is known as a typical coating material used for a long time. Many Japanese lacquers are used also the Nikko Toshogu Shrine. The part used is widely used not only for indoor but for outdoor paint. Many of chromatics at this time are a black color and a red color, and it is known that it will be hard to take out green and a yellow color. Because the paint on the basis of a Japanese lacquer of the because of such a chromatic cannot take out vividness easily since the black color of a Japanese lacquer serves as a substructure. There is a method which used the drying oil as skillful coloring on the other hand.

From the old article, the Yomeimon Gate was recorded as it is the drying oil painting (a tung oil, a perilla oil ... ) colored. The sample was extracted from eight places. These samples were analyzed by Py-GC/MS of 500 °C conditions. As a result, it turned out that it is coloring which used oil as the old article. In addition, the element of glue or rosin was also detected. It is expected that these were used for the regulation of a viscosity or an adhesion force. Moreover, it became clear that the As and the mercuric were used for the pigment. These elements are pigments detectable also by Py-GC/MS[1]. An As is an arsenic sulphide and is usually carrying out the yellow colored. By adding an ultramarine to an arsenic sulphide, I can make it green. A mercuric is a mercury sulfide and is carrying out the skillful red color.

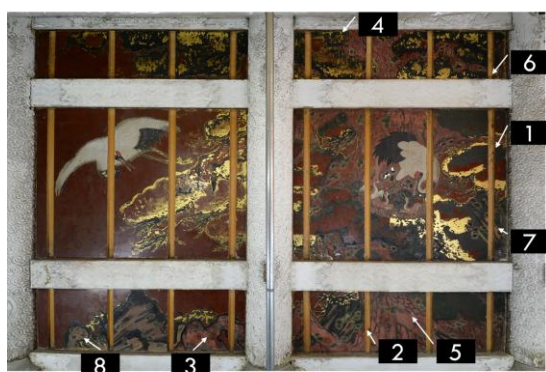


Figure The place of the sample of a Yomeimon Gate

Table Result of Yomeimon Gate samples

| Sample | Japanese lacquer | Drying oil  | Pine resin | Glue        | Pigment           |
|--------|------------------|-------------|------------|-------------|-------------------|
| 1      | ×                | ○           | ×          | ×           | Hg                |
| 2      | ×                | ○           | ×          | Δ(a little) | As · Hg           |
| 3      | ×                | ○           | ○          | ○           | As · Hg(a little) |
| 4      | ×                | ○           | ×          | Δ(a little) | As · Hg(a little) |
| 5      | ×                | Δ(a little) | ×          | ○           | Hg(a little)      |
| 6      | ○                | ○           | ×          | ×           | Hg                |
| 7      | ○                | ○           | ×          | Δ(a little) | As · Hg(a little) |
| 8      | ×                | ○           | ×          | ×           | As · Hg           |

### Acknowledgment

On the occasion of this study, received the great synergize in Association for the Preservation of the Nikko World Heritage Site Shrines and Temples.

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## SCIENTIFIC ANALYSIS OF IMITATION LACQUERWARE USING “PAPIER-MÂCHÉ”

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In this study, analyzing the “papier-mâché”. It is a term that has been applied to three dimensional objects of recycled paper fiber whether layered in sheet form with an adhesive or cast as beaten pulp [1]. Also, it has been known that imitation lacquerware is modeled on Japanese lacquerware. The studied Sample is a crafted object that has been purchased in Vienna, and fabricated age of the sample is unknown. This sample is small box decorated like mother of pearl, and coated with like Japanese lacquer. The sample was analyzed by cross section analysis, energy dispersive x-ray fluorescence (ED-XRF), and Py-GC/MS. It shows that the five regions of analysis sample were analyzed using those analytical instruments (Figure).

First, the results of cross section analysis showed that the base coat was used paper or wood chip, the paint was used black pigments. Second, the result of ED-XRF showed that black pigments were regarded organic pigments. Finally, the results of Py-GC/MS showed that  $m/z = 60$ ,  $m/z = 202$  chromatograms of (I) and pyrogram of sample (V) are shown in Figure. At  $m/z = 60$  in the chromatogram, paint was found to have using dry oil. At  $m/z = 202$  in the chromatogram, black pigments are used lowest layer. In addition, pyrogram of sample (V) has the same property with polyvinyl acetate (PVAc). Therefore, the sample is painted between iron and wood which regarded as adhesive PVAc.

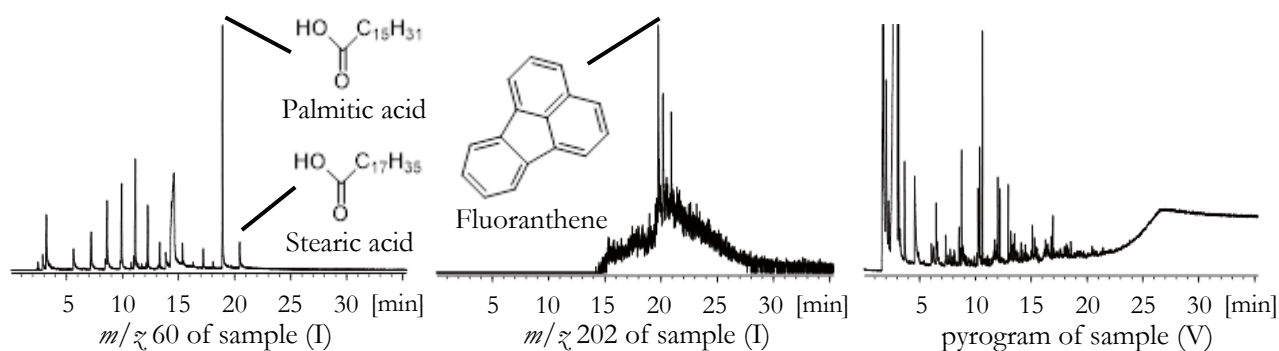


Figure Overview of sample and Py-GC/MS results

Table Five regions of analysis sample

| Sample      | (I)                    | (II)                   | (III)                           | (IV)                               | (V)                            |
|-------------|------------------------|------------------------|---------------------------------|------------------------------------|--------------------------------|
| Explanation | Box of outside surface | Lib of outside surface | Decoration like mother of pearl | Lib of non-restored inside surface | Box of restored inside surface |

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## INFLUENCE OF THE TEMPERATURE RISE TIME ON PYROGRAMS IN ANALYTICAL PYROLYSIS

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Thermal degradation by pyrolysis is highly temperature dependent, and the distribution of pyrolysis products is strongly dependent on the actual temperature at thermal decomposition. This leads to problems with reproducibility since the pyrogram is highly influenced by not only the steady-state temperature of the pyrolyzer, but also how the final temperature is reached. Therefore the time to reach the temperature in isothermal pyrolysis, the temperature rise time, is a vital characteristic of the pyrolysis process. Indeed, if the half decomposition time is of the same order of magnitude as the temperature rise time, most of the sample will be pyrolyzed below the steady state temperature [1]. The temperature rise time shall be as short as possible to ensure reproducibility and well-defined pyrolysis conditions.

In the present work a filament pyrolyzer is used to investigate the influence of the temperature rise time on the resulting pyrograms, with temperature rise times ranging from milliseconds to minutes. The sample is placed directly on the heated filament, and the pyrolysis temperature is measured by two independent methods: by resistance and by light emission.

[1] H. Jönsson, I. Ericsson, Analytical pyrolysis beyond fingerprinting techniques. Poster presented at Pyro2014, Birmingham, UK.

## High pressure tandem catalytic reactor-GC/MS system and its applications

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Due to the increased demand generation for bio-energy, catalytic pyrolysis of biomass already became an important research area. Many kinds of catalytic reaction system were used for the various kinds of catalytic reaction such as deoxygenation, hydrolysis, and so on. The reactor systems were also varied depends on the target products and the scale of the catalytic reactor system. For the micro-reaction system, pyrolyzer-GC/MS was used by many researchers because catalytic reaction together with the product analysis can be performed in a short time using this system.

By developing a tandem micro reactor-GC/MS system, in-situ and ex-situ catalytic pyrolysis over catalysts also became possible to be performed in one system. Various kinds of reaction parameters such as temperature and reaction gas can be controlled in this system. However, high pressure reaction was the technical barrier of this system because independent pressure control of catalytic reactor and GC/MS column head pressure was difficult.

Recently, we introduced the high pressure tandem micro reactor-GC/MS system which can overcome these difficulties by applying additional high pressure flow controller. By these system, catalytic pyrolysis of biomass under high pressure up to 35 bar can be performed under various kinds of reaction gas such as helium, hydrogen and so on. This system also can do the online monitoring of the non-isothermal catalytic pyrolysis under high pressure which can not be performed by other conventional high pressure reactor system such as batch reactor.

In this study, we introduced the several applications using this high pressure tandem catalytic reactor-GC/MS system together with the brief explanation of the system.

## ChromIdent – towards a comprehensive utilization of pyrolytic fingerprints for sample comparison and quality control

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Pyrolysis - gas chromatography/mass spectrometry (Py-GC/MS) is regarded as a valuable fingerprinting technique for solid organic materials including polymers, lignocellulosic biomass, soil organic matter and solid fuels amongst others. The intriguing fact that Py-GC/MS is capable to provide highly reproducible fingerprints with a potentially large amount of structural information is, in many cases, opposed by the immense complexity of pyrograms, which may contain several hundred pyrolysis fragments. Many of the peaks are overlapping and demand deconvolution processing or can not be identified by commercially available mass spectral libraries. Consequently, the user of this analytical technique is often faced with a tedious and time-consuming analysis of the generated data – in particular when long measurement series were acquired and the complex fingerprints are to be compared against each other or against reference measurements.

It is this tremendous drawback which motivated the development of ChromIdent<sup>®</sup>, a software extension for the chromatography software OpenChrom<sup>®</sup> [1]. ChromIdent has been designed for the comprehensive comparison of fingerprints generated by Py-GC/MS or Thermodesorption-GC/MS. After peak detection and deconvolution, peak identification and other common processing steps in OpenChrom, ChromIdent allows to build reference libraries on the basis of peak patterns characteristic for each sample. By the library building process a global peak table valid for all considered samples is constructed, where next to mass spectral match quality also the retention time or retention index may be utilized to ensure a correct peak matching. This resulting peak matrix is the basis for subsequent analysis of unknown samples or, alternatively, may be exported to perform e.g. chemometric approaches with other software solutions.

In order to build useful libraries the user may decide to utilize all detected peaks or just a subgroup within the measurement, e.g. the lignin fragments only. Thereafter unknown fingerprints, e.g. composite materials, can be compared against the libraries to find similarities with reference fingerprints, or sub-fingerprints, and, additionally, elucidate whether there are unique marker components hinting towards particular references.

In the present study the applicability of ChromIdent for sample authentication and marker component detection is verified on two Py-GC/MS datasets, a measurement series on genetically modified poplar samples and a set of tropical hardwoods, which has been discussed before [2].

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# STUDY ON CHINESE HISTORICAL LACQUER CULTURE AND TECHNOLOGY

## – ANALYSIS OF CHINESE QIN-HAN DYNASTY LACQUERWARE –

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### ABSTRACT

A Chinese lacquerware belong to personal collection was analyzed by cross-section, field emission scanning electron microscope with energy dispersive X-ray spectrometry (EDX), strontium isotope ratios ( $^{87}\text{Sr}/^{86}\text{Sr}$ ), carbon 14 age determination, and direct and on-line dervatisation using THMA (tetramethylammonium hydroxide)-pyrolysis-gas chromatography/mass spectrometry (GC/MS). The carbon 14 analyzed results showed that the wood species of the lacquerware was *Zelkova schneideriana* tree growth in the Yangtze River are a about 2300 years ago, and the lacquer film was the sap collected from lacquer tree about 2200-2250 years ago. The  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope ratios was 0.7115 consistent with that of the Chinese mainland ( $>0.7110$ ). In direct pyrolysis-GC/MS, 3-heptylphenol (C7) and 3-pentadecylphenol (C15) were detected in the mass chromatograms at  $m/z = 108$  extracted ion pyrogram, and palmitic acid and stearic acid were detected in the mass chomatograms at  $m/z = 60$  extracted ion pyrogram, suggesting that the sap collected from *Toxicodendron vernicifluum* lacquer tree and was added in much additives when be used. The cross-section and EDX revealed the coating technique and pigment species of lacquerware. Based on these results, the Chinese Qin-Han Dynasty lacquer culture are discussed.

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## THE DRAMATIC EFFECT OF THE ALUM TREATMENT ON THE OSEBERG WOOD COLLECTION: A PY-GC/MS AND ICP-OES STUDY

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The Viking Age alum-treated archaeological wood artefacts from the Oseberg collection are today highly degraded, a condition partly attributed to the alum-treatment performed at the beginning of last century. The wood preservation is non homogeneous, and also the alum content is different in the various objects and also in different areas of the same object. Samples collected from “alum poor” and “alum rich” regions of same fragments were analysed by analytical technique as pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS), inductively-coupled plasma – optical emission spectroscopy (ICP-OES) and ionic chromatography (IC). Relevant information about the chemical composition were obtained, and related to the state of preservation.

Py-GC/MS showed that the wood was highly depleted of carbohydrates. The lignin fraction was also highly degraded. Specifically, Py-GC/MS showed the “alum-rich” wood to have a lower content of pyrolysis products deriving from unaltered lignin with respect to samples from “alum poor” regions. Furthermore, in the same samples there was a higher content of pyrolysis products deriving from altered lignin. The main degradation reactions involved oxidation, side-chain cleavage and demethylation of lignin. Although the mechanisms of these reactions are very complex, results from ICP-OES suggested that the degree of deterioration is related to the metal content of the samples, in particular iron and calcium [1]. The relative abundance of pyrolysis products with carboxyl functionalities, detected as major products and markers of oxidation, also correlated with the content of aluminium, potassium, sulphur and sulphates. Similar trends were observed for the results obtained by all the different applied techniques, highlighting successful complementarity. The chemical composition and the states of preservation of the artefacts were related to the alum content in the samples.

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## CHEMICAL CHANGES OF THERMO-HYDRO TREATED BIRCH VENEERS

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Wood thermal treatment is a widely explored technology of wood modification in the field of solid wood. Expanding the use of thermo-hydro treatment (THT) technology towards wood composites, THT of veneers is a lesser explored area, however it could be used for the production of plywood with increased dimensional stability and enhanced resistance against biological attacks. Low thickness of veneers results in a more extensive thermal degradation at lower treatment temperatures and shorter treatment duration than solid wood. In the process of thermal treatment part of the wood is volatilized, which leads to mass loss, and the remaining residue can be extracted with acetone, since the constituents are poorly bound to the material. From the environmental point of view, it is important to identify volatiles, since they can cause emissions when the material is applied for plywood production. The aim of this research was to study chemical changes in birch veneers after thermo-hydro treatment in various regimes and identify compounds extracted with acetone.

In the present study rotary cut birch wood veneers were subjected to one-step thermal treatment in water vapor environment under elevated pressure. The highest treatment temperatures – 150°C, 160°C and 170°C were maintained for 50 minutes. After the treatment mass loss was determined and the material was extracted with acetone. Chemical composition of extracted, treated as well as untreated material was investigated by analytical pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS), Fourier transform infrared spectroscopy (FTIR-ATR) and elemental analysis. Surface functional groups were studied by wet-chemistry methods.

It was found that the mass loss during the process of hydrothermal treatment varies from 2.8% at 150°C to 13.9% at 170°C. The quantitative composition of volatiles resulting from analytical pyrolysis differed between extracted and non-extracted samples (mass loss in the process of THT was taken in account when calculating results in relative %). Py-GC-MS study of extracted and non-extracted samples shows that thermal treatment decreases total content of volatiles – both carbohydrate (58% to 51% for non-extracted, 57% to 44% for extracted) and phenolic derivatives (15% to 12% for non-extracted and 15% to 8% for extracted). Among carbohydrate derivatives ratio of acids, esters, and pyranes decreases, however ratio of aldehydes, ketones, furanes and sugars increases. Changes in the lignin derivatives content are accompanied with increase of phenyl and benzyl compounds ratio, which points at lignin condensation, and decrease of syringil compounds.

Formation of furans is also supported by FTIR-ATR data, and coincides with GC-MS results of acetone extracts - content of furans significantly increases with temperature increase for the treated samples, when no furans are observed in extracts of unmodified veneer. Thermal destruction of hemicelluloses is responsible for obtained tendency.

More compelling results can be obtained, if changes in each identified substance are analyzed separately.

Key words: birch veneer, thermo-hydro treatment, wood chemical composition, FTIR, Py-GC-MS

## CHARACTERIZATION AND AGEING STUDIES OF AQUAZOL RETOUCHING PAINTS USING TECHNIQUES BASED ON PYROLYSIS

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Aquazol is the commercial name of a family of thermoplastic polymers made up of poly(2-ethyl-2-oxazoline) (PEOX), which has only been investigated to a limited extent. PEOX is a non-ionic tertiary amide formed by the cationic ring opening polymerization.

This class of polymers have found several applications in the field of conservation consolidants and coatings, thanks to their high flexibility and their reversibility with deionised water or polar solvents [1]. Nevertheless to date, the stability and ageing behaviour of Aquazol have only been tested on a limited basis [2,3].

We investigated the possibility of using Aquazol 500 as paint binder in the production of retouching paints. Pyrolysis and mass spectrometry (Py-GC/MS and EGA-MS) and thermal analysis techniques were used to characterize the raw materials used in the formulation of the retouching paints and to evaluate the stability of the resulting paints during artificial ageing. The study involved not only the characterization of the Aquazol polymers but also the study of the additives and of several synthetic pigments, such as Alizarin, Irgazin<sup>®</sup> red, Quindo<sup>®</sup> pink. In order to evaluate the performances of the home-made retouching paint the results were compared with those obtained from the characterization of the commercial paints based on Aquazol available from the Golden Artist Colors [2].

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## The combination of pyrolysis-based techniques to evaluate the state of preservation of archaeological wood in the presence of consolidating agents

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The evaluation of the degradation state of archaeological wood can be performed at different levels of detail using optical microscopy, SEM, TAPPI methods, FTIR, NMR and Py-GC-MS techniques. Analytical pyrolysis presents a series of advantages, such as small sample size (*ca.* 100  $\mu$ g), short time of analysis (*ca.* 30 min.), and negligible pre-treatment of the sample. These are often fundamental requirements in the field of cultural heritage.

A correct interpretation of the results obtained by analytical pyrolysis enables precious information at a molecular level about wood degradation to be achieved. In particular, the ratio between holocellulose and lignin content (H/L ratio) is a commonly used parameter to evaluate the degradation state of archaeological wood in terms of loss of wood components. In addition, a categorisation of holocellulose and lignin pyrolysis products according to their molecular structure and pyrolytic formation, achieves information about the degradation reactions undergone by the single wood components (holocellulose and lignin), allowing to integrate the information obtained by the calculation of the H/L ratio.

Waterlogged archaeological wood usually needs to be consolidated and most of the consolidating agents are not reversible, thus the evaluation of the degradation state of consolidated archaeological wood is dramatically complicated by the presence of the consolidating agent.

In this work we present an analytical method based on Evolved Gas Analysis (EGA-MS) and Py-GC-MS with *in situ* silylation using hexamethyldisilazane (HMDS) suitable to establish the degradation state of wood even in presence of consolidating agents. EGA-MS allows to identify the principal zones of thermal degradation of the different materials simultaneously present in a composite sample. It is then possible to perform several single-shot pyrolysis experiments at different temperatures on the same sample, thus selectively thermally degrading the different components. Alternatively, a single-shot pyrolysis experiment can also be performed and the different components can be studied simultaneously by overcoming the presence of overlapping peaks using the AMDIS (Automated Mass spectral Deconvolution and Identification System) software to deconvolute the pyrogram.

The method was applied to some samples from “L’Aimable Grenot”, a corsair boat dating back to the 18<sup>th</sup> century and sunken in 1750 out of the Saint Malo harbour (France), and from the shipwreck called “Lyon”, which is part of sixteen wrecks discovered during the salvage excavations of the Parc Saint-Georges in Lyon, Rhone region (France), and dating back to the 2<sup>nd</sup> century AD. The results highlighted that different zones of thermal degradation for wood and conservation materials can be identified and used to separately investigate their chemical changes, using EGA-MS. Py(HMDS)-GC-MS allowed to characterise the wood and obtain molecular information on the degradation state of its components. In addition, this method can be applied on every kind of lignocellulosic material with the aim to highlight chemical changes in biopolymers such as cellulose, hemicelluloses and lignin.

The research was performed in the framework of the ArCo project (2014-2016), funded in the framework of JPI-JHEP Joint Pilot Transnational Call for Joint Research Projects on Cultural Heritage.

## END GROUP ANALYSIS OF STYRENE-BUTYL ACRYLATE COPOLYMERS PREPARED USING BENZOYLPEROXIDE INITIATOR BY STEPWISE CHEMOLYSIS-PYROLYSIS GAS CHROMATOGRAPHY

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Pyrolysis-gas chromatography (Py-GC) has been widely utilized for structural characterization of various synthetic polymers. Even for the end groups in a polymer sample, which are generally difficult to be analyzed because of their trace concentrations compared to polymer main chains, can be characterized qualitatively and quantitatively by Py-GC due to its high sensitivity [1]. In general, the fragments of initiators and chain transfer agents are incorporated in to the polymer chain end. In the case various types of terminal groups are coexisting, their detailed characterization becomes much more difficult. Moreover, as for copolymer samples, the observed pyrograms frequently become so complicated that it is not an easy task to evaluate in detail the characteristic products of the end groups among the complex pyrolysis products in the pyrograms.

For the Py-GC analysis of such complex polymer structures, stepwise measurements, especially the combination of chemolysis (thermally assisted hydrolysis and methylation) and pyrolysis, are often effective. So far stepwise Py-GC in the presence of TMAH at different temperatures was applied to the determination of the end group functionalities of polystyrene macromonomers with methacryloyl (ML) end groups [2]. In this case, stepwise pyrolysis using a two-stage pyrolyzer consisting of two independent furnaces was utilized to decompose the ML end group moieties hydrolytically into their methyl derivatives such as methyl methacrylate (MMA) at 250 °C and then to pyrolyze the polystyrene main chains thoroughly at 650 °C. The concentration of the ML end groups was determined by comparing the peak intensity of MMA observed in the former pyrogram with those of the characteristic products formed from the polystyrene main chain in the latter pyrogram. In this work, the stepwise chemolysis-pyrolysis GC was applied to the end group determination in more complex styrene (St)-butyl acrylate (BA) copolymers radically polymerized using benzoyl peroxide (BPO) initiator.

A series of St-BA copolymer (St : BA = 80 : 20 in molar feed) samples were prepared through radical polymerization with various contents (1.5 - 10 wt%) of BPO. In this polymerization reaction, it is well-known that two kinds of BPO fragments, benzoyloxy and phenyl groups are incorporated into the polymer chain ends. The stepwise chemolysis and pyrolysis-GC measurements were performed using GC-MS (for peak identification) or GC-FID (for quantification) equipped with a microfurnace pyrolyzer (Frontier Lab PY-2020iD). In the first chemolysis step, the copolymer sample (ca. 0.3 mg) mixed with tetramethylammonium hydroxide (TMAH, 25 wt% methanol solution, 2  $\mu$ L) was introduced into the pyrolyzer and heated at 250 °C for 10 min. During this step, the formed products were cold trapped at the inlet part of the metal capillary separation column dipped in liquid N<sub>2</sub>, then the trap was removed with drawing up the sample in the cup to the waiting position and GC measurement was started. In the resultant chromatograms, only the peak of methyl benzoate formed through chemolysis reaction selectively and quantitatively at the benzoyloxy terminals by TMAH. During the first step, the temperature of the pyrolyzer was raised to 600 °C, and after the GC measurement of the chemolysis products, the second step Py-GC of the residual copolymer sample was carried out. In the observed pyrograms, the peaks of the characteristic products formed from phenyl end groups, benzene and stilbene, were clearly detected among the various pyrolyzates of polymer main chain.

Based on the peak intensities of these characteristic products, relative contents of the individual end groups were able to be estimated, and was proved to be almost proportional to the feed amounts of BPO for both end groups. Moreover, it was suggested that the content of benzoyloxy end group was roughly twice larger than that of phenyl terminal.

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## Chemical Analysis of UV irradiated B-72 by Py-GC/MS and EGA-MS

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Relics of various countries including Japan have been restored using some synthetic resin until now. Paraloid™ B-72 (B-72) is one of the most widely used synthetic resins in restoration. However, B-72 film appeared discoloration, cracks and mold after restoration have been reported in recent years. The degraded B-72 film may cause deteriorations of aesthetics and state of preservation. In consequence, the degraded B-72 film must be removed. But, it's difficult to remove the degraded B-72 film because it is impossible to be redissolved in organic solvent. For this reason, B-72 film was considered to have changed composition after degradation.

In this study, B-72 film was degraded by ultraviolet irradiation (185 nm, 120h) and the degradation fragments were characterized by pyrolysis gas chromatography mass spectrometry (Py-GC/MS) and Evolved Gas Analysis mass spectrometry (EGA-MS). Figure 1 presents the Py-GC/MS spectra of the UV-irradiated and Non-irradiated. Compared with Non-irradiated, UV-irradiated appears four peaks at 14.47–15.57 min from T.I.C.. Figure 2 presents the EGA-MS spectra of UV-irradiated and Non-irradiated. A two-step appearance of gas was observed at around 200–400°C in Non-irradiated, whereas UV-irradiated shows a one-step appearance of gas at around 100–450°C. Thus, the appearance of gas behavior change with UV irradiated because of scission process by radical [1].

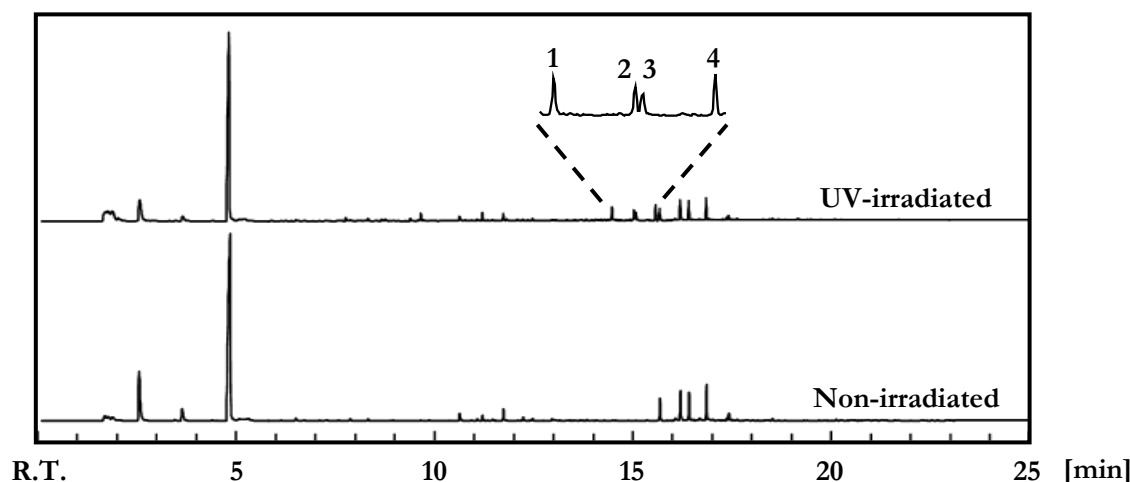


Figure 1 Py-GC/MS spectra of the UV-irradiated and Non-irradiated B-72 film

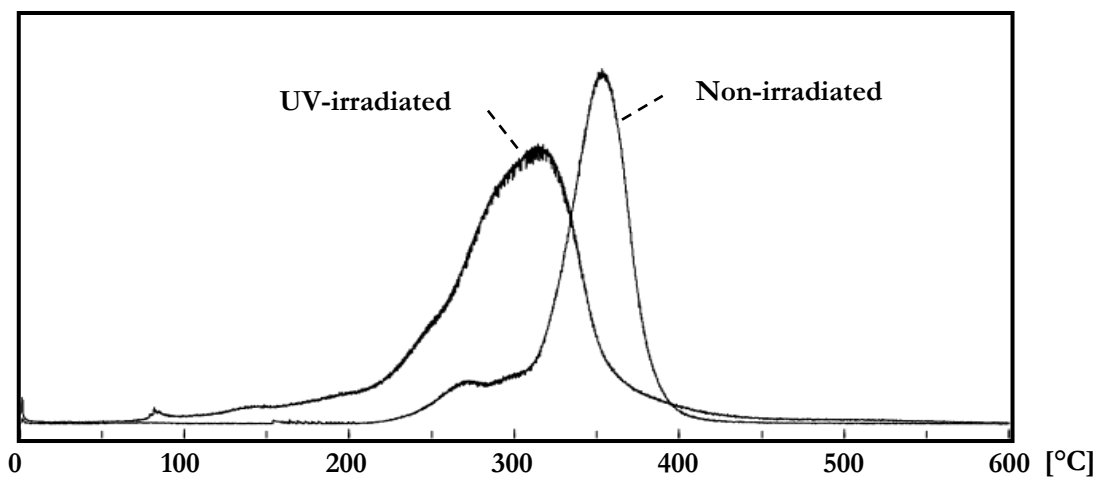


Figure 2 EGA-MS spectra of the UV-irradiated and Non-irradiated B-72 film

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## Quantification of polyvinylpyrrolidone (PVP) and polyvinylalcohol (PVOH) in polyamide films by pyrolysis GC-MS

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Polyvinylpyrrolidone (PVP) and polyvinylalcohol (PVOH) are used in combination with polyamide for food contact applications like water-soluble packaging films. For quality control/quality assurance purposes PVP and PVOH concentrations need to be measured in the final products and therefore pyrolysis GC-MS was applied as this method is supposed to perform with the requested sensitivity, selectivity and accuracy. FTIR spectroscopy was used for identification purposes; however, from the FTIR data no real quantification (weight% ratio) could be given. For this application the polymer composition is generally known before (supplier, FTIR data) and with this a priori knowledge, target peaks can be selected for pyrolysis GC-MS. For the pyrolysis analysis up to 20 mg of sample was placed in an 80  $\mu$ l sample cup and by free fall injected and heated up to 650°C for 2 minutes in a helium stream. The hardware configuration uses a thermal desorbing/pyrolysis unit coupled to GC-MS (PY-2020iD, Frontier laboratories, Japan/ GC-MS QP2010 Plus, Shimadzu, Kyoto, Japan) using an Ultra ALLOY-5 column (0.25 mm i.d. x 30 m x 0,25  $\mu$ m film thickness, Frontier laboratories, Japan). The mass spectrometer was programmed in single ion monitoring prior to the selected target analytes using electron impact ionization (70 eV) and a detector dwell time of 0.30 seconds.[1] [2]

For this measurement external calibration has been chosen by using in-house mixed reference materials (PVP and PVOH concentrations ranging from 15-40 weight %). A 4-point calibration has been used were beside linearity, as a method requirement, the obtained results should fall within the range of the calibration. The sample and calibration points must be measured at least in double to document either the sample homogeneity as well as the uncertainty of the instrument analysis. Each measurement is joined with a cleaning blank (no cup, no sample) for checking the cleanness of the sample path and a blank (cup without sample) before injecting the samples/calibration. The method stands and falls with the selection of the right quantifiers. The quantifiers for PVOH and PA6 are the area ratio of 2-butenal and caprolactam while the quantifiers for PVP and PA6 are n-vinylpyrrolidinone and caprolactam. For calculation; one quantifier fragment comes from polymer A ( $Q_A$ ) while this signal is relatively compared to the sum of the both quantifiers from polymer A and polymer B ( $Q_A$  and  $Q_B$ ). These numbers (ranging from 0 to 1) in combination with the corresponding concentrations are given in the calibration curve.

As an example the measured results for 7 samples are given in Table 1. For samples 1 till 5 (PVOH in PA6) the standard deviation is below or meeting 1,0 while for samples 6 and 7 (PVP in PA6) a higher standard deviation has been obtained. Higher standard deviations coming from technical samples might be caused by local homogeneity issues as there have to be noted that such film samples have a very limited thickness ( $\mu$ m-range).

Table 1: overview of test results on the quantification of PVOH/PVP in PA6 films by pyrolysis GC-MS

| Sample # | Parameter   | Weight %<br>(average $\pm$ standard deviation; n=2) |
|----------|-------------|---|
| 1        | PVOH in PA6 | 19,0 $\pm$ 0,8                                      |
| 2        | PVOH in PA6 | 31,1 $\pm$ 1,0                                      |
| 3        | PVOH in PA6 | 30,9 $\pm$ 0,4                                      |
| 4        | PVOH in PA6 | 26,6 $\pm$ 0,1                                      |
| 5        | PVOH in PA6 | 22,2 $\pm$ 0,8                                      |
| 6        | PVP in PA6  | 21,7 $\pm$ 3,8                                      |
| 7        | PVP in PA6  | 17,2 $\pm$ 2,8                                      |

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## Feasibility of pyrolysis GC-MS for the characterization of chemical modified polymer surfaces

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Many polymer applications can be improved by modifying surface properties like roughness, hydrophilicity, surface charge, surface energy, reactivity, biocompatibility, permeability, UV-stability, chemical and heat resistance. Surface modification techniques like surface roughening, surface patterning, chemical surface modification and molecular attachment are commonly used. Surface-engineered material finds its field in chemistry, mechanical engineering and electrical engineering. In several cases the customer would like to confirm the presence of surface specific chemicals after modification which is a challenge with common analytical tools as techniques like electron microscopy-EDX or FTIR are suffering from sensitivity or specificity problems.

By using pyrolysis GC-MS, having a nanogram sensitivity, chemical surface modification systems can be confirmed after mechanical separation of the surface. Knowledge of the matrix (substrate) is an advantage as these signals can be subtracted from the obtained data in the pyrogram. For this analysis a common pyrolysis GC-MS configuration can be used. Generally, 650°C for 2 minutes in a helium stream were the applied pyrolysis conditions. The hardware configuration uses a thermal desorbing unit coupled to GC-MS (PY-2020iD, Frontier laboratories, Japan/ GC-MS QP2010 Plus, Shimadzu, Kyoto, Japan) having an Ultra ALLOY-5 column (0.25 mm i.d. x 30 m x 0,25 µm film thickness, Frontier laboratories, Japan). The mass spectrometer was programmed in full scan mode from 30-1000 Da with electron impact ionization (70 eV) and a detector dwell time of 0.30 seconds.[1] [2] [3]

2 applications, where a chemical surface modification was performed, are demonstrated by using pyrolysis GC-MS; one example shows the characterization potential for polyurethane adhesive identification on a polyolefin based matrix while another example proves the presence of a fluorine based coating on polyethylene terephthalate (PET) fabrics.

Polyolefin based films might be modified on their surface by a µ-layer of embedded glass pearls glued by polyurethane based adhesives improving heat resistance, scratch resistance or improving water repelling properties. By pyrolysis GC-MS the complete polyurethane adhesive system can be revealed as polyurethanes pyrolytic fragmentise at the urethane bond remaining isocyanates and alcohols followed by the release of CO<sub>2</sub> forming the primary amine corresponding to the initially amine before the phosgenation process in the isocyanate production.[4] Not only small quantities of polyurethane glue on a polyolefin surface but as well polyurethane based primers, chain extenders and the diol (ester and ether) part can be revealed. Beside common isocyanate adhesive systems like MDI and TDI also more complex systems using IPDI, HMDI or diisopropylphenyl type diisocyanates can be evaluated. In all cases a small amount of sample was mechanically removed from the surface and pyrolyzed.

Beside the use of fluoroelastomers having an excellent high temperature and chemical resistance also PET fabrics might be coated by fluorinated compounds as perfluoroalkyl-grafted fabrics have as well improved chemical/thermal stability and improved oil/water repellence.[5] In certain cases pyrolysis GC-MS could distinguish between fluorine coated PET fibres and non-fluorine coated PET fibres, this, by the detection of tridecafluoro-1-octene. Vinyl based fluoroalkenes are appearing in the pyrograms as monomer resulting after the back-to-monomer process in the pyrolyzer. In this case the PET fiber was taken as a whole as the fluorinated part cannot be separated from the matrix.

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## ANALYTICAL PYROLYSIS OF PRETREATED HEMP SHIVES LIGNOCELLULOSE TO LEVOGLUCOSAN AND LEVOGLUCOSENONE

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The utilization of biomass is imperative for a bio-based society. While many sources of biomass exist, this study focuses on industrial hemp (*Cannabis Sativa* L.) shives as a feedstock for producing value added products. Levoglucosan (LG) has the potential to be used in the synthesis of dextrans, bioethanol, various polymers and complex asymmetric molecules. High yields of LG can be achieved if lignocellulosic biomass is pyrolysed after optimal pretreatment conditions (usually at 500°C). Levoglucosenone (LGO) - a pyrolytic product of cellulose, used as a chiral source for synthesizing natural products - can be produced with high selectivity and yield from the fast pyrolysis of cellulose/biomass impregnated with phosphoric acid at 500°C.

Pretreatment of industrial hemp shives with 5%  $\text{Al}_2(\text{SO}_4)_3$  as a catalyst was performed at 170°C for 90 min. The yield of furfural and acetic acid was 9.2% and 7.0%, respectively; and the amount of residual lignocellulose was 75.5%. The lignocellulose fraction (washed and unwashed) was subjected to cellulose compositional and thermogravimetric analysis, as well as analytical pyrolysis at 400°C and 500°C, which resulted in 40% total condensable products, with LG and LGO as the target chemicals.

The yield of  $\alpha$ -cellulose decreased from 41.7% to 16.2%, while the yield of  $\beta$ -cellulose increased from 0% to 18.8%. The larger amount of  $\beta$ -cellulose yield infers that the structure of the cellulose matrix was more effectively degraded and became more digestible due to the catalytic effect of  $\text{Al}_2(\text{SO}_4)_3$ . This implies that  $\text{Al}_2(\text{SO}_4)_3$  catalyses not only the decomposition of  $\gamma$ -cellulose but also the depolymerisation of  $\alpha$ -cellulose. Thermogravimetric analysis shows that maximal decomposition temperature for unwashed LC is 246°C while that for washed LC sample 336°C and untreated hemp shives 350°C. Lower maximal decomposition temperature can be attributed to the presence of catalyst left in LC after pretreatment process. Therefore, special attention was paid to the pyrolysis temperature. Washing resulted in a higher formation of carbohydrates (3.1%), especially hydroxyacetaldehyde (1.1%) and LG (8.7%), but decreased the yield of furfural and its derivatives. This is because LC samples did not contain many water-soluble hemicellulose degradation products or free aluminum sulfate. Washing the LC fraction before pyrolysis at 500°C increased the yield of LG by approximately fivefold (from 1.73 to 8.7%) while LGO was absent. Pyrolysis of unwashed LC at 400°C resulted in elevated amounts of LGO (5.7%) in the condensable products.

These results demonstrate that the LC residue that is left after furfural production can be used as a feedstock for the production of LG after washing the remaining catalyst and inorganic substances using fast pyrolysis at 500°C. However, more economical efforts could be obtained if LGO was considered to be a final product. Washing with water would therefore not be necessary, and fast pyrolysis could be performed at a temperature of 400°C.

## CHEMICAL CHARACTERISATION OF TARS FROM THERMAL CONVERSION OF BIOMASS BY 1D GAS CHROMATOGRAPHY COMBINED WITH SILYLATION

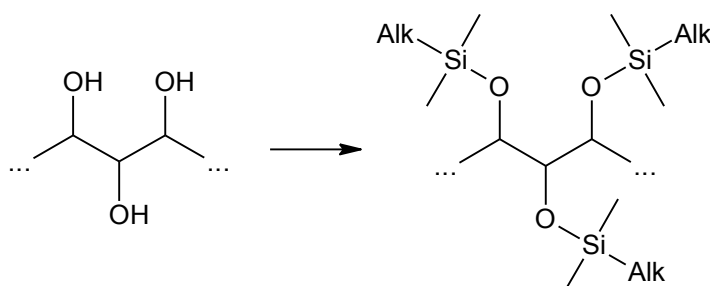
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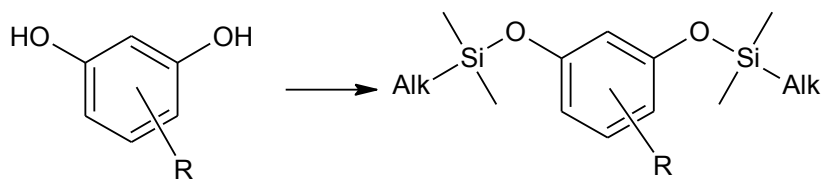
Tars obtained from thermal conversion of biomass are an incredibly rich source of information on type and composition of feed-biomass as well as process parameters. So far that information remains hidden due to lack of analytical and data processing methods that can handle with such an enormous set of chemical individuals. Herein we would like to present our partial research based on results obtained from gas chromatography combined with chemical derivatization with the use of silyl agents.

That approach extended the range of compounds that can be analysed with gas chromatography technique by polyalcohols and polyphenols with low-volatility and medium thermal stability. All results were studied with chemometric methods which proved to be excellent tools when handling large sets of data.

Examined tars originated from batch and continuous pyrolysis of wood-biomass, straw and waste-plant biomass in temperature range between 400 and 600°C.



Silylation reaction of polyphenols and polyalcohols



Silylation reaction of polyphenols and polyalcohols

## ANALYTICAL PYROLYSIS AS A METHOD TO QUANTITATIVE ANALYSIS OF FOSSIL FUELS CONTAMINANTS IN BIOCHAR

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The primary goal of this research was to apply analytical pyrolysis technique (Py-GC-MS) combined with chemometric methods (Partial Least Squares Regression - PLSR and Principal Components Regression - PCR) in order to determine the pyrolysis behaviours of biochars mixed with fresh low-rank fuels. Biochars from wheat straw, forestry wood and waste wood (waste furniture) were prepared using a 1 kg fixed-bed reactor at 500°C with a residence time of 20 min. The Py-GC-MS pyrolysis experiments were carried out at 500, 700 and 900°C. Biochars were mixed with low-rank fuels (acid hydrolysis residue, peat and brow coal) at the level of 2, 4, 16 and 32 wt. %.

Obtained chromatographic and mass spectral data were pre-processed using a MATLAB software and the correlation between the concentration of added external low-ranks fuels, intensity of mass fragment ions and peak areas was determined by PLSR and PCR regression methods. This chemometric approach of the Py-GC-MS data processing accomplishes the non-quantitative Fourier transform infrared spectroscopy (FTIR) data analysis [1, 2].

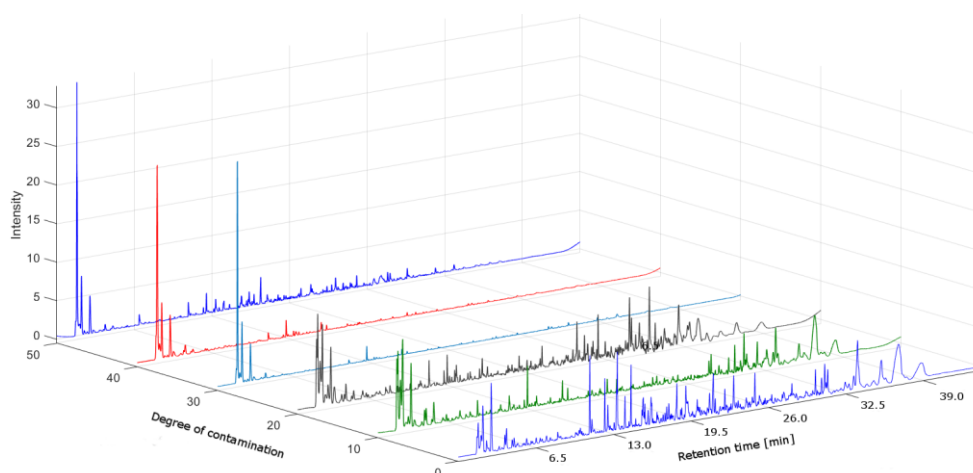


Fig. 1. Py-GC-MS chromatograms of wheat straw biochar and acid hydrolysis residue mixtures pyrolysed at 500°C.

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## THERMALLY ASSISTED CHEMOLYSIS USING HYDROGEN DONOR REAGENT FOR STRUCTURAL ANALYSIS OF INTRACTABLE CROSS-LINKING POLYMERS

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Thermally assisted hydrolysis and methylation gas chromatography (THM-GC) using tetramethylammonium hydroxide (TMAH) is widely utilized for the characterization of condensation polymers in terms of precise chemical composition and microstructures such as branching and end groups, which are often difficult to be analysed by conventional pyrolysis (Py)-GC. However, THM reaction is practically effective only for ester and carbonate linkages. Accordingly, to characterize various intractable materials, a novel thermally assisted chemolysis technique applicable to a wide variety of cross-linking polymers has been required.

On the other hand, from the point of view of polymer recycling, it has been reported that thermosetting phenol and epoxy resins are solubilized in hydrogen-donor solvent such as tetralin at around 450 °C [1]. This process could be achieved through thermal bond cleavages in polymer chains followed by hydrogen supply from solvent although the detailed reaction mechanisms were unclear. Recently, it was demonstrated that lignin was also liquefied with hydrogen-donor solvent [2] in a micro reaction sampler set in a vertical microfurnace pyrolyzer of Py-GC system [3]. In this work, to develop a unique thermally assisted chemolysis technique useful for structural analyses of various cross-linking polymers, the conversion reactions of thermocured epoxy and phenol resins in tetralin were investigated in detail.

The ground resin sample was weighed and put into an autoclave made of a stainless steel tube (1.4 inch  $\Phi$ , ca. 7 cm long) together with given amount of tetralin. The sealed autoclave was heated for prescribed period and temperature up to 450 °C. The recovered products of the resin samples were then analysed both by matrix assisted laser desorption ionization-mass spectrometry (MALDI-MS) and Py-GC-MS.

As for epoxy resin samples cured with imidazole compounds, the samples were thoroughly solubilized in tetralin at 400 °C for 1 hour. MALDI mass spectra of the products showed a number of peaks of the species which should be formed through bond cleavage with hydrogen donation. Meanwhile the cured phenol resins were also completely liquefied in tetralin in the sealed autoclave at 450 °C for 1 hour. In the MALDI mass spectra of the liquefied products, various oligomeric species, which should be also formed through bond cleavages with hydrogen supply, were observed. Moreover, when the products from the phenol resin samples were subjected to Py-GC measurements, mono and diaromatic compounds were mainly observed in the pyrogram. It is quite interesting to note that 2, 4, 6-trimethyl phenol was clearly observed in the pyrogram of the decomposition products of phenol resin. This product should directly reflect the cross-linking structure of the cured phenol resins, whereas it is hardly observed in the pyrograms obtained by ordinary Py-GC measurements. This observation suggests the potential of chemolysis with tetralin useful for the analysis of the cross-linking structure of cured resin samples.

Moreover, the cured resin samples were also subjected to the measurements using micro reaction sampler with tetralin in Py-GC system. Based on the observed results, the possibilities of the chemolysis with hydrogen-donor tetralin on the structural analysis of intractable cross-linking polymers were discussed in detail.

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## DETERMINATION OF FORMALDEHYDE AS A PYROLYSIS PRODUCT USING ANALYTICAL PYROLYSIS DERIVATIZATION-GC/MS

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Formaldehyde is a volatile organic compound with a low molecular weight and a low boiling point (-21°C). A common air pollutant and health hazard, it is typically sampled from indoor atmosphere onto a sorbent tube coated with a derivatizing agent, Dinitrophenyl Hydrazine (DNPH), and taken back to a lab to be analyzed by HPLC. Alternatively, formaldehyde can be analyzed using GC with help of fluorinated derivatizing agents. These include pentafluorobenzyl hydroxyl amine (PFBHA), and Pentafluorophenyl Hydrazine (PFPH). Both react with formaldehyde on sorbent tubes to produce thermally stable derivatives, and PFPH has shown to be more effective and versatile (than PFBHA) for GC analysis of aldehydes[1].

GC/MS and FTIR are most commonly used to analyze polymer pyrolysates; PY-FTIR allows for the detection of volatile gases such as formaldehyde. While PY-GC/MS is useful for analyzing semi-volatile pyrolysis products, small volatile gases are more difficult. However, pyrolysis coupled with derivatization on a sorbent trap can facilitate the detection of formaldehyde as a pyrolysis product with GC/MS.

In this presentation, we will use analytical pyrolysis GC/MS to study the detection of formaldehyde using a derivatization method. Pyrolyzed vapors flow to a sorbent trap coated with PFPH, and the trap heats to release aldehyde derivatives directly to the GC/MS for analysis. Polymers such as phenol-formaldehyde resin, tobacco, and sugars are studied. Detecting small molecules, such as formaldehyde can be used confirm reaction mechanisms, and to study combustion reactions.

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## Analytical Pyrolysis in the investigation of turquoise imitations and treatments

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Turquoise is a complex basic copper aluminum phosphate best represented by the formula  $\text{Cu}(\text{Al,Fe})_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$ . The color turquoise has been named after the mineral and is typical for the species, although variations between green and blue can occur.

The material has been used in jewelry since ancient times, especially in Persia and by Indian tribes in America. Nowadays it is still popular and besides the purely natural material several imitations or modifications are on the market. Starting from inorganic materials which are simply soaked with color or coated with a varnish, via natural material which has been reinforced or sintered with binders, to fully synthetic products – almost everything is available and has been used.

Conventional gemological identification methods are rather limited with non-transparent materials; one way of identifying polymer imitations is by sticking a hot needle into the material and checking if there is smoke - a simple pyrolytic approach. We have used pyrolysis-GC/MS to identify fakes such as polyurethanes, polymethylmethacrylates, melamine resins, but also treatments of natural turquoise such as impregnation with wax or cyanoacrylate can be easily identified. The results have been verified with other techniques such as FTIR and Raman spectroscopy.



Fig. 1. Different turquoise samples, from left to right : chinese matrix turquoise, polymer stabilized turquoise, polyurethane coated stone, turquoise stabilized with melamine resin.

## Analysis of the aromatic composition of internal common rail injector deposits via thermal degradation

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Increasing reports about malfunctions in common rail injector (CRI) systems lead to a more intensive research on diesel fuel injection systems, which are working under higher pressures and temperatures. Under these conditions, deposits are formed leading to problems with the injector performance. Relatively few information is available on the origin of such deposits and their actual chemical composition. Previous studies have identified different substance classes such as alkanes and aromatic hydrocarbons in the deposits. In particular, aromatics and polycyclic aromatic hydrocarbons (PAHs) are suspected to produce insoluble solid precipitates. In this study, thermal degradation of deposits and subsequent characterization of the formed products by resonance-enhanced multi-photon ionization time-of-flight mass spectrometry (REMPI-TOFMS) was employed to reveal the aromatic-pattern of deposits on injector parts.

Experiments were carried out using a home-built injection test bench. Mineral diesel fuel (no biodiesel content) with or without deposit control additive as well as hydrated vegetable oil (HVO) were used as fuels. The influence of temperature, injection pressure, injection amount of used fuel, and fuel composition on the tendency to form deposits on the metal surface of commercial CRI parts was investigated. After the test bench run, small rings of the injector system were directly investigated without any sample preparation. Aromatic species desorbing from the ring's surface indicate a strong influence of temperature and fuel composition on the actual amount of aromatic compounds. A strong enrichment was observed in additive-free diesel fuel. HVO revealed almost no aromatic compounds in the deposits, since there is a measurable deposit layer observable, it has to be contained of non-aromatic substances. This is indicating that depending on the applied fuel there are several possible mechanisms leading to the formation of injector deposits.

## SCIENTIFIC ANALYSIS OF *JŌMON* RELIC EXCAVATED THE MINAMIKŌNUMA RUINS

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Many important historical products are excavated from ancient ruins all over Japan. The relics excavated from ruins are the vestiges on which people lived. Material and technique of the relics is valuable key to understand the culture of that era. Archaeological investigation is mainly studied by observation and reference records of past. However obtained information is not sufficient and the accuracy is questionable. This study purpose is clarifying material and fabrication technique by using scientific analysis.

In many studies of Japanese archaeology, lacquer and lacquerwares are the excavated from ancient ruins all over Japan [1, 2]. Lacquer sap is polymerized in the natural environment, is formed a coating film having excellent appearance and high hardness. Therefore lacquer is a natural paint that has been used in a wide range of fields from daily commodities to craft products since ancient times. This announcement was performed on Analysis of *Jōmon* relic excavated from the Minamikōnuma ruins in Japan. That the red iron oxide and mercury is used as red pigment have been reported by previous studies. Two red samples of the *Jōmon* period were excavated from the Minamikōnuma ruins. Sample A is wooden earring, B is wooden bowl (Figure). From results of Py-GC/MS, the samples were confirmed to contain *Toxicodendron vernicifluum* that is the Japanese, Chinese and Korean lacquer species. Moreover they were observed multilayer-coating from cross section and identified pigments from ED-XRF.

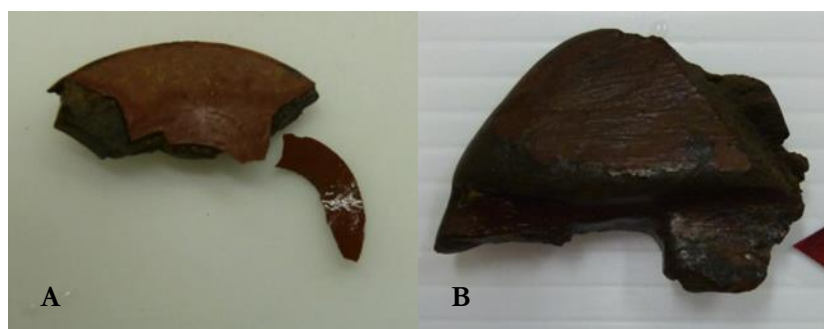


Figure Relics excavated from Minamikōnuma ruins A) earring B) bowl.

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## Analysis and identification of Ryukyu lacquerwares decorated with wisteria vine by pyrolysis-gas chromatography/mass spectrometry and <sup>87</sup>Sr/<sup>86</sup>Sr isotope ratio measurements

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### ABSTRACT

Three kinds of Ryukyu lacquer trays decorated with wisteria vine produced in the 17-19th century in Ryukyu Kingdom, and belonging to the Urasoe Art Museum were analyzed by cross-section, field emission scanning electron microscope with energy dispersive X-ray spectrometry (EDX), strontium isotope ratios (<sup>87</sup>Sr/<sup>86</sup>Sr) measurement, radioactive carbon 14 dating, and direct and on-line derivation using tetramethylammonium hydroxide (THMA) pyrolysis gas chromatography/mass spectrometry (Py-GC/MS). The carbon 14 dating analyzed results showed that the lacquer film was about 1728-1785 years ago. The <sup>87</sup>Sr/<sup>86</sup>Sr isotope ratios of lacquer film was 0.7107 consistent with that of the Japanese mainland (<0.7110). The wood species of lacquerware body was *Pinus parviflora* tree growth in the Japanese islands. In direct Py-GC/MS, 3-heptylphenol (C7) and 3-pentadecylphenol (C15) were detected in the mass chromatograms at m/z = 108 extracted ion pyrogram, and palmitic acid and stearic acid were detected in the mass chromatograms at m/z = 60 extracted ion pyrogram, implying that the sap collected from *Toxicodendron vernicifluum* lacquer tree and was added in much additives when be used drying oil at lacquerware making. The cross-section and EDX revealed the coating technique and pigment species of ancient lacquerware, suggesting an high lacquer technology in Ryukyu Kingdom period. In order to better conserve and restore valuable antique Ryukyu lacquerwares, identification of the lacquer species of Oriental lacquer is very important. Furthermore, the investigation definitely will provide scientific support for the conservators, restorers, and archaeologists.

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# Verification of the Absence of Combustion in an Electrically Heated Tobacco System<sup>1</sup>

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## I. ABSTRACT

The main purpose of this research is to verify the absence of combustion processes occurring in the solid porous media of a newly developed electrically heated tobacco system (EHTS)[1]. First, we define combustion as the phenomenon which happens after ignition and discuss the validity of the combustion criteria for the solid porous media as  $d^2T/dt^2 > 0$  and  $dT/dt > 0$  in the range of  $T > 400K$ . Then a universal numerical model for solid porous fuel with air flow in and out has been established. Finally, based on the definition of combustion and developed numerical model, we give a critical assessment on the presence or absence of combustion in the solid porous media as a simulation of the EHTS using product operating conditions. Based on the numerical calculations performed, combustion phenomena do not take place in the EHTS. Further, critical ignition maps for the solid porous media under different heat power input, puff frequency and puff duration have been drawn.

## II. FIGURES

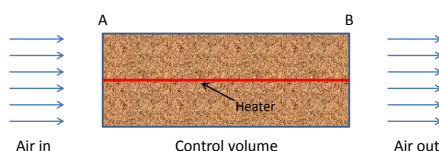


Fig.1. Porous media with Electrical heater

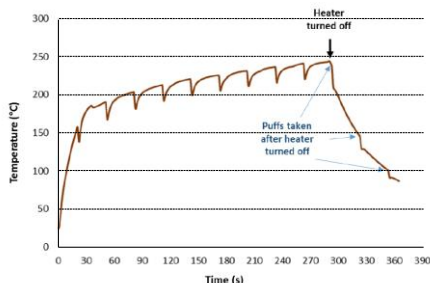


Fig.1. Experimentally measured tobacco plug average temperature (measured 0.5mm from the heater) when the heater is turned off during product use

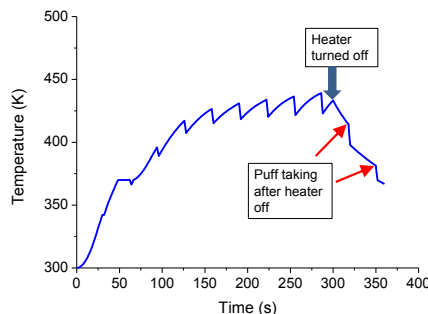


Fig.2. Simulated temperature history under the given heater temperature during heating and when the heater is turned off

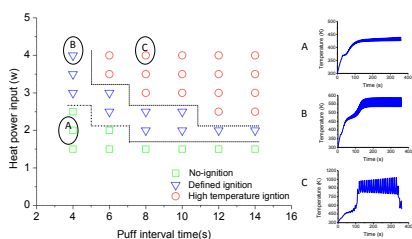


Fig.4. Ignition map (puff duration:2s, puff volume:55ml)

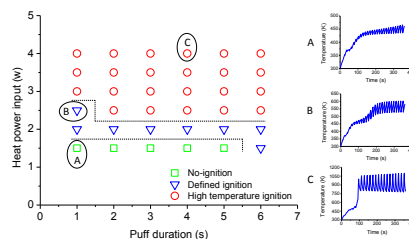


Fig.5. Ignition map (puff interval:12s, puff volume:55ml)

[1] The Electrically Heated Tobacco System (EHTS) was developed by Philip Morris International (PMI). All calculations performed were based on the thermophysical properties / product operating conditions provided by PMI and from published scientific literature.

## ODOR ANALYSIS OF PEROXIDE DEGRADED POLYPROPYLENE BY PYROLYSIS GAS CHROMATOGRAPHY-MASS SPECTROMETRY

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Polypropylene with high melt index (HMIPP) is widely used in fibers, large size products with thin wall and other complex shapes. There are two methods to obtain HMIPP. One is adding chain transfer agent (generally H<sub>2</sub>) during polymerization to adjust the molecular weight of PP to a lower value. The other way is adding peroxide during granulation procedure to degrade PP [1]. The peroxide degradation method is easy to carry out. The molecular weight and the melt index are easy to adjust by changing the concentration of peroxide. Therefore, this method is more used in industry.

However, unpleasant odor often emits in HMIPP prepared by the peroxide degradation method. The odor components and the correlation with peroxide type and concentration are concerned by the industry. In the literatures, head-space gas chromatography-mass spectrometry, thermodesorption gas chromatography-mass spectrometry and solid phase micro-extraction gas chromatography-mass spectrometry were used to analyze the small molecular weight volatiles in PP [2-4]. Alkanes, alkenes, ketones, carboxylic acids and phenols were detected.

In this paper, flash evaporation technique of pyrolysis gas chromatography-mass spectrometry (PGC-MS) was used to detect the volatiles in HMIPP by the peroxide degradation method. Characteristic peaks related only to peroxide degradation were identified by comparing chromatograms of PP with and without peroxide. The characteristic peaks corresponded not to the thermal decomposition products of peroxide, but the new thermal degradation fragments of PP with the initiation effect of peroxide. By quantitative analysis of these characteristic peaks, the correspondence between the odor and the peak intensity was established. This also supplies a possibility to evaluate the degradation degree of PP by peroxide.

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ABSTRACTS

# **Biomass / Catalysis**

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**Oral presentations**

## FAST PYROLYSIS OF BIOMASS AND IN-LINE STEAM REFORMING PROCESS FOR HYDROGEN PRODUCTION

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In recent years, renewable fuels have attracted significant interest due to the uprising price of fossil fuels and their environmental problems such as large amount of CO<sub>2</sub> emissions to the atmosphere, which is one of the most important causes of global warming and climate change [1]. Among different alternatives, hydrogen has been projected as one of the cleanest energy carriers and it is also a compound which is widely used in chemical industry. Hydrogen can be produced from many different feedstocks, including fossil fuels such as natural gas, oil derived feedstocks or coal, as well as renewable resources or wastes such as biomass or plastics. Thus, biomass will play an important role in medium to long term, because it is CO<sub>2</sub> neutral source and chemicals or fuels produced from biomass are considered sustainable.

The thermochemical conversion of biomass represents a renewable alternative for the full-scale production of hydrogen, where pyrolysis is the most efficient method due to the lower temperature required for the process comparing with gasification. An alternative to produce hydrogen from biomass that has gained growing attention is the indirect route by bio-oil reforming. Several authors carried out studies with different representative compounds of bio-oil, such as acetic acid, acetone or phenol, which are important to understand the reactivity and the coke formation in the catalyst [2]. Bio-oil aqueous fraction and raw bio-oil reforming have also been extensively studied in the literature. However, the bio-oil is unstable and it polymerizes under storage, provoking an increase of its viscosity and average molecular weight and therefore, it can generate operational problems, which can be avoided using a two step pyrolysis-catalytic steam reforming process.

In this study, the continuous fast pyrolysis of pine wood sawdust followed by in-line steam reforming of pyrolysis volatiles has been studied. The first step has been carried out at 500 °C in a conical spouted bed reactor (CSBR), which has several advantages for pyrolysis of biomass. The characteristic cyclic movement of CSBR gives way to high heat and mass transfer rates, and the vigorous movement of bed particles allows handling solids of irregular texture [3]. Moreover, this reactor is appropriate for continuous operation, which is essential for implementation of biomass pyrolysis at large scale [4]. On the other hand, the second step (catalytic steam reforming of pyrolysis volatiles) has been carried out in a fluidized bed reactor on a Ni commercial reforming catalyst.

At zero time on stream, 11.2 g of hydrogen are obtained per 100 g of biomass fed into the process, obtaining a conversion of 99.7 % and a hydrogen yield of 93.45 % at 600 °C, with 0.28 g<sub>catalyst</sub> h g<sub>biomass</sub><sup>-1</sup> and S/B=4. The high conversion obtained evidences the good performance of the two-step reaction system. The initial gas composition is the following one: 66.1 % H<sub>2</sub>, 30.1 % CO<sub>2</sub>, 3.6 % CO and 0.2 % CH<sub>4</sub>.

The temperature has a positive effect on conversion and hydrogen yield. At 550 °C, low conversion of volatiles is obtained, while above 600 °C the volatile products of biomass pyrolysis are almost fully converted to gas. Moreover, an increase in space-time from 0.14 to 0.42 g<sub>catalyst</sub> h g<sub>biomass</sub><sup>-1</sup> gives way to a higher conversion (from 91.6 % to 99.7 %). The influence of steam/biomass ratio (between 2 and 5) on initial conversion is not very significant, achieving a conversion higher than 99.5 % in the range studied.

Finally, the catalyst deactivation is significant increasing time on stream, due to the blocking of active centres by carbon deposition and thus, secondary reactions take place, obtaining higher CO, CH<sub>4</sub> and light hydrocarbons (ethylene, ethane, propylene, propane) concentrations.

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## PRODUCTION OF RENEWABLE AROMATIC COMPOUNDS BY CATALYTIC FAST PYROLYSIS OF LIGNOCELLULOSIC BIOMASS WITH CE-ZSM-5 AND V-ZSM-5 CATALYSTS

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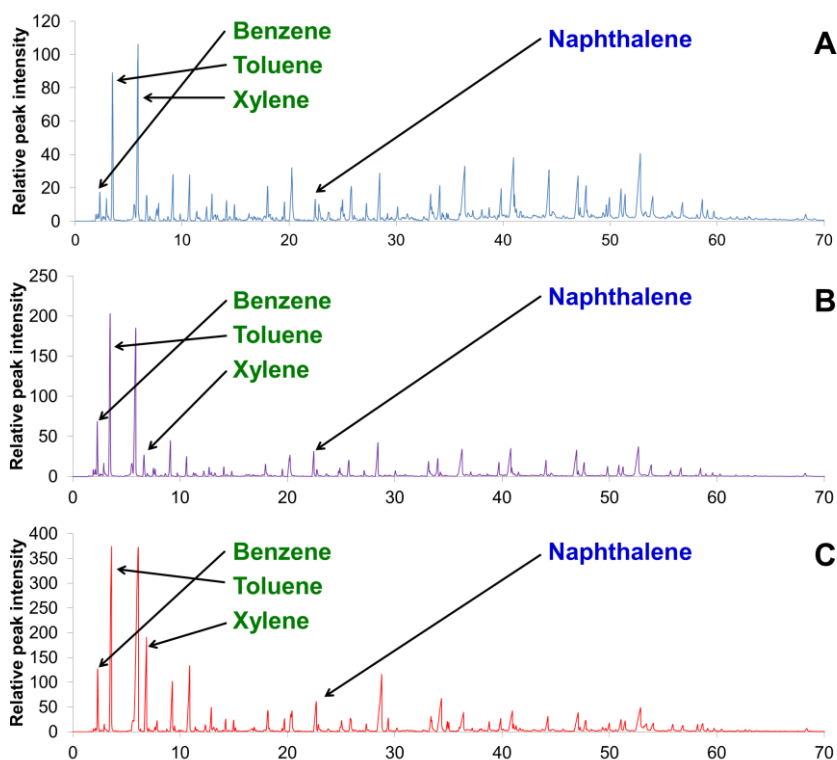
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Upgrading bio-oil to a conventional transport fuel requires full deoxygenation and can be achieved by catalytic cracking of fast pyrolysis vapours. Catalytic cracking accomplishes deoxygenation through simultaneous dehydration, decarboxylation, and decarbonylation reactions occurring in the presence of a zeolite catalyst. Zeolite catalysts have been used for the pyrolysis of biomass and related materials and shown high aromatic selectivity but are deactivated rapidly due to coke formation on the zeolite surface. By limiting the production of polycyclic aromatic hydrocarbons, which led to coke formation, can help to overcome this problem. This can be achieved by incorporating transition metals and other metals in the zeolite framework.

A series of cerium and vanadium doped ZSM-5 catalysts were prepared and the catalytic performance of these catalysts was tested. Pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) tests carried out at 550°C for both uncatalysed and catalysed biomass samples were performed using a CDS 5200 pyrolyser closed coupled to a PerkinElmer Clarus 680 GC-MS. This study focused on the incorporation of cerium and vanadium in the zeolite framework for their effect on mono-aromatic selectivity and ability to limit the production of polycyclic aromatic hydrocarbons. Aromatic hydrocarbon yields are increased when ZSM-5 has been impregnated, but also result in a slight increase in yields of polycyclic aromatic hydrocarbons which is not desired.



Example of product distribution for beech wood pyrolysis with **A** – ZSM-5, **B** – V-ZSM-5 (10), **C** – Ce-ZSM-5 (10)

## THE MECHANISM OF CATALYTIC FAST PYROLYSIS

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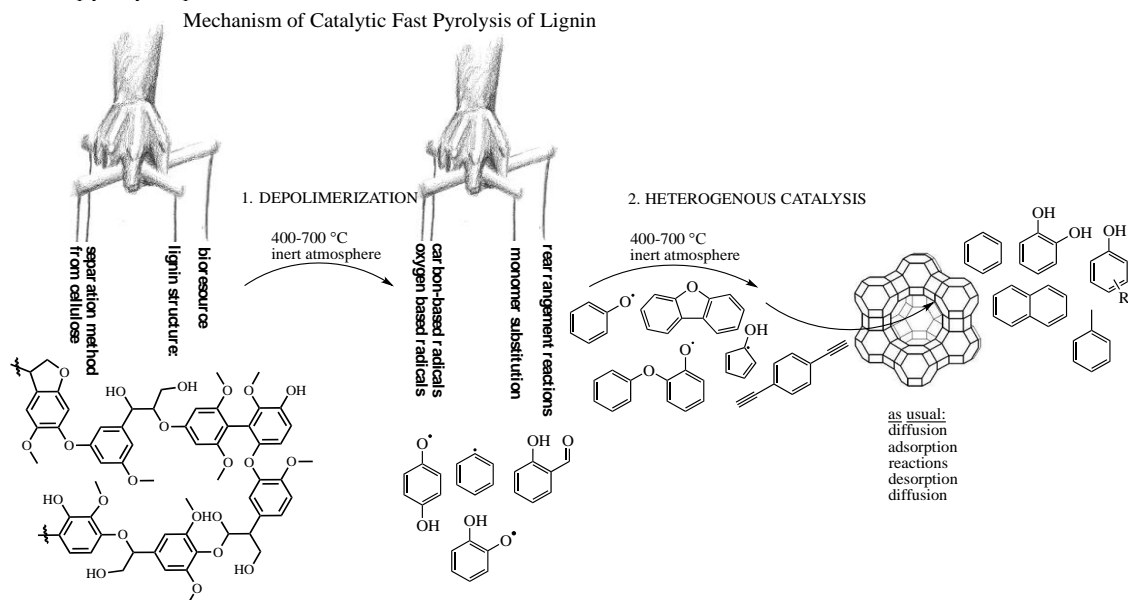
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Lignin is one of the three most abundant biopolymers and currently regarded as a waste product from paper and pulp production. While cellulose and hemicellulose are regular biopolymers and thus easily converted,[1] lignin is highly disordered comprising differently substituted phenols connected by various bonds, such as carbon-carbon and ether bonds. Efficient and fast depolymerization is achieved by pyrolysis[2] and catalytic fast pyrolysis (CFP) to temperatures up to 650°C yields the largest amount of phenolic monomers.[3]

The process of catalytic fast pyrolysis of lignin is much more complicated than standard heterogeneous catalytic processes. Additionally to the constraints of diffusion, adsorption and desorption, primary depolymerization and diffusion out of the polymeric matrix of lignin is necessary.[4] The depolymerization is mainly driven radically and has to be considered when improving the process of CFP. We study the mechanism of primary depolymerization at high vacuum with iPEPICO at the Swiss Light Source together with actual process conditions bridging the different conditions. We investigated the influence of structural differences resulting from the separation method of lignin onto the catalytic fast pyrolysis products.



**Figure 1** schematic view on the catalytic fast pyrolysis of lignin.

During depolymerization, ether bonds are not broken down easily, but rather stay intact until the whole aromatic/phenolic ring is decomposed at high temperatures, eg. by decarbonylation. The reactions of primary products are mainly determined by the nature of the formed radical: Substituents, such as methoxy-groups, enable stabilization and internal rearrangements of the radicals, while plain aromatics and phenols rather recombine immediately, to form dibenzofurane.[5] This observation is supported by the fact that lignins with a high content of multiple methoxy-substituted phenolic subunits produce more monomers at high temperature, thus less recombination occurs. The prominent bonds –main difference between carbon-carbon and ether bonds- require different active sites in the catalyst to convert effectively.[6] While carbon-carbon bonds are easily broken by H-USY, as known from FCC, ether bonds result in lower monomer yield and higher selectivity for phenols instead of aromatic hydrocarbon. Thus the lignin structure is crucial for the product distribution of CFP and must be optimized accordingly.

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## INVESTIGATION ON METAL MODIFIED ZEOLITES: CATALYST SCREENING FOR PYROLYSIS OF PINE WOOD AND SUNFLOWER STALK

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The aim of this work was to investigate the effect of different types of metal based ZSM-5 catalysts synthesized by both hydrothermal method (ht) and ion exchange method (ion) on catalytic upgrading of pyrolysis vapors. For this purpose, catalysts were screened using pinewood and sunflower stalk. The catalytic screening experiments were carried out in a bench- scale fixed-bed reactor under nitrogen atmosphere at 500 °C. Catalyst were characterized by XRD, SEM/EDS, pyridine adsorption and BET methods. The bio-oil produced was initially in two phases of the liquid; organic and aqueous phase. Dichloromethane fraction of liquid phase was considered as bio-oil.

Keeping in mind that pine wood pyrolysis produced bio-oil more than sunflower stalk, the bio-oil amount decreased with the use of catalysts tested for both biomass type. XRD results showed that the crystallinity of ZSM-5 increased with hydrothermal preparation method although metal peak did not clearly observed in XRD patterns.

TGA of spent catalyst was also performed in order to determine the exact amount of coke deposited on the catalyst surface. In case of catalysts prepared by ion exchange method by commercial HZSM-5 catalyst, the amount of coke deposited on catalyst was higher than that synthesized by hydrothermal method. The highest coke deposition was observed in the case of NiZSM-5 ion catalyst while the lowest coke was deposited on NiZSM-5 ht for both biomass pyrolysis. Although coke on each catalysts showed the similar behaviour for both biomass types, the amount of coke from pinewood was more than that from sunflower stalk. Product gas evolved from sunflower stalk pyrolysis mainly contained CO<sub>2</sub> and CO whereas pinewood pyrolysis produced more CO gases than CO<sub>2</sub>. It is also noticed that Ni based catalyst led to increase on H<sub>2</sub> formation.

GC/MS results revealed that the catalysts exhibited different catalytic activity on pinewood and sunflower stalk pyrolysis. For pinewood pyrolysis, the use of all catalysts led to decrease on aldehydes and ketones with increasing the aromatic compounds. The highest increase on amount of aromatic compounds was found to be in the case of metal (Ni,Co,Zn) doped catalyst by ion exchange method. For sunflower stalk, HZSM-5 ht had the highest effect on aromatization in expense of phenolic compounds.



# INTEGRATED CATALYTIC PYROLYSIS: TOWARDS RENEWABLE BUILDING BLOCKS FOR THE CHEMICAL INDUSTRY

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The growing world population and increasing welfare levels will result in a steady growing demand for materials, including plastics. The foreseen reduction in fossil resource supply, in combination with the demand for more environmentally friendly processes (CO<sub>2</sub> reduction) make biomass an attractive candidate for the preparation of plastics in the near future. Especially from the (packaging) industry (Coca-Cola, Danone, NIKE), there is a strong demand for the production of green polyesters, resulting in the recent market introduction of BioPET30. In this case the ethylene glycol moiety is obtained from bioethanol. However, up till now there is no green alternative for the other monomer, p-terephthalic acid (PTA).

Recently BioBTX and the University of Groningen were able to convert lignocellulosics towards PTA using an integrated catalytic pyrolysis process. Whereas in most cases biomass, including wood, is pyrolyzed in the presence of excess catalyst<sup>[1]</sup>, we utilized an *in situ* up-grading process in which the biomass is first pyrolyzed and the vapours obtained are subsequently aromatized by a zeolite catalyst. Main advantage of the process is that the zeolite catalyst is prevented from deactivation by inorganics present in the biomass fraction, thereby increasing the life time of the catalyst significantly<sup>[2]</sup>. In a subsequent downstream process the small aromatics were converted by an oxidation reaction to e.g., benzoic acid, isophthalic acid and PTA. The latter building block was polymerized to fully green PET using bio-ethylene glycol (see Figure 1).

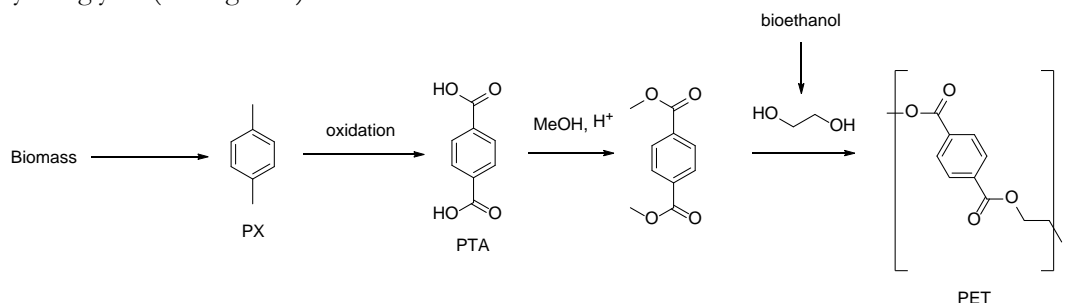


Figure 1. Synthesis of fully green PET by integrated catalytic pyrolysis of biomass (lignocellulosics).

Our process concept is not restricted to lignocellulosics but also crude glycerol, a waste stream from the biodiesel industry, could be converted to PTA in high yields. Our process results in a significant reduction of the carbon footprint; LCA analysis showed a CO<sub>2</sub> reduction of 80-85% compared to synthesis from petrochemical sources. It results in high yields of BTX and the full valorization of by-products such as char, ethene and propene in combination with extended life time of the zeolite catalysts makes it an attractive candidate for the synthesis of several green drop in building blocks for the chemical industry.

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## Understanding the effects of catalyst properties on biomass pyrolysis over ZSM-5 type zeolites: comparison of micro and process development scales

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Catalytic pyrolysis over zeolites has been a well-researched method for producing biomass pyrolysis oils with chemical and physical properties that are superior to those of analogous non-catalytically produced pyrolysis oils. The zeolite catalysts act to reject oxygen from the pyrolysis vapors, producing pyrolysis oils with a higher concentration of hydrocarbon components, often aromatic hydrocarbons. While ZSM-5 based zeolites have been widely reported to be most effective for this process, this study aimed to learn the role of several catalyst properties on production of aromatic hydrocarbons, coke formation and the resulting catalyst deactivation. The approach taken was to first study the role of catalyst acidity (Si/Al ratio), crystallite size, role of added binder (used to form extrudates for fluid bed studies) and addition of gallium on the microscale to access yields and rate of catalyst deactivation. In the case of catalyst acidity, the highest acidity catalyst tested (Si/Al = 11.5) was found to be most active but also subject to rapid catalyst deactivation whereas a moderately acidic catalyst (Si/Al = 40) had nearly the same initial activity but deactivated less quickly. These and similar observations were used to advise the use of moderately acidic HZSM-5 on the process development scale which was done using a fluidized bed reactor with a capacity of ~ 3 kg/h. Again effects of the catalyst properties were evaluated based on yield of deoxygenated products and rate of deactivation, measured by changes in pyrolysis gas composition; both in situ and ex situ mode catalytic pyrolysis were assessed. In this presentation we will discuss the comparison of the results between the microscale and pilot scale studies and access the translation of the microscale trends to the larger scale.

# MICROPYROLYSIS COUPLED TO GC/MS AS A SET-UP TO INVESTIGATE FAST PYROLYSIS BEHAVIOR OF BIOMASS CONSTITUENTS AND THE EFFECT OF INTRINSIC CATALYSTS

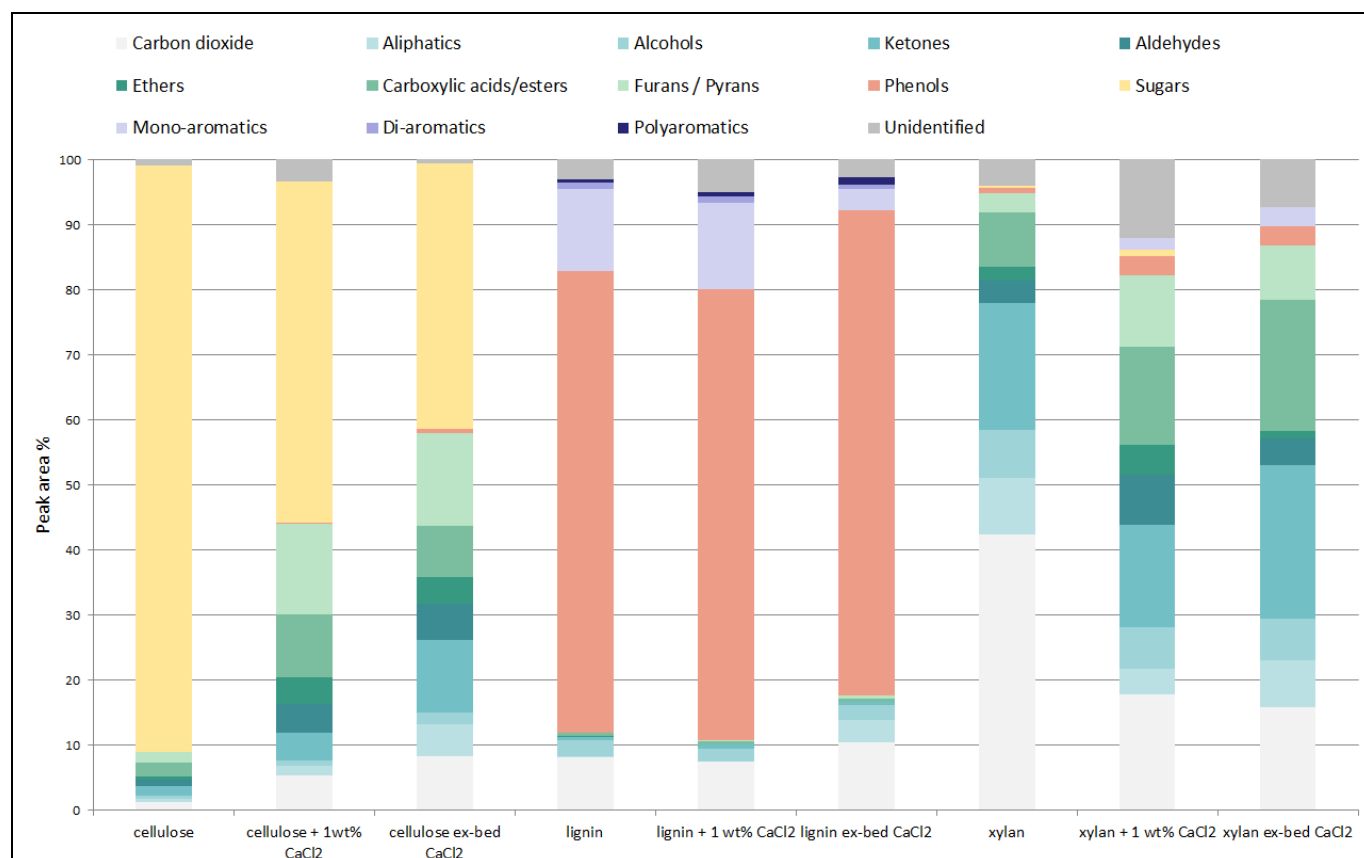
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Analytical pyrolysis coupled to GC-MS (pyGC-MS) was applied for the thermochemical degradation analysis of biomass constituents (cellulose, hemicellulose and lignin) and to investigate the effect of alkali and earth alkaline metals (potassium and calcium salts). These intrinsic catalysts, naturally present in biomass, were applied both in- and ex-bed and their influence on respectively primary and secondary decomposition reactions was analyzed. The FrontierLab EGA/PY3030-D microfurnace oven was set at 500°C for in-bed experiments (biomass mixed with catalyst) and extended with a tandem pyrolyzer, a second reaction tube filled with the catalyst bed, for ex-bed catalysis also called vapor phase upgrading.

The bottom-up approach of this study is different from work in literature where biomass pretreatment changes the mineral content in biomass and its catalytic capacity. It is known that the removal of metal ions by acid-washing pretreatment increases the yield of pyrolysis bio-oil and its anhydrosugar fraction markedly, while that of char and gas is significantly reduced. The opposite effect is noticed for biomass samples doped with inorganic salts. [1, 2] The focus of this study was more specific on the pyrolysis reactions in the vapor phase, relating the both primary and secondary decomposition products to the original biomass fraction. The attached figure gives an overview of the product range for the calcium catalysed pyrolysis experiments conducted in this study.



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# ACHIEVEMENTS AND CHALLENGES IN CATALYTIC FAST PYROLYSIS OF WOODY BIOMASS

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Renewable energy sources like solar, wind, hydropower, etc., are not suitable for the production of transportation fuels and bulk chemicals used in the current industries [1]. To increase the sustainability of the petro-chemical economy while continuing the production of petroleum-like products, chemicals, and (transportation) fuels, biomass may be put in service.

In recent years, catalytic fast pyrolysis (CFP) of biomass as a means of producing bio-oil with improved physico-chemical properties, has received lots of attention. This technique, carried out either by adding catalyst particles to the pyrolysis reactor (in situ) or by ex situ vapour treatment, is meant to enhance the cracking of heavy molecules in the primary pyrolysis vapours as well as to induce reactions to eliminate oxygen from the resulting bio-oil [2]. In order to produce a high-quality liquid product in sufficient quantities (CFP-oil), various aspects of the CFP process need to be considered. The most relevant ones are the biomass feedstock selection (woody biomass, forestry or agricultural residues, etc.), the reactor types (bubbling/circulating fluidized beds, auger reactors, etc.), the catalyst types (microporous or mesoporous zeolites, metal oxides, etc.) and the process conditions (temperature, vapour residence time, catalyst-to-biomass ratio, etc.) [3].

Most of the literature studies concerning CFP of biomass deal with catalyst screening in small scale laboratory systems. Unfortunately there is a lack of research concerned with the process operation and design. In recent years, project developers like KiOR [4], Anellotech [5], and the Gas Technology Institute, GTI (IH2 technology) [6] have tried to push catalytic fast pyrolysis to the pilot and commercial scale, but with varying degrees of success. Logically, such process developers are careful in revealing precise performance data such as the obtained product yields, the relevant product properties (e.g. acidity, viscosity, chemical composition), and the total operation time. Websites of private enterprises do not provide such data although it appears that the companies are sending out large product samples for closer inspection by future clients.

The intention is to contribute to PYRO 2016 with a critical review of catalytic fast pyrolysis of woody biomass. The review will summarise the current status and the achievements of research and technology development, based on the scientific literature, the available reports on commercial/industrial attempts, and also the scientific expertise in CFP obtained in our research group. The way of implementing CFP technology is discussed while focusing on the most feasible process modes in relation to proper heat integration and the catalyst sustainability. It is important to decide on the optimal properties of a catalyst for CFP, the consequences of long-term usage of catalysis, and the presence of biomass originated ash in large scale continuously operated CFP systems. The ultimate goal is to come up with some recommendations and suggestions regarding the design of a CFP process on a commercial/industrial scale.

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ABSTRACTS

# **Biomass / Catalysis**

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**Poster presentations**

## Effect of alkali and acid pre-treatment on Grass Pyrolysis

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Pyrolysis of biomass is a process which yields high quality, clean, and green products like bio-oil and bio-char. Bio-oil has a wide range of applications and also includes liquid fuels and raw chemical products. Therefore, it will be attractive to tailor the bio-oil properties to improve the yields of specific compounds that are economically interesting. In particular, pyrolytic sugar can be used for fermentation while phenolic compounds have an array of industrial applications such as adhesives; moreover, they can substitute petroleum-based phenols. However, it is difficult to achieve high yields of specific chemicals in the bio-oil without adequate biomass pre-treatments.

The purpose of this work is to evaluate and optimize the pre-treatment process in order to firstly, maximize the sugar yields and, secondly, to maximize the phenolic compounds. To achieve this, different acid and alkali additives, such as  $\text{CH}_3\text{COOH}$ ,  $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{KOH}$ ,  $\text{NaOH}$ , and  $\text{CaCO}_3$  have been used.

A Mechanically Fluidized Reactor (MFR) has been used to pyrolyze pre-treated grasses (e.g. Phragmites) in order to produce bio-oil and bio-char. The process can be either continuous or batch-wise.

Pre-treatment of phragmites with acetic acid demonstrated a positive effect on bio-oil yield with a 5-10 % increase. The results clearly show the effect of pH for the pre-treatment on bio-oil properties, and determine whether acid or alkali composition is also important. The effect of this pre-treatment on primary and secondary reactions has also been investigated.

## A DETAILED QUALI-QUANTITATIVE ANALYSIS OF PRODUCTS FROM PYROLYSIS-ZEOLITE CRACKING OF THE MICROALGAE SPIRULINA

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The recent EU directive 2015/1513 encourages research efforts for the developments of advanced biofuels, such as those made from algae, that could provide greenhouse gas emission savings with low risks of indirect land-use change and food/feed competition. Harvesting algal biomass is a major obstacle for economical sustainability, but there are species profitably cultivated at industrial scale for non-energetic purposes, such as the microalgae *A. platensis* (Spirulina). Spirulina is not an oleaginous or carbohydrate-rich microalgae, therefore not a suitable species for biodiesel or bioethanol production. An organic liquid (here named as bio-oil) with potential fuel properties (high C and low O/N content) was recently obtained by catalytic pyrolysis of Spirulina with zeolite HZSM-5 [1]. However, further investigations are needed to fully evaluate the prospective of zeolite cracking in the development of liquid biofuels from protein-rich microalgae. In this study, *A. platensis* was cultivated in a 70 L indoor vertical photobioreactor and harvested when the dried biomass reached a concentration of 1 g L<sup>-1</sup>. In triplicate runs, about 4 g of lyophilised algal biomass were pyrolysed at 500 °C under nitrogen flow that swept vapours through 40 g of pelletized HZSM-5 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, 38) leaving behind a char. Downstream the zeolite bed, two liquids, a bio-oil floating over an aqueous phase, were condensed inside a cold trap (0 °C); thereafter, uncondensed vapours (light fraction) were adsorbed onto a poly(styrene-divinylbenzene) resin (XAD-2), and permanent gas was collected in a Tedlar bag. The yields, carbon C and nitrogen N contents of all the fractions excluding gas were determined directly by weight difference and elemental analysis; molecular analysis was performed on the liquid (SPME/GC-MS with internal calibration, <sup>1</sup>H-NMR), gas (GC-TCD) and char (Py-GC-MS) fractions. C was distributed as inorganic C into the aqueous and gas (CO<sub>2</sub>/CO) phases, all representing 20% of the original algal C. Most of the feedstock C ended up in char (30%); about 15% of initial Spirulina mass deposited onto the catalyst as coke. Bio-oil with over 80% C content was obtained with a molecular composition dominated by mono and polyaromatic hydrocarbons; a similar pattern was observed in the light fraction and at trace levels in the aqueous phase. Overall, bio-oil and light fraction were obtained with a 10% mass yield accounting for 20% C and energy of algal biomass. Large part of original N was dissolved into the aqueous phase (38% of initial N) and incorporated into char/coke (40%). A minor fraction of N ended up in bio-oil (about 6%); part of it was attributed by GC-MS to N-containing organic compounds derived from the thermal degradation of proteins or their reactions with lipids and carbohydrates (alkyl indoles, pyrroles, nitriles, pyrazines, carbazoles). Decoupling pyrolysis and zeolite cracking enabled the collection of char that could be employed as a fuel to increase the utilization of C and energy from the original biomass. The detailed mass, C and N balance and molecular analysis confirmed previous studies on a similar zeolite/algae system [1] and provided additional information for the quantitative evaluation of the potential of the process towards third generation biofuels.

Acknowledgments: Italian Ministry of Economic Development of the program Agreement MISE-CNR “Ricerca di Sistema Elettrico”.

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## Catalytic pyrolysis of waste lignin from pulping process for bio-oil production

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Catalytic pyrolysis of waste lignin on various noble metals was investigated at 400 - 600°C for bio-oil production. Lignin was extracted from black liquor, pulping waste steam, including kraft (KL) and soda process (SL). This research focused on study the liquid products from fast pyrolysis of extracted lignin. As a high thermal stability and the properties of thermoplastic polymer, lignin is difficult for absolutely decomposed [1]. Therefore, catalytic pyrolysis was compared with non-catalyst tests. The metal catalysts which included Ni, Pd, and Ru were prepared by impregnation on ZrO<sub>2</sub>. The catalytic and non-catalytic reactions were carried out using Py-GC/MS. In addition, lignin model compound (LMC) was also tested as base case to study the influence of spent chemicals in black liquor on this thermal conversion process. The results of FTIR analysis illustrated the different structure of KL and SL (Fig.1). TGA and <sup>13</sup>C NMR revealed the effect of the pulping process on lignin in black liquor, led to dissimilar of degraded compound in bio oil. Various aromatic compounds in liquid yield of KL were higher than LMC and SL pyrolysis (Fig.2). Moreover, Ru/ZrO<sub>2</sub> showed the remarkable effect on the composition of liquid yield. However, the main degraded compounds of all lignin were guaiacol, creosol, 4-Ethylguaiacol, and syringol. The effect of temperature was not significant for the composition of bio oil production. Lignin from waste steam would yield better conversion compared with lignin model compound. As a result, catalytic pyrolysis could be an appropriate conversion method for lignin waste to high value products.

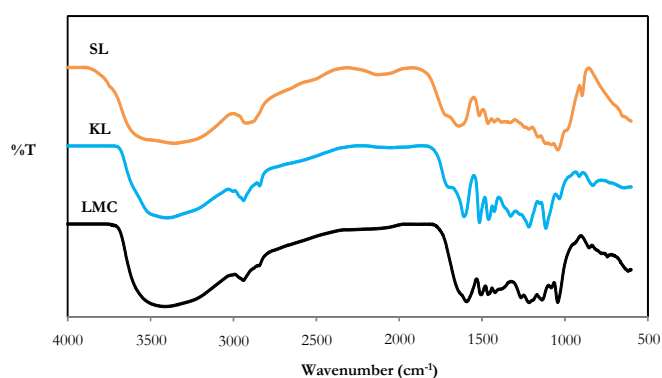


Fig. 1 FTIR results of KL, SL, and LMC

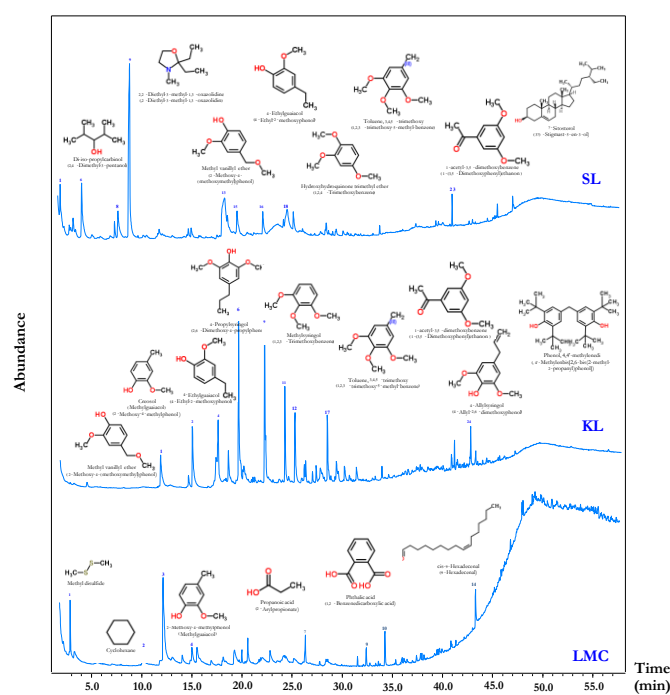


Fig.2 Py-GC/MS Chromatograms of KL, SL, and LMC with non-catalytic at 500°C

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# CATALYTIC PYROLYSIS OF BIOMASS USING AN INTEGRATED CONCEPT

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Catalytic pyrolysis is a technology that integrates pyrolysis and catalytic conversion in a single process. It has shown to be a suitable technology to convert a wide range of biomass into biofuels and biobased chemicals like benzene and toluene [1]. Catalysts may either be used during the pyrolysis process (*in situ* catalysis) or in the vapour phase (*ex situ* catalysis) to steer the product portfolio to the desired composition and products. Typical catalysts are strong Bronsted acid catalysts, for example zeolites. A major concern for in-situ catalytic pyrolysis is irreversible deactivation of the catalysts by the inorganic components present in the biomass.

We here report experimental studies on catalytic pyrolysis using an integrated catalytic concept of *in* and *ex-situ* catalysis for aromatics (benzene, toluene, xylene, BTX) synthesis from biomass, with the intention to maximize the BTX yield. In this integrated catalytic pyrolysis concept, the *in-situ* catalyst is a cheap mineral catalyst whereas a dedicated aromatization catalyst is used for vapour phase upgrading (*ex situ* catalysis). As such, we intend to reduce catalyst cost while having the possibility to tune the composition of the vapour phase during pyrolysis to achieve high yields of BTX in the subsequent vapour phase aromatization step [2].

Proof of concept was obtained using a pyrolysis GC-MS using a tandem microreactor RX-3050 from Frontier lab and on gram scale using a in house built integrated catalytic pyrolysis set-up. Some of the results obtained in the Py-GC-MS are given in Figure 1 (left) using Bentonite as the *in-situ* catalyst for in the pyrolysis process and H-ZSM-5 for vapour phase upgrading. Clearly, the BTX yields are higher for the integrated concept. These findings were confirmed by gram scale experiments with good mass balance closure.

In addition, various biomass sources were tested and the effect on BTX yield was determined. It was shown that particularly the use of vegetable oils, as well as glycerol resulted in considerably higher BTX yields (Figure 1 right). Particularly crude glycerol is an attractive source as it is abundantly available as a byproduct from the biodiesel industry. Our novel concept convincingly shows the potential for high BTX formation from biomass via a commercially attractive process.

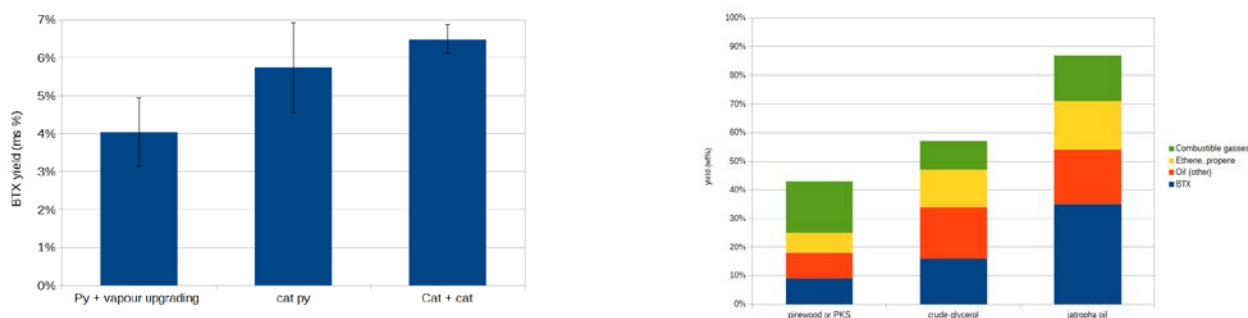


Figure 1. BTX yields for integrated catalytic pyrolysis versus in and ex-situ catalytic pyrolysis (left) and versus the biomass feed (right)

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## **Studying Catalyzed Biomass Pyrolysis and Catalyst Deactivation and Regeneration by using a Tandem Micro Reactor GC-MS**

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A pyrolysis tandem micro-reactor coupled to GC-MS was used to study catalysed and un-catalysed pyrolysis of biomass and was also used for studying exsitu ZSM5 catalysts-deactivation and -regeneration. The deactivation procedure is based on performing multiple pyrolysis cycles of biomass. The regeneration procedure is based on heating the deactivated catalyst to 600°C for 1 hour using an air flow. Deactivated spent catalyst could be regenerated to almost full activity by performing this regeneration procedure. Furthermore for quantification purposes an internal standard procedure was developed. The internal standard procedure proved to be robust and easy to perform and showed reproducible results.

## CATALYTIC PYROLYSIS OF EMPTY FRUIT BUNCH IN A BENCH-SCALE FIXED BED REACTOR

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Pyrolysis is being considered as one of the promising thermochemical conversion technologies to convert solid biomass to bio-oil. Although many studies were reported to maximize the yield of bio-oil via the optimized pyrolysis system, the bio-oil is difficult to be used directly because of its low quality due to high oxygen content, low heating value, low pH, and low stability. Therefore, many researchers are investigating the catalytic pyrolysis of biomass over various kinds of catalyst such as metal oxides, inorganic materials, and zeolites to upgrade the quality of bio-oil. Among various catalysts, calcium-based materials such as CaO, CaCl<sub>2</sub>, and Ca(OH)<sub>2</sub> were also applied to the catalytic pyrolysis of biomass due to their low cost and abundance [1].

In this study, catalytic pyrolysis of empty fruit bunches (EFB) over calcium-based catalysts such as dolomite, CaY and CaX zeolite were performed using a bench-scale fixed bed reactor. The quality of bio-oil produced from each catalytic pyrolysis experiment was evaluated in terms of water content, pH, and heating value. Chemical composition of bio-oil was also analysed by a gas chromatography/mass spectrometry (GC/MS).

Non-catalytic pyrolysis of EFB produced the large amounts of bio-oil (46.6 wt.%) having pH of 3.3. Meanwhile, by applying calcium-based catalysts, the quality of bio-oils such as pH value and heating value was improved although the water content of bio-oils was slightly increased. Chemical composition of bio-oils was also changed into the more stable deoxygenated chemicals. This study will be helpful for the understanding of the role of calcium-based catalysts in vapor-catalyzed pyrolysis reaction and their influence on the quality of bio-oil.

### Acknowledgement

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## EFFECTS OF SUPPORTS ON THE PRODUCTION OF FUEL-RANGE HYDROCARBONS IN THE HYDROTREATMENT OF SOYBEAN OIL WITH PLATINUM-BASED CATALYSTS

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Declining reserves of fossil fuels and growing environmental concerns have made renewable energy exceptionally attractive for the future. The conversion of biomass into hydrocarbon fuels (biomass-derived fuels are named biofuels) is becoming an attractive solution for overcoming this problem. Vegetable oils in particular are promising resources for the production of biofuels [1-3].

More recently, research on the conversion of vegetable oils into biofuels has attracted more interest because the European Union implemented a carbon-emission tax on airlines in 2011 [1,3]. Depending on the reaction conditions and on the type of catalyst used, a series of complex reactions occurs during hydroprocessing. This includes the saturation of double bonds, breakage of C–C bonds, heteroatom (sulfur, nitrogen, or oxygen) removal, isomerization, and cyclization [4,5]. The reaction conditions and the catalyst have significant effects on the composition and quality of the liquid product. The choice of catalyst is crucial in determining the composition and fuel properties of hydroprocessed triglycerides.

The present study focused on the effects of various Pt/zeolite catalysts on the selectivity for fuel-range hydrocarbons obtained by hydroprocessing soybean oil. Soybean oil is a renewable feedstock that is currently being used for the production of biofuels from sustainable biomass resources. Supports that are used include ZSM-5 (Si/Al<sub>2</sub> ratio = 30 and 280), zeolite-beta (Si/Al<sub>2</sub> ratio = 25 and 300), and HY zeolite (Si/Al<sub>2</sub> ratio = 5.2, 12, and 30). Platinum was impregnated as an active metal. Zeolite HY and zeolite-beta have microchannel structures that are composed of 12-membered oxygen rings (12-MR), whereas ZSM-5 is composed of 10-membered oxygen rings (10-MR). ZSM-5 zeolite has a structure with straight 10-ring channels running parallel to the corrugations and sinusoidal 10-ring channels perpendicular to the sheets. Zeolite-beta has a three-dimensionally (3D) intersecting channel structure composed of two perpendicular straight channels with a cross section of 0.64 × 0.76 nm and a sinusoidal channel with a cross section of 0.55 × 0.55 nm. On the other hand, HY has a 1D straight channel structure with a cross section of 7.4 × 7.5 nm.

Catalytic tests were carried out in a fixed-bed reaction system at 400 °C and 50 bar. The hydroprocessing conversion and the selectivity for hydrocarbons in the fuel range were determined by simulated distillation. In addition, the compositions of the liquid products (including the *n*-alkane content and the oxygen/carbon and hydrogen/carbon ratios) were determined in detail. The zeolite supports with higher acidities show better selectivities for (and conversions into) fuel hydrocarbons than zeolites with lower acidities. Thus, ZSM-5 (30), HY (5.2), and zeolite-beta (25) supports, having higher acidities, are superior to ZSM-5 (300), HY (30), and zeolite-beta (300) supports, respectively, having lower acidities. The ratio *n*-C<sub>8</sub>–C<sub>17</sub>/total-C<sub>8</sub>–C<sub>17</sub> is strongly dependent on the zeolite supports in Pt/zeolite catalysts. A zeolite with a smaller pore size, such as ZSM-5, is an efficient support for the higher ratio of *n*-C<sub>8</sub>–C<sub>17</sub>/total-C<sub>8</sub>–C<sub>17</sub>.

The effects of WHSV and Pt loading on hydrotreatment activities were also studied, using the Pt/zeolite-beta (25) catalyst. Relatively light fuel hydrocarbons, such as gasoline and jet-fuel hydrocarbons, have a maximum value (gasoline 25%, jet fuel 46%) at an optimum WHSV of 4.0 h<sup>-1</sup>, whereas the heavier fuel hydrocarbons, such as diesel, shows a trend similar to the conversion into liquid product, which decreases with an increase in WHSV. Among the catalysts used, Pt/zeolite-beta (Si/Al<sub>2</sub> = 25) gives the highest conversion into liquid product (72%) and the highest selectivity for jet-fuel-range (46%) and diesel-range (51%) hydrocarbons. A Pt loading of 3 wt % in this catalyst results in the best catalytic performance because of the optimal balance between the acidic and metallic sites.

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## SUPERCritical ETHANOLYSIS OF LIGNIN IN THE PRESENCE OF Ru-Ni BIMETALLIC CATALYST

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Recent studies in the field of lignin depolymerization have led to a renewed interest in developing new concept catalyst for improving the selectivity of the target compound in lignin-oil such as phenol, guaiacol, syringol, and so on. Bimetallic catalysts have received great attention because they showed different catalytic properties depending on corresponding monometallic catalysts, resulting in the enhanced catalytic activity with different product distribution. Previous studies reported that the addition of noble metals (Ru, Rh, Pd, and Au) to Ni catalyst or Pd-Fe catalyst enhanced catalytic activity as well as products selectivity in the hydrogenolysis of lignin model compounds [1,2]. However, to date, there is a lack of research dealing with lignin macromolecules in this field.

In this work, bimetallic Ru–Ni catalyst with different metal ratio (Ru to Ni 1:0, 0.8:0.2, 0.6:0.4, 0.4:0.6, 0.2:0.8, and 0:1) supported on mesoporous silica (SBA-15) was prepared by a hydrothermal method and a subsequent incipient wetness impregnation method (Figure 1). The catalytic properties of prepared catalysts will be investigated by XRD, XPS, BET, HR-TEM, and TEM-EDX soon. In lignin depolymerization process, soda lignin generated from the soda pulping process of wheat straw and sarkanda grass was directly depolymerized to phenol-rich oil fraction (lignin-oil) over Ru-Ni bimetallic catalysts under supercritical ethanol state (350 °C). As lignin depolymerized products, lignin-oil, char, and gas are produced. Lignin-oil, a high value-added chemical resource, composed of monomeric phenols, higher molecular phenolics, polyaromatic hydrocarbon, and heavy aliphatic hydrocarbon, will be in-depth analysed using various instruments such as GC/MS, GPC, elemental analyzer, and 2D-NMR. From GC/MS and GPC results, we will evaluate synergetic effect as well as catalytic activity of bimetallic catalysts for improving selectivity of target monomer. In addition, the ability for catalyst recycling will be also evaluated because it is directly connected to economic feasibility of the catalyst.

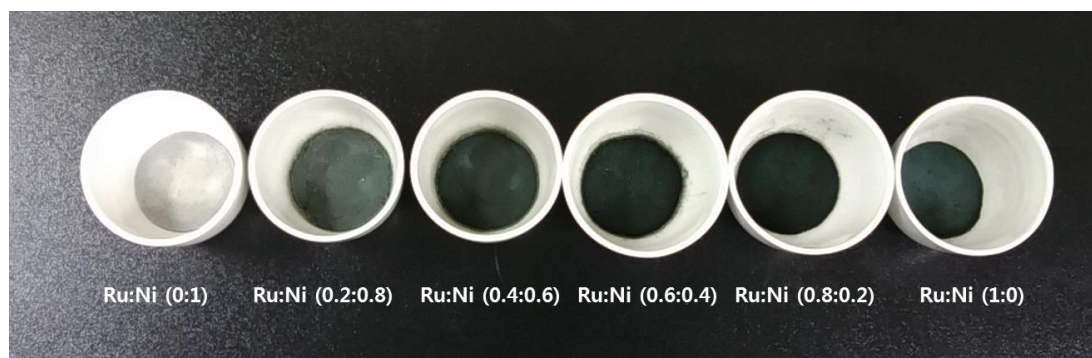


Figure 1. RuNi/SBA-15 catalysts with different metal ratio

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## CATALYTIC DEPOLYMERIZATION OF LIGNIN IN SUPERCRITICAL ETHANOL/WATER MIXTURES

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Lignocellulosic biomass has received attention as a renewable liquid fuel feedstock [1]. Lignin is the major component of biomass; however, their utilization for the production of fuels or chemicals is relatively limited compared to other components of biomass, including cellulose and hemicellulose due to the absence of an effective method for breaking lignin structures into monomer units that can be used as building blocks for synthesis of fuels and chemicals [2]. Hydro-/solvolysis is a decomposition method which is conducted in water or in a solvent under a pressurized liquid or supercritical state [3]. Compared to pyrolysis, its advantages are the low oxygen content of the liquid product, known as bio-crude oil (BCO) due to hydrodeoxygenation catalyzed by the ability of the solvent to donate hydrogen and the reduction of char due to retarded repolymerization of degraded intermediates by the role of the solvent as an alkylating/stabilizing agent [4]. In this research, catalytic hydro-/solvolysis of lignin with a range of solid base and transition metal catalysts were studied using water and ethanol as a solvent with the goal of maximizing the yield and quality of BCO. Two different lignin samples, kraft lignin and acid hydrolysis lignin were used as feedstocks. Kraft lignin was purchased from Sigma-Aldrich, while acid hydrolysis lignin was prepared by two-step concentrated acid hydrolysis of oil palm empty fruit bunches (EFB) using 20% sulfuric acid. A stainless steel 160 ml batch autoclave equipped with a magnetic stirrer was used for the catalytic hydro-/solvolysis experiments.

Initial solvent screening experiments were performed in the absence of the catalysts, using water, ethanol, and 2-propanol. The reactions were carried out at 373-473 K for 1 hour. The results showed that the overall BCO yield is higher in water, while the molecular weight of BCO is lower and the yields of monomeric aromatic chemicals (MACs) are higher in ethanol and 2-propanol. These results indicate that hydrolytic cleavage of the lignin ether bond is faster than solvolytic cleavage, whereas the alcoholic solvents retard the recondensation of degraded intermediates by hydrogen donation and alkylation. The effect of water-to-alcohol ratio was further investigated to optimize the solvent properties. A 50:50 water:ethanol mixture markedly enhanced the yields of BCO and total MACs compared to water or ethanol alone, showing the synergistic effect of combinations of different solvent properties. Catalytic hydro-/solvolysis were also investigated using a range of solid base and supported metal catalysts, including CaO, MgO, Ru/C, Pd/C, and Ni/C to promote the lignin depolymerization. The BCO yield generally increased in the presence of catalysts and the highest yield of BCO was obtained with Ru/C catalysts, possibly due to the enhanced hydrogenolysis activity. In order to maximize the hydrogen donation effect, formic acid was added to the water-ethanol mixture in the presence of Ru/C. The addition of formic acid further promoted the depolymerization of lignin, exhibiting the highest yields of BCO (70%) and the total MACs (22%) and the lowest yield of char (8%). The elemental analysis of BCO revealed that O/C ratio decreases and H/C ratio increases in the presence of catalysts and formic acid due to the enhanced hydrodeoxygenation activity by the hydrogen generated from the in-situ decomposition of formic acid. Overall, our results demonstrate that catalytic hydro-/solvolysis is an effective method for the depolymerization of lignin.

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## CATALYTIC PYROLYSIS OF LIGNIN WITH SOLID ACID CATALYSTS

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Lignin is an important lignocellulosic component occupying the second largest amount in plant biomass. Although lignin is a candidate aromatic source, the large amount of char formation and the low quality of bio-oil is being considered as the problems of lignin pyrolysis. Recently, many researchers are focusing on the catalytic pyrolysis to produce the large amount of high quality bio-oil from lignin. Catalytic pyrolysis of lignin is also more difficult than other lignocellulosic components of biomass because of the low reactivity of lignin-derived phenolic compounds [1]. Additionally, faster deactivation of the catalyst due to the large amounts of coke formation made by the thermal resistant structure of lignin. Therefore, more research to improve the bio-oil quality and increase the catalyst life time is highly recommended.

In this study, in-situ catalytic pyrolysis of lignin over zeolite (e.g., HZSM-5 and HY) and silica-alumina was performed using a lab-scale fixed bed reactor. To increase the catalyst life time, sequential two stage catalytic pyrolysis of lignin was also performed by applying silica-alumina and zeolite as in-situ and ex-situ catalyst, respectively.

In-situ catalytic pyrolysis of lignin over each catalyst showed the different product distribution. In case of silica-alumina, the amounts of light phenolic compounds were increased with decreasing heavier phenolics. Meanwhile, HZSM-5 showed high production performance of mono aromatic compounds such as benzene, toluene, and xylenes due to its high acidity and proper pore size. By applying sequential two stage catalytic pyrolysis with in-situ silica alumina and ex-situ HZSM-5 catalysts, higher amounts of aromatic compounds were produced with the smaller amount of coke formation. This indicates that silica-alumina is very helpful to promote the catalytic activity and increase the lifetime of HZSM-5 catalyst during catalytic pyrolysis of lignin.

### Acknowledgement

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# INVESTIGATION OF THE CATALYTIC EFFECT OF TRANSITION METALS ON THE SUBCRITICAL HYDROTHERMAL LIQUEFACTION OF NON-WOODY BIOMASS

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Subcritical hydrothermal liquefaction (HTL) of two different non-woody biomass (empty fruit bunch (EFB) and coconut shell (CCNS)) was performed at 300 °C in the presence of various transition metal catalysts (ZnCl<sub>2</sub>, CuCl<sub>2</sub> and NiCl<sub>2</sub>) to investigate the catalytic effects on the properties of HTL products; crude-like oil (HTL oil) and water soluble fractions. In the presence of ZnCl<sub>2</sub>, a dramatic decrease in the HTL oil yields was detected. The HTL oil yields decreased from 22.8% (control) to 10.6-14.1% for EFB and from 13.9% (control) to 5.6-6.5% for CCNS, respectively, by increasing catalyst loading from 2.5 to 10.0%. Similar trends of mass balance were also found in HTL oil with CuCl<sub>2</sub> and NiCl<sub>2</sub>. The change in the amount of water soluble fractions was varied by using different kinds of feedstock or catalysts. Both in case of EFB and CCNS, water content of HTL oil increased by increasing catalyst dosage from 2.5 to 10.0%. The TAN value of HTL oil increased with use of 2.5% catalyst, but decreased when 5.0-10.0% of catalyst was used. GC/MS analysis revealed that carbohydrates and lignin-derived compounds in the HTL oil gradually decreased with increasing amounts of catalyst. Instead,  $\gamma$ -valerolactone (GVL) was identified which was not detected in HTL oil without catalysts. In addition, levulinic acid was detected in HTL oil from both feedstock with CuCl<sub>2</sub> catalyst. We suggest that Cu<sup>2+</sup> from CuCl<sub>2</sub> disrupted the hydrogenation of levulinic acid to form GVL. So much of levulinic acid remained in HTL oil. Figure 1. shows the proposed pathway of cellulose decomposition in presence of transition metals. Physicochemical properties and chemical compounds in water soluble fraction will be determined in the near future.

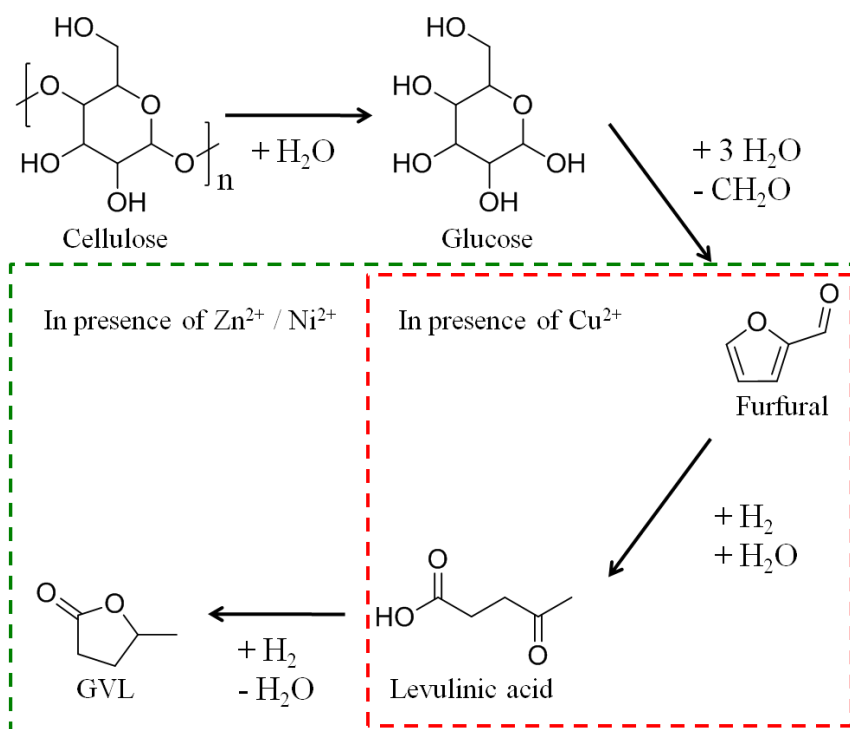


Figure 1. Proposed pathway of hydrothermal decomposition of cellulose with transition metal catalysts

## Production of valuable products by catalytic upgrading of pyrolytic oil from *Jatropha* waste over metal/zeolite catalysts

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*Jatropha* waste was mainly consisting of organic compounds and thus, was needed to directly convert into bio-oil by fast pyrolysis process. This bio-oil has various potential applications such as heat resource, etc and as a feedstock for chemical processes, but has limited properties to use as the following problems; oxygen-rich composition, low heating value, corrosiveness, etc. Thus, pyrolytic bio-oil may be upgraded to be used as a transportation fuel.

Pyrolytic oil produced from fast pyrolysis of *Jatropha* waste was separated into both water soluble pyrolytic oil (WSPO) and water insoluble pyrolytic oil (WIPO), which was weight percentage ratio of about 90 : 10 (WSPO : WIPO). In this study, catalytic upgrading of water soluble pyrolytic oil (WSPO) with high proportion in pyrolytic oil, in order to produce valuable products, was investigated using zeolites (ZSM-5, USY, Beta) and also metal (Ga, Mg, etc) impregnated on zeolite (metal/zeolite). The metal/zeolite showed a little less BET surface area than pure zeolite, because of closing micropores of zeolite by the metal. Performance of zeolites and metal/zeolite catalysts was compared in a continuous fixed-bed reactor system, at 400°C reaction temperature and 20 h<sup>-1</sup> weight hourly space velocity (WHSV). According to zeolite type, the catalytic activity and the product distribution of aromatics in liquid product, and also light olefin hydrocarbons in gas product, as valuable products, were clearly differed, which was influenced by the physicochemical properties of zeolite. Also, the type of metal impregnated on zeolite showed an influence on the product distribution from catalytic upgrading of WSPO. These results were discussed.

Table 1. Elemental analysis of water soluble pyrolytic oil from *Jatropha* waste

| Items  | C<br>(wt%) | H<br>(wt%) | O<br>(wt%) | N<br>(wt%) | S<br>(wt%) |
|--------|------------|------------|------------|------------|------------|
| Values | 16.13      | 10.09      | 68.85      | 4.88       | 0.05       |

Table 2. Pore structure and BET surface area of zeolites

| Zeolite type | Pore dimension | Pore size (Å)           | BET surface area (m <sup>2</sup> /g) |
|--------------|----------------|-------------------------|--------------------------------------|
| ZSM-5        | 3              | 5.1 x 5.5<br>5.3 x 5.6  | 400                                  |
| USY          | 3              | 7.4 x 7.4               | 780                                  |
| Beta         | 3              | 6.6 x 6.75<br>5.6 x 5.6 | 680                                  |

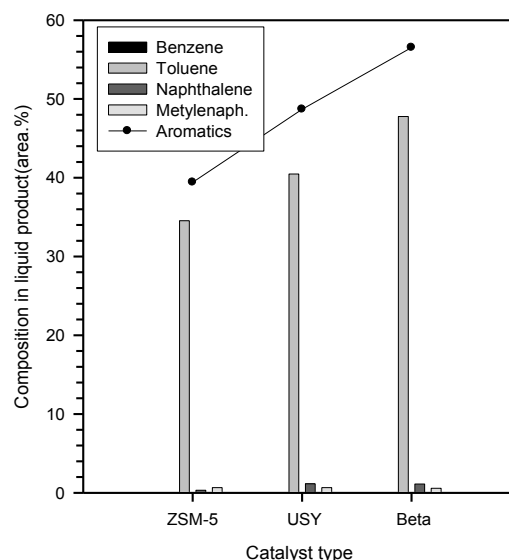


Fig. 1. Aromatics in liquid products from catalytic upgrading of WSPO over zeolite catalyst (400°C, 20 h<sup>-1</sup> WHSV).

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# CATALYTIC PYROLYSIS OF BIOMASS IN NH<sub>3</sub> GAS WITH FLUIDIZED BED

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## I. Introduction

Biomass contains large proportion of O (say 50% w/w), with which hydrogen bonds are formed. Inexpensive process to deoxygenate and hydrogenate biomass is needed to produce useful products. Anaerobic pyrolysis leads to bio-oil with high content O, which upgrades by hydrogenation with difficulties. Conversion of biomass to synthesis gas causes great loss of carbon resource to CO<sub>2</sub> emission by the following H<sub>2</sub> production or F-T synthesis.[1] Catalytic thermal treatment in H<sub>2</sub> aiming to direct production of hydrocarbons involves dissociation of H-H on the catalyst and subsequently reaction with biomass derivatives from heating. A poor selectivity therefore is resulted with great production of CH<sub>4</sub>. However, NH<sub>3</sub> molecules would react with C atoms adjacent to O under mild conditions,[2] which makes the degradation more selected. Here we propose a method of biomass pyrolysis at 200-500°C in controlled concentration of NH<sub>3</sub> gas with catalysts. Hydrocarbons, amines and N-doped carbons are obtained. The process can be operated with fluidized bed, which would facilitate the contact between biomass and catalyst particles.

## II. Method and discussion

The cracking process was first analysed by synchrotron vacuum ultraviolet photoionization mass spectrometry. Biomass molecules crack into smaller segments, water, and CO under the help of heat and NH<sub>3</sub>. The possible conversions are illustrated in fig. 1 and fig. 2. Lignin, which contains lower O, even reacts with NH<sub>3</sub>. N-doped carbons formed during the process facilitates the conversion. Different heating temperature results in various intermediates.

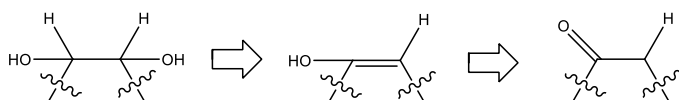


Fig. 1 Dehydration and transformation of biomass by heat

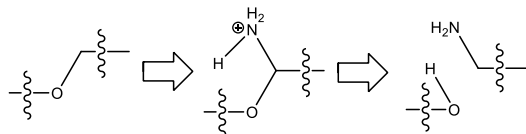


Fig. 2 Degradation of biomass by NH<sub>3</sub>

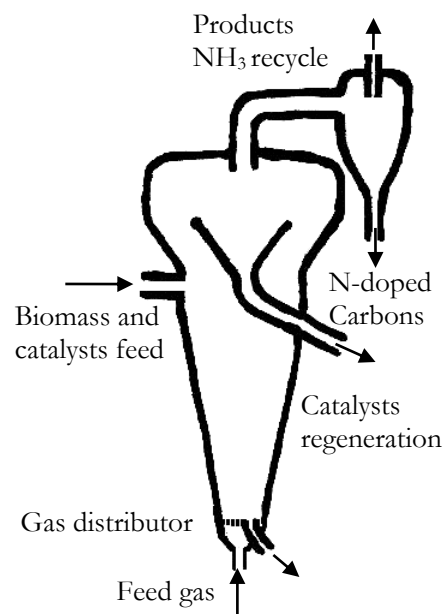


Fig. 3 Scheme of a fluidized bed reactor

These intermediates can be either cracking with catalyst or undergoing catalytic condensation to heavier carbon chain. Definite analysis of these intermediates will help the design of the catalysts. Products with and without catalysts are compared. Possible catalytic mechanism is proposed for further optimization.

## III. Prospective

With the studies, an intact conversion can be integrated to a fluidized bed with different heating zones as well as catalysts pellets with proper size in the designated heating zone (fig. 3).

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## CATALYTIC CONVERSION OF PYROLYTIC VAPORS OF WOODY BIOMASS

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Rising energy demand requires new available energy sources that can be converted into fuels efficiently. Biomass and bio-residues can be converted to more valuable energy forms via different thermochemical processes including pyrolysis. For thousands of years, pyrolysis has been applied for charcoal production but it is only during the last 30 years that fast pyrolysis was developed. The concept is the rapid heating of biomass at moderate temperatures around 500°C with short reaction times of up to 2 seconds in an oxygen-free environment to optimize the yield of liquids [1]. Pyrolytic bio-oils contain a significant amount of reactive oxygenated species and they have to be stabilized and deoxygenized to be compatible with traditional fuels. Catalytic pyrolysis is an approach that allows a partial deoxygenation before vapor condensation. Since 2007, the number of publications concerning catalytic pyrolysis increased drastically but the characterization of the liquid products are often poor and none so far have focused on the liquid yields in relation to the quality [2].

To produce upgraded bio-oils, a semi-continuous pyrolysis experiment on lab-scale was developed. It consists of a quartz tube containing two porous frits. The first retains the wood and char, while the second holds the catalyst. This reactor is placed inside a cylindrical oven. Beech wood chips are introduced into the top part of the reactor by means of a solid powder dispensing system (Parimix). Each 6 seconds 100 mg grams of wood chips are dropped into the reactor. A flow of nitrogen of 500 mL/min inerts the biomass injector and drives pyrolysis vapors through the catalyst fixed bed (catalyst-to-biomass ratio of 1:10). At the reactor exit a condenser collects the bio-oil at 4°C. This condenser is followed by an electrostatic trap -5°C to capture the very fine oil droplets. A last trap with silica gel protects the micro-GC used for on-line gas analysis.

Bio-oils were characterized by CHONS, GC-MS, GCxGC-MS, -FID and GPC. For this work, the selected catalysts are zeolites, H-ZSM-5, H-MCM, H-Y and silica-alumina and supported metals on the same these zeolites.

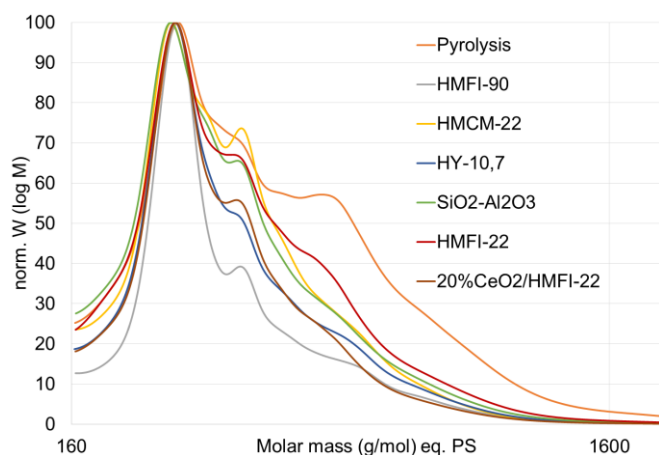


Figure 1: GPC analysis of bio-oils

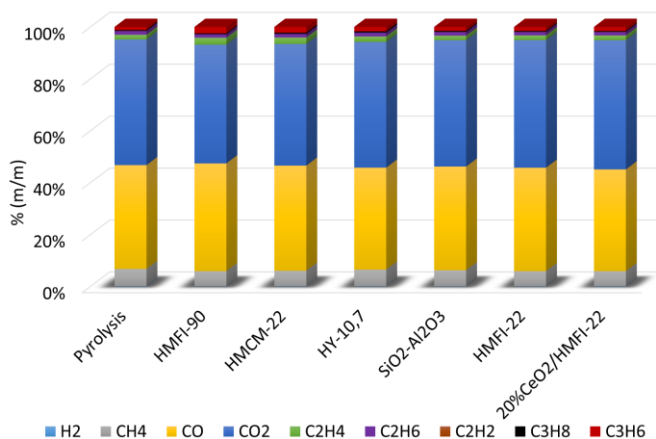


Figure 2: Mass composition of gas phase

With the use of catalyst, an aqueous phase is appearing in addition to the bio-oil. GPC analysis showed a decrease of the average molecular mass (Figure 1) with respect to thermal pyrolysis oil. Although the overall gas composition did not seem to be dependent on the type of catalysts (Figure 2) some significant differences were observed on the time-dependent C2 production.

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## PY-GC/MS AND EGA-MS INVESTIGATION ON FRUCTOSE, INULIN AND TOPINAMBOUR: THE PYROLYSIS PRODUCTS AND THE EFFECTS OF CATALYSTS

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Biomass are an important natural resource becoming more relevant in the last years as they represent a renewable source of energy and sustainable source for the production of high added-value products. To develop conversion processes for the efficient use of biomass resources, it is important to understand their chemistry and to know how they interact with catalysts. They are in fact normally used during conversion processes to increase the yield and rate of reaction of specific products.

Our work is focused on the study of fructose, inulin and topinambour (*Helianthus tuberosus* L.) also known as Jerusalem artichoke, a tuber particularly rich in inulin, using evolved gas analysis coupled with mass spectrometry (EGA-MS) and Py-GC/MS in the presence of hexamethyldisilazane (HMDS) for the in situ derivatisation of pyrolysis products.

During the last years, interest in inulin and inulin-containing biomass has become more and more important due to their often unique and various range of potential uses. Inulin could be found in various plant sources but only in a few crops such as Jerusalem artichoke, its quantity (> 80% of the dry matter) and quality can be considered in terms of its utilization. In our work, EGA-MS was used to investigate the thermo-chemistry of inulin and *Jerusalem Artichoke* and to understand their depolymerization pattern. On the other hand, Py-GC/MS provided insights into the decomposition pathways and allowed us to identify and semi-quantify the pyrolysis products of fructose, inulin and *Jerusalem artichoke* also in the presence of two different catalysts, niobium phosphate  $\text{NbOPO}_4$  and niobium oxide  $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ .

## EFFECT OF ZEOLITE PORE SIZE ON CATALYTIC CONVERSION OF LIGNIN MODEL COMPOUNDS DURING PYROLYSIS

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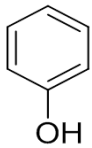
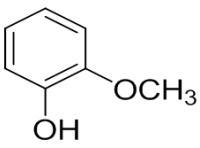
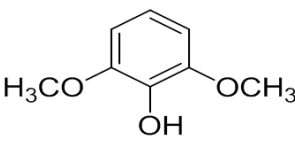
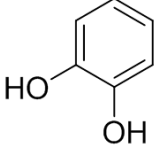
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The goal of this study was to investigate the effect of pore size of zeolite catalysts on catalytic pyrolysis of lignin model compounds. Up to date, research about catalytic conversion of cellulose/cellulose pyrolysis products over zeolite catalyst had been widely studied, but a little study had been progressed in the field of catalytic conversion of lignin/lignin pyrolysis products [1, 2]. In this study, phenol, guaiacol, syringol and cathecol (C6 type) were selected as representative lignin model compounds, and these were pyrolyzed at 600 °C over three kinds of zeolite catalysts having different pore size (ZSM-5: 5.6 Å, BETA : 6.4 Å, Y : 7.4 Å) for 20 seconds. The acidity of catalyst had similar values, ranged from 0.25 to 0.27 mmol/g of catalyst, where surface area of Y was the largest among the three types of zeolite catalysts (Table 1). We assumed that lignin model compounds having various molecular dimensions (Figure 1) could pass (or not) internal pore of zeolite, followed by converted into aromatic/phenolic compounds depending on its molecular size. In the case of ZSM-5, lignin model compounds could not be effectively converted to aromatic hydrocarbons over ZSM-5 compared with other zeolite catalysts due to its smaller pore dimensions. Among the three type zeolite catalysts, Y was found to be the most effective catalyst for producing monocyclic aromatics such as benzene, toluene and *p*-xylene. However optimal zeolite catalyst for the production of naphthalenes was BETA. These results revealed that product selectivity was clearly affected by pore size of zeolite catalysts. Other lignin model compounds (C1C6, C2C6, and C3C6) will be also pyrolyzed in same condition to investigate the effect of side chain of lignin model compounds in this catalytic conversion. In addition, we will also investigate the effect of pyrolysis temperature and catalyst ratio on this conversion mechanism in the future works.

**Table 1** Properties of zeolite catalysts.

|       | Si/Al ratio | Surface area (m <sup>2</sup> /g) | Pore dimensions(Å)   | Pore shape | Acidity (mmol/g) |
|-------|-------------|----------------------------------|----------------------|------------|------------------|
| ZSM-5 | 23          | 425                              | 5.1 x 5.5, 5.3 x 5.6 | Elliptical | 0.25             |
| BETA  | 25          | 680                              | 7.4 x 7.4            | Elliptical | 0.27             |
| Y     | 5.2         | 750                              | 6.6 x 6.7            | Circular   | 0.25             |

| Phenol  | Guaiacol  | Syringol   | Cathecol  |
|---|---|--|---|
|  |  |  |  |
| 8.098 Å x 6.477 Å*  | 9.476 Å x 8.101 Å   | 10.738 Å x 7.856 Å   | 7.364 Å x 7.325 Å   |

\* Å wide x Å long

**Figure 1** Dimensions of lignin model compounds

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## CATALYTIC PYROLYSIS OF LIGNIN USING CO- AND NI-DOPED ZEOLITE CATALYSTS

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Lignin is a highly heterogeneous polymer composed of hydroxycinnamyl alcohols, including p-coumaryl, coniferyl and sinapyl alcohol building blocks. Upon thermal treatment, lignin is degraded to a mixture of phenols. The composition of degradation products is highly dependent on the feedstock and the type of chemical linkages present in lignin. Catalytic cracking fractionate lignin to simple structures and most common cracking catalysts are zeolites, of which HZSM-5 has the best potential to deoxygenate lignin and form aromatic hydrocarbons.

Catalytic pyrolysis of lignin for the production of aromatic hydrocarbons was investigated to evaluate the performance of H-ZMS-5 zeolites with different loadings of cobalt (Co) and nickel (Ni) (5 and 10 wt.%). Catalysts were synthesised using as a support commercially available ZSM-5 zeolite (Si/Al=40). Cobalt and nickel were incorporated to the supports by “ball-milling” (mechanochemical grinding). Characterisation of synthesised catalysts was focused on their acidic and textural properties. Lignin samples (ALM, ETEK, Organosolv, Alkali, pyrolytic) with and without catalyst were pyrolysed at 400-900°C using a CDS 5200 pyroprobe coupled to a Clarus 600 Series GC-MS/FID system.

Experiments show that the selectivity to particular aromatic hydrocarbons varies with the composition and purity of the lignin for both catalysts. It was observed that the use of nickel-doped catalysts promoted with a higher efficiency production of saturated hydrocarbons such as ethylcyclohexane, benzene and 1-ethyl-2-methyl-benzene through the hydrogenation, dehydration and decarboxylation of oxygenated aromatic compounds.

## EFFECT OF CALCIUM OXIDE ON YIELD AND COMPOSITION OF BIO-OIL OBTAINED FROM SUGARCANE BAGASSE FAST PYROLYSIS.

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Fast pyrolysis of biomass allows the production of liquid products, which can be used as fuels or partial replacement of these after a deoxygenation treatment or as chemical precursors due of the great diversity of species that are contained in these products [1]. However, the process of pyrolysis and technologies of improving bio-oil are still immature due to unknowledge of different factors that affect the quality and composition of the resulting bio-oil [2]. This paper shows the results of the addition of calcium oxide as a catalyst to the process of fast pyrolysis of sugarcane bagasse, the products distribution was determined, the physical characteristics of the bio-oil and elemental analysis of products. The oxygen content in bio-oil is decreased by the presence of the catalyst during the process, achieved a 14% decrease in oxygen with the addition of 10% catalyst. In addition, a decrease of total bio-oil yield of 17% w/w (see Figure 1) was detected.

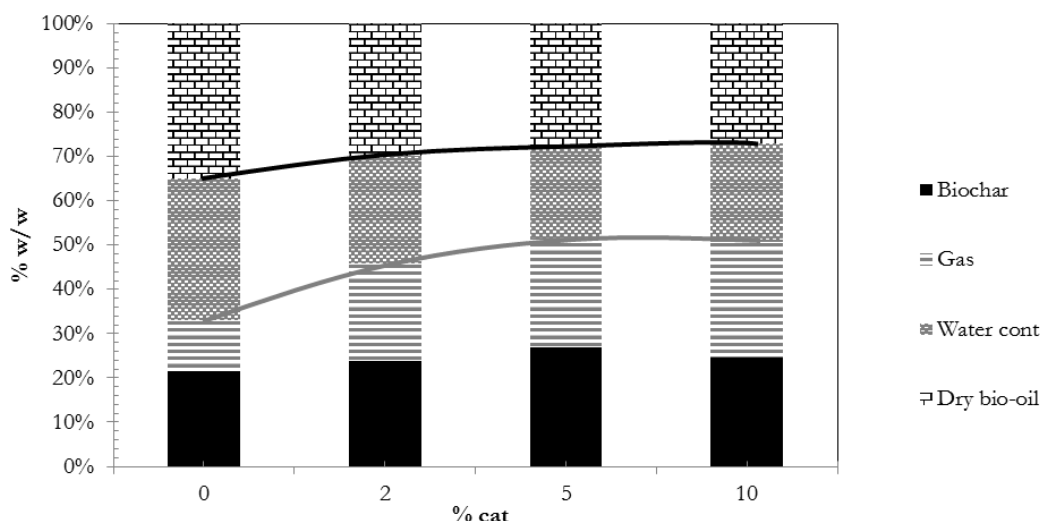


Figure 1. Products distribution of fast pyrolysis process with different relations of catalyst

As shown in Figure 1 an important aspect of use the catalyst relates to reducing the amount of water present in the bio-oil obtained. The performance of the gases is greater when the participation of the catalyst is 10% and reduce the performance of bio-oil and the water contain in this. Regarding the composition of bio-oil were detected by GC/MS over 150 compounds, the distribution of the main functional groups and the aging effect of bio-oil for these groups was analyzed [3-5].

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## CATALYTIC FAST PYROLYSIS OF PONGAMIA PINNATA WASTE USING ZEOLITE Y PREPARED FROM COAL FLY ASH

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Pongamia pinnata (Karanja) is promising plant oil for biodiesel production due to its 30-40% oil content in kernel [1]. However, de-oiled cake are produced in large amounts after extraction process. These raw wastes are invaluable and consist of toxicity such as karanjin and di-ketone pongamol [2]. The conversion of karanja wastes via pyrolysis is one of the potential approaches for producing bio-fuel. Unfortunately, bio-oil derived from pongamia pinnata wastes exhibited poor properties such as high acidity and viscosity. To improve quality of produced bio-oil for transport fuels, zeolite catalyst was introduced in the pyrolysis of pongamia pinnata wastes for decreasing oxygenated and nitrogenated compounds. Zeolite Y were synthesized from coal fly ash, as silica and alumina sources, by hydrothermal method and subsequently characterized on pore size, specific surface area, particle size, morphology and acidity. Non- and catalytic fast pyrolysis of pongamia pinnata wastes were carried out in micro-batch pyrolyzer connected directly to Gas Chromatography-Mass Spectrometry instrument (Py-GC/MS). Effect of catalysts on activity and selectivity on chemical species of produced vapours were investigated. Selectivity of catalysts were determined based on 5 main categories of chemical composition including oxygenated compounds, hydrocarbon, nitrogenated compound, sulfur compound, and sugar. From ultimate analysis of de-oil cake obtained from the southern part of Thailand, the carbon and hydrogen content were 45-51% and 5-7%, respectively. Heating value was 17-22 MJ/kg with 81-85% combustible compounds including fixed carbon and volatile matter. Thermal behaviour under inert atmosphere showed completely degradation at 400-500°C with maximum degradation rate around 380-400°C. Thus, non- and catalytic pyrolysis of pongamia pinnata wastes were performed at 400, 500, and 600°C. Oxygenated compounds, especially ester is the main products from fast pyrolysis of pongamia pinnata via non-catalytic process with 79.21%. With introduction of zeolite catalysts, oxygenated species underwent via decarbonylation, decarboxylation, and dehydration reactions and further converted to aliphatic and aromatic hydrocarbon. Pyrolysis temperature at 600°C showed the highest aliphatic and aromatic hydrocarbon production when Zeolite Y was applied with biomass to catalyst ratio of 1:5. Selectivity of monocyclic aromatic hydrocarbon (MAHs) and polycyclic aromatic hydrocarbon (PAHs) increased to 52.49% and 45.84%, respectively when catalyst to biomass ratio increased from 1:1 to 1:5. Enhancement of hydrocarbon compounds is correspond to the decrease of oxygenated compounds which were reduced from 46.54% to 1.13%, respectively. Moreover, solid residue is increased corresponding with enhancement of MAHs selectivity.

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## Ni-, Fe-, Co- AND Cu-BASED CATALYSTS FOR HYDROGEN PRODUCTION FROM CATALYTIC GASIFICATION OF BIOMASS

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Biomass gasification is a promising technology to produce renewable hydrogen or hydrogen enriched syngas for a sustainable chemical industry. However, producing hydrogen from the biomass gasification process has several challenges such as low hydrogen production and high tar formation. Recently, biomass catalytic gasification has received great interest due to the increase of hydrogen yield and the decrease of tar formation. One significant challenge for catalytic gasification is to develop an efficient catalyst with high catalytic activity for hydrogen production and high catalyst stability in terms of coke deposition and metal sintering. In this work, several active metals including Ni, Co, Cu and Fe were investigated using  $\text{Al}_2\text{O}_3$  as catalyst support for hydrogen production from biomass gasification. Additionally, different catalyst promoters such as Ca, Ce, Mn were studied. The experimental results show that the highest hydrogen production ( $24.32 \text{ mmol g}^{-1}$  biomass) was obtained with the Ni-Ce/ $\text{Al}_2\text{O}_3$  catalyst, indicating the effective promotion of Ce metal. Fe-based catalysts produced a much higher molar ratio of  $\text{H}_2/\text{CO}$  (2.87), while the Cu/ $\text{Al}_2\text{O}_3$  catalyst only produced a gas with a  $\text{H}_2/\text{CO}$  molar ratio of 0.89. The high concentration of  $\text{CO}_2$  and low concentration of CO produced from the Fe-based catalyst demonstrated that the catalyst might be effective for promoting water gas shift reaction. In addition, although the carbon deposition was low on the surface of the reacted Fe/ $\text{Al}_2\text{O}_3$  catalyst, filamentous carbons could be easily identified, compared with other catalysts. From temperature programmed oxidation analysis of the reacted catalysts (Figure 1), reducing the injection of water into the process with the Fe-based catalyst, carbon deposition was shown to be significantly increased.

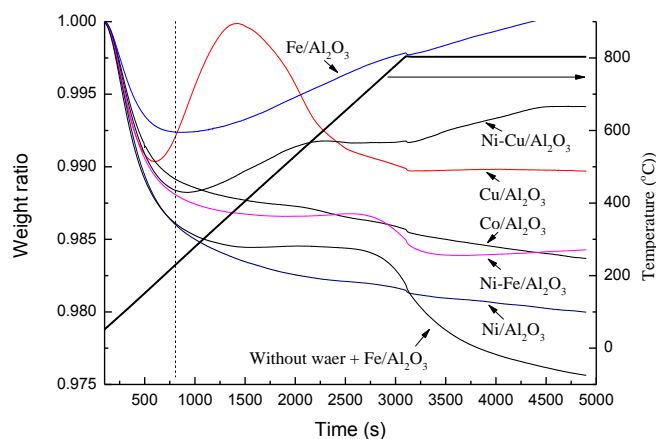


Figure 1 Temperature program oxidation of the reacted catalysts

## STEAM REFORMING OF PYROLYSIS VAPORS OVER CHAR BASED CATALYST

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In this study, thermal and catalytic steam reforming of bio-oil was investigated in a dual reactor system to increase overall gas production as well as hydrogen yield. The chars (biochar and coal char) and metal supported chars (Ni and Fe) were used as catalysts. To deduce the catalytic activity of the inorganic constituents of char, both non-demineralized and demineralized chars were used. In case of thermal reforming, the steam had no influence on overall gas yield and hydrogen production. In catalytic runs, Ni/char exhibited the highest catalytic activity on H<sub>2</sub> production and the increase on catalytic bed temperature from 500 °C to 700 °C led to increase both overall gas amount and tar decomposition. Inherent inorganic content of char did essentially affect both bio-oil decomposition and gas distribution. On the other hand, Fe/char had also catalytic activity on overall gas production, eventually H<sub>2</sub> amount.

It is noteworthy to mention that the biochar decomposed during steam reforming of bio-oil while coal char was relatively stable. Decrease on the mass of biochar during steam reforming could be attributed to steam gasification of biochar itself. As conclusion, this study showed that the metal loaded char, especially coal char, can be considered as steam reforming catalyst for H<sub>2</sub> production from biomass.

## CATALYTIC PYROLYSIS OF OLIVE POMACE

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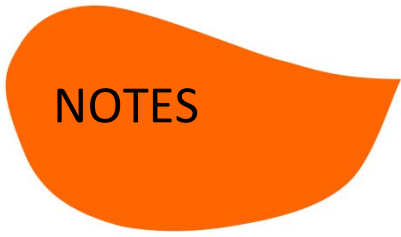
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The aim of this study is to understand the zeolite behavior during catalytic upgrading of pyrolysis vapors. For this purpose; an agroindustrial waste, olive pomace, was pyrolyzed in presence and absence of catalyst in a “two-step pyrolysis” system. Various types of zeolites (FCC, EFCC, REFCC, HZSM-5, HZSM-5/FCC mixture) were used as catalyst. The effect of catalyst type on yield and composition of products (char, bio-oil and gas) was investigated. The composition and fuel properties of bio-oils were characterized.

Although, the catalysts had no considerable effect on the yield of the pyrolysis product, they affected the bio-oil composition. REFCC gave the highest catalytic activity in terms of decomposition of pyrolytic lignin into extractives. Both HZSM-5 and FCC alone had no considerable effect on composition of bio-oil, whereas the addition of HZSM-5 on FCC provided synergic effect, leading to increase aromatic compounds and decrease phenolic compounds. Before and after pyrolysis, the surface area of catalysts was determined. It was observed that their surface area dramatically dropped after pyrolysis.

The stability of REFCC catalysts was also tested by repeatedly reusing in pyrolysis without regeneration. After the first cycle, the activity of catalyst on bio-oil composition was almost lost due to blocking pores with coke formation. It is concluded that the commercial zeolites should be modified in order to improve its stability against coke deposition for bio-oil upgrading.



# NOTES

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ABSTRACTS

# **Biomass / Fast pyrolysis**

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**Oral presentations**

## HEAT TRANSFER BETWEEN SOLID PARTICLES: APPLICATION TO FAST PYROLYSIS

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Fast pyrolysis of biomass is often conducted in fluidized bed reactors (FBR) and the majority of commercial fast pyrolysis plants exploit this technology. FBR's can be regarded a very well investigated technology and many rules for their design have been developed on a scientific basis. There are also some new reactor concepts that have been specifically adapted to optimize fast pyrolysis conditions. The optimisation usually aims at achieving a high heating rate for the biomass particles as high as possible and a vapour residence time at reaction temperature as short as possible. Given the wealth of literature on these new reactor concepts indicates that there exists good experience with their operation. But there is very little published on the scientific basis for design principles. This contribution elaborates principles of heat transfer between solid particles and/ or between a heated surface and solid particles. This type of heat transfer is relevant for almost all industrial and pilot plant installations that realize fast pyrolysis conditions, namely those based on FBR'S, rotating cone reactors, and auger reactors with a heat carrier system. As an example, the heat transfer coefficient in a twin-screw mixing reactor is calculated and compared to the 'reference system' of an FBR. Design and optimisation criteria are being discussed.

The heat transfer between solids is governed by two major resistances: one resistance is defined by geometrical features of the particles (shape and distance) and a second is defined by the quality of mixing. This holds true for the heat exchange between a wall and particles and the heat exchange between different particles. A discrete element model (DEM) of the particle flow in a twin-screw mixing reactor has been used in order to identify the distance between a biomass particle and its surrounding heat carrier particles. The DEM model has been implemented with Liggghts and is capable to track  $1.3 \cdot 10^6$  particles representing a mass flow of  $10 \text{ kg h}^{-1}$  of biomass and  $1.2 \cdot 10^6 \text{ kg h}^{-1}$  of heat carrier. These conditions represent the process development unit that is under operation at IKFT/ KIT [1]. The results indicate that the upper limit of the heat transfer coefficient that can be achieved in a twin-screw mixing reactor is around  $400 \text{ W m}^2 \text{ K}^{-1}$ . This is in the same order of magnitude as in FBR's. Whether this upper limit can actually be achieved during operation depends on the mixing conditions in the reactor. Figure 1 illustrates that the mixing is characterized with a goodness of mixture between 0.8 and 0.9 at the currently applied operating conditions [2]. Mixing models are applied in order to evaluate the operational window that is required to achieve the upper limit of the heat transfer based on the goodness of the mixture.

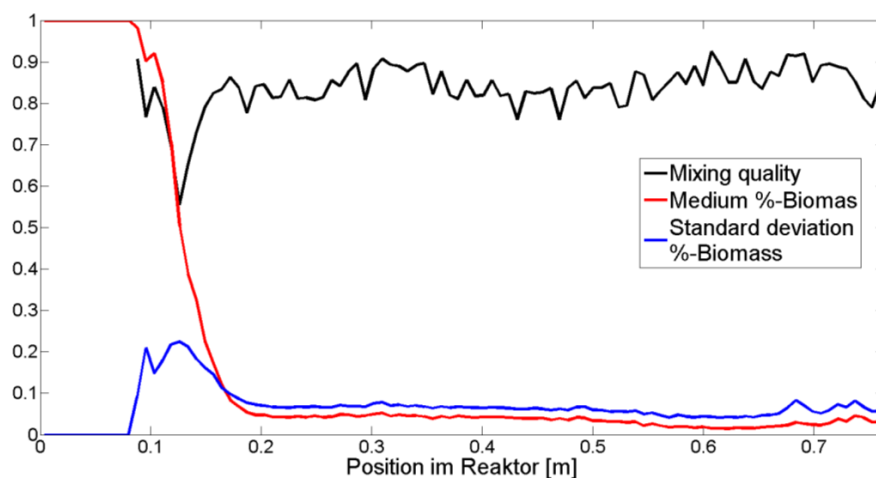


Figure 1: Spatial development of the mixing quality in a twin-screw reactor.

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## FLASH PYROLYSIS OF TORREFIED BIOMASS

- an experimental investigation on the conversion rate and kinetics in a cyclonic TGA -

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Flash pyrolysis oil from biomass has the advantage of a high mass and energy density per volume compared to the originating feedstock. Bio-oil can play a significant role in the future green energy system as a fuel in the transportation and electric energy production fields, or as a drop-in fuel for refineries. However, the major drawbacks of this bio-oil are its high oxygen content and high acidity in comparison to fossil fuels, leading to lower calorific values and corrosion of prime movers. Hemicellulose in the biomass is seen as one of the major precursors for the formation of acids in bio-oil. Removing a part of the hemicellulose by a torrefaction pre-treatment can lead to an improved bio-oil quality. Moreover, torrefied material has a markedly improved grindability, which matches very well with flash pyrolysis' need for finely ground biomass particles. Therefore flash pyrolysis of torrefied biomass can be seen as a promising route.

The cyclonic TGA setup at the University of Twente [1] offers the possibility to analyse the conversion rate of materials undergoing flash pyrolysis. The setup consists of a pre-heated disc shaped reactor mounted on a fast responding electronic balance. A pre-heated inert gas enters the reactor tangentially and swirls around its walls. Injected material will come into contact with both the pre-heated gas and the hot reactor wall, assuring a very high external heat transfer to particles, which facilitates flash pyrolysis conditions. Gaseous products leave the reactor with the inert gas stream, and this mass loss is registered by the balance.

The purpose of this work is to study the conversion rate and decomposition kinetics of torrefied material during the flash pyrolysis process in the cyclonic TGA. As feedstock, hardwood (ash and beech), softwood (European spruce) and wheat straw were used, both in virgin and various torrefied conditions. Furthermore, a number of samples was pelletised after torrefaction to study the influence of pelletisation on the flash pyrolysis rate. In the first series of experiments, the conversion times of virgin and torrefied material of various particle sizes between 0-400  $\mu\text{m}$  were measured at a fixed temperature of 550°C. Next, the kinetic regime was determined by establishing the region where the particle size has no longer any influence on the conversion time. Experiments with particle sizes within this region at different conversion temperatures between 450-550°C were used to determine the kinetics from Arrhenius curves.

The results show that the flash pyrolysis kinetics of torrefied material are slower compared to virgin material. Furthermore, the experiments with the various feeds show that at a low torrefaction severity ( $T = 250^\circ\text{C}$ ,  $t = 45$  minutes), conversion times of virgin and torrefied material are very similar. With increasing torrefaction severity (up to  $T = 280^\circ\text{C}$ ), the results show increased conversion times for the torrefied material, with 70% conversion times of typically 1.5-2 seconds for virgin material to 2.5-3 seconds for torrefied material. This effect was more prominent for biomass species containing a higher hemicellulose content, as well as species containing more reactive hemicellulose. Thus, the conversion time of softwood was significantly longer than for hardwood. The pelletised biomass streams had on average about 10% longer conversion times than the non-pelletised streams. This is presumably caused by changes in the biomass' microstructure due to the pelletisation process.

To assess the hemicellulose contents of the biomass streams, a conventional TGA was used to generate TG/DTG curves. It was observed that for the lowest torrefaction severities, the mass loss from virgin to torrefied material was insignificant, while torrefaction at the highest severity led to an almost complete vanishing of the hemicellulose shoulder in the DTG curve.

Concluding, it can be said that torrefying biomass has a profound effect on the ensuing flash pyrolysis process. For reactor design purposes it is important to increase the particle residence times because of the larger conversion times of torrefied biomass compared to the virgin biomass. The kinetic data on decomposition of virgin and torrefied biomass during flash pyrolysis can be used to enhance the modelling of these processes.

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## Characterization of chars from fast pyrolysis of biomass in a fluidized bed reactor

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In the present work, characterization of chars from fast pyrolysis of two different biomass samples (beech in stick form and oak in pellet form) in a fluidized bed reactor was carried out. The effect of pyrolysis temperature was studied in the range of 450°C to 850°C. The results are compared to the characterization of char from slow pyrolysis of oak in pellet form.

The char was characterized in terms of its elemental composition and by Scanning Electron Microscopy (SEM), Fourier Transform Infrared (FTIR) and Raman spectroscopy, X-Ray diffraction (XRD), solid-state cross-polarization and Carr-Purcell/Meiboom-Gill [1,2] <sup>13</sup>C nuclear magnetic resonance (CPMAS and CPMG NMR). Specific surface area was measured by nitrogen adsorption at 77K. Moreover, the mechanical strength of the products was studied by sieving and stretching tests as well as particles attrition phenomena in fluidized bed. Finally, the reactivity of char towards the combustion and steam gasification is discussed.

The results showed that the char properties are highly dependent on the pyrolysis process parameters. Elemental analysis reported a higher value of C/O and C/H at high temperatures indicating that char underwent a deeper carbonization process. The surface area increased dramatically from 3m<sup>2</sup>/g to 129m<sup>2</sup>/g for the pellet char prepared at 650°C then remained constant for pyrolysis temperatures ranging from 650°C to 850°C. The low surface area at 450°C suggested that the pellet char is mainly constituted of macropores.

Besides, an increase in the pyrolysis temperature leads to:

- A decrease in the mechanical strength induced by an increase of disorder in the char structure (SEM).
- A progressive loss of hydroxyl and aliphatic groups which completely vanished above 650°C. The char became more and more aromatic at high temperatures (FTIR).
- An increase in the concentration of larger aromatic rings (with a minimum of six rings) assuming the absence of any sign of graphite structure in the char as revealed by X-Ray diffraction [3].

These results were confirmed by <sup>13</sup>C CPMAS NMR indicating a loss in aliphatic, ketonic, carboxyl and phenolic groups at temperatures below 650°C leading to a highly aromatic cluster. Finally, <sup>13</sup>C CPMG-MAS NMR showed the presence of paramagnetic centers at 850°C which are attributed to structural disorder.

The reactivity of char towards the combustion and steam gasification decreased with increasing pyrolysis temperature. This is believed to be due to the presence of aliphatic groups, oxygen functionalities and volatile compounds in the char since they are parameters influencing the overall reactivity [4]. Indeed, these functionalities are significant especially at low pyrolysis temperatures. Besides, chars from pyrolysis of oak in pellet form are more reactive than chars from pyrolysis of beech in stick form.

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# CHARACTERIZING THE ROLE OF INTRA-PARTICLE PROCESSES DURING BIOMASS THERMOCHEMICAL CONVERSION USING HIGH PERFORMANCE COMPUTING

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Modeling and simulations are playing an increasingly important role for the design and optimization of biomass thermochemical conversion reactors, as they have the potential to provide unique insight into the prevailing complex phenomena occurring during conversion. While significant progress has been achieved recently, predictive and reliable computational fluid dynamics (CFD) tools able to simulate the complex, reactive, multiphase flows found in fluidized-bed reactors are still lacking. Of specific interest here is the description of the chemical processes, occurring both inside the biomass particle and in the gas phase, and how they interact with dense, sometimes turbulent, particle-laden flows. Particle-level chemical processes involve complex dynamics between intra-particle heat and mass transfer coupled with phase-change reactions, occurring in a highly anisotropic porous structure. Numerous works have shown strong evidence that those intra-particle phenomena do impact overall conversion strongly. Yet, virtually all CFD studies done at the reactor level neglect those due to a lack of proper models and integration framework, or prohibitively high computational costs, and use simple, homogeneous and spherical particle descriptions instead. Secondary gas phase reactions have also been characterized experimentally and theoretically, albeit to a lesser extent, but again, are most often neglected in reactor simulations, especially at the relatively low temperatures relevant for biomass pyrolysis processes.

This work aims at investigating the validity of these strong modeling assumptions, and characterizing quantitatively the impact that the level of detail included in the various chemistry and particle models has on overall reactor performance by integrating particle-scale models into large-scale Lagrange-Euler fluidized bed simulations. The presentation is organized around three main axes:

We first present a theoretically and numerically sound algorithm for the resolved simulation of single biomass particle conversion, which will then serve as reference for further larger-scale model development. While a one-dimensional configuration is considered initially, particular attention is given to the description of the chemical processes, including secondary charring reactions from intra-particle mass transport, and secondary gas phase reactions. Detailed comparisons of key quantities, such as heating rate, conversion time, and primary products release obtained using homogeneous and one-dimensional approaches are provided.

The two particle descriptions are then integrated into the massively parallel Lagrange-Euler multiphase flow solver NGA [1-3], in which individual particles are tracked in space and time using a point-particle approach, while the conservation equations for gas phase variables (velocity, density, pressure, compositions) are solved on a Eulerian mesh. Careful considerations of boundary conditions at the surface of the biomass particles, along with appropriate sub-iterations of the governing flow equations allow both the homogeneous and PDE-based particle models to be accurately coupled to the flow solver. Simulations of pseudo-two-dimensional fluidized bed reactors are conducted with the different particle models and with and without secondary gas phase chemistry. A sensitivity analysis study of the results is performed to clearly identify the controlling aspects, that is, those that should be targeted in priority for further improvement.

Finally, in order to transfer the intra-particle models to the more practical Eulerian-Eulerian framework, largely favored to simulate realistically-sized reactors, we propose a model reduction framework based on averaged reaction rates to replace the expensive 1D, PDE-based biomass particle evolution equations by a computationally cheaper system of ordinary differential equations describing the particle variables of interest (temperature, composition, and any quantity transferred to the gas phase.) Validation is performed through comparisons with the above detailed fluidized bed simulations.

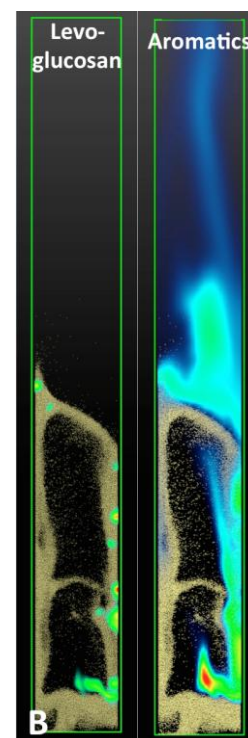


Figure 1. Detailed meso-scale simulation of reactive particle-laden flows in NGA: Individual tar species production during biomass gasification in a pseudo-2D fluidized bed reactor.

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## WOODY BIOMASS FAST PYROLYSIS IN A DROP TUBE REACTOR

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Bio-oil produced from biomass fast pyrolysis could constitute an alternative to fossil liquid fuels, especially to be combusted for local district heating. This work was performed in this context with the participation of the CCIAG Company.

Production of bio-oil by biomass fast pyrolysis in an entrained flow reactor has not been studied a lot up to now [1], but could constitute an alternative to the better-known fluidised bed pyrolysis process. In the context of the development of such a process, woody biomass fast pyrolysis experiments were performed in a drop tube reactor as a first step laboratory-scale study.

Beech powder was continuously fed into the 1.2 m long electrically heated reactor, while the products – char, tar and gas - were recovered and quantified. Temperature – 450, 500, 550 and 600 °C - and beech particle size – from 315 to 800 µm – were the two parameters investigated in this study.

Gas species were analysed by micro-gas chromatography. Char and bio-oils underwent elemental composition analysis, Higher Heating Value (HHV) measurement, and degradation tests in a Thermo-Gravimetric Analyser (TGA). Moreover, bio-oils were submitted to water content, acidity and viscosity measurements. Their chemical composition was also analysed by GC-MS.

The drop tube reactor experiments were simulated using a modelling tool previously developed for high temperature - 800-1400 °C – biomass gasification [2]. The model was specially adapted for this study, introducing a new devolatilisation reaction and a global tar cracking reaction, both associated with kinetic parameters.

For all the tests, the mass balance closure was checked and always laid between 88 and 104%. The maximum bio-oil yield – about 63 wt.% - was reached at 500 °C, with beech particles in the 315-450 µm range. For a lower temperature – 450 °C – or a higher particle size, the bio-oil yield was significantly lower due to incomplete wood powder pyrolysis. This was confirmed with solid residue observations, which showed that particles were not completely devolatilised, as well as by their thermogravimetric analysis showing a substantial residual mass loss. Moreover, the model showed that this incomplete pyrolysis was due on one hand to the too low temperature, and on the other hand to the too short solid residence time in the reactor.

The highest temperature tests – 550 and 600 °C – led to lower bio-oil yields than the 500 °C one, because of enhanced cracking of bio-oil into gas, whose yield was then higher. This cracking was correlated to composition modifications of the bio-oils analysed by GC-MS.

Except from the highest temperature at 600 °C, the operational conditions of the tests had a low impact on the properties of the bio-oil. In particular, their HHV was always comprised between 13.5 and 15.5 MJ/kg. Thus, the optimum conditions to obtain the highest energy content in the bio-oil are the same as the one for maximization of the bio-oil yield: temperature of 500 °C and beech powder of 315-450 µm.

The developed model was validated by confrontation with the experimental results. The devolatilisation and tar cracking reactions, as well as kinetic laws, could now be used for the design and simulation of a pilot entrained flow reactor for biomass fast pyrolysis.

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## PREDICTIVE MODELING OF SWITCHGRASS THERMOCHEMICAL PRODUCTS FROM BIOMASS COMPOSITIONAL FEATURES

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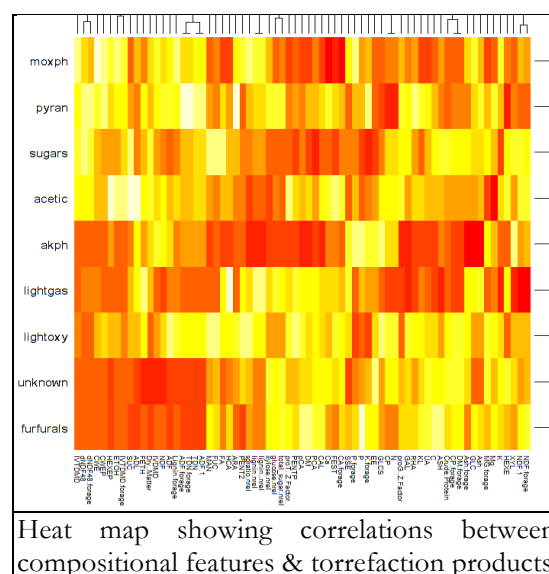
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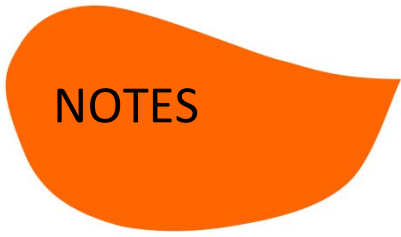
Thermochemical conversion of biomass to fuels and chemicals may be the most economical replacement for traditional fossil-sourced hydrocarbons in the long term. However, the current viability of thermochemical biomass conversion is limited by both processing & feedstock development constraints. Various biomass feedstocks for thermochemical conversion have been proposed, investigated, and compared in the literature [1–2]. Additionally, studies have been done which explore primary thermochemical products of individual biomass components [3–5] and secondary thermochemical products of these components when mixed or otherwise reacted with catalytically active materials [6–7]. However, to our knowledge no studies exist which compare the thermochemical products of well-characterized samples of a single species and seek to establish relationships between the compositional features of this species and the thermochemical products formed. By better understanding which of these compositional features influence the thermochemical product distribution, we may be able to promote favorable feedstock characteristics that improve processing ability.

In this work we investigate the links between the compositional features and the thermochemical (torrefaction / fast pyrolysis) products of biomass. Twenty-two different switchgrass samples were characterized by biochemical & spectroscopic methods (including NIRS with forage equation fitting, Py-MBMS, enzymatic digestion, and others). These were then subjected to analytical pyrolysis/torrefaction with a CDS Analytical 5250T pyroprobe coupled to a Shimadzu QP-2010+ GC/MS-FID. The detected compounds were lumped into catalytically relevant functional groups for analysis.

Interpretable mathematical models were then built to predict the thermochemical products as functions of the biomass composition. The techniques used included LASSO (least absolute shrinkage and selection operator), random forests, and ordinary least squares with forward & backward stepwise feature selection using the Akaike Information Criterion (AIC) [8]. These models incorporate automatic feature selection to avoid over-fitting. The models developed predict the yields of furfurals, pyran derivatives, and alkyl phenols with  $R^2 > 0.7$ ; methoxyphenols & acetic acid were predicted with  $R^2 > 0.5$ . The predictive ability of the models is used to formulate hypotheses about underlying mechanisms. The information gained may help to shape the direction of thermochemical conversion strategies.



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NOTES

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ABSTRACTS

# **Biomass / Fast pyrolysis**

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**Poster presentations**

## POTENTIAL OF VIRGINIA MALLOW AS AN ENERGY FEEDSTOCK FOR FAST PYROLYSIS PROCESSING

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The aim of this study is to compare the potential of virginia mallow to other high yielding perennial grasses and hardwoods by characterising and comparing fast pyrolysis product yields. Feedstocks selected for this study include: miscanthus (*Miscanthus x giganteus*), virginia mallow (*Sida hermaphrodita*), willow short rotation coppice (*Salix viminalis*) and oak (*Quercus robur*). The experimental work was split into two sections: analytical (Py-GC/MS) and laboratory scale processing using a 300 g h<sup>-1</sup> continuous bubbling fluidised bed reactor. Pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) has been used to quantify pyrolysis products from these feedstocks by simulating fast pyrolysis heating rates using a CDS 5200 pyrolyser closed coupled to a PerkinElmer Clarus 680 GC-MS. High bio-oil yields were achieved for virginia mallow, willow SRC and oak (65.36, 62.55 and 66.43 wt. % respectively). Water content within the bio-oil is highest in the miscanthus (17.64 wt. %) and relatively low in the perennial virginia mallow and hardwoods willow SRC and oak (12.49, 13.88 and 14.53 wt. %). Similar high yields of bio-oil and low yields of char and non-condensable gas to willow SRC make the perennial virginia mallow an attractive energy feedstock for fast pyrolysis processing.

## CARBON-13 ISOTOPE SPECTROMETRY FOR FAST PYROLYSIS CHEMISTRY

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The production of pure and/or enriched <sup>13</sup>C labelled products from plant biomass has been receiving an increasing interest over the years, especially in life science research, as the use of stable isotope tracers can provide detailed chemical analysis of whole plant cell wall [1][2] but can also bring further insights on degradation mechanisms.

In this study, we propose to provide an overview of existing and current spectrometric analytical techniques using stable isotopic techniques that have permitted further progress in the field of pyrolysis revealing important mechanistic features. The mass spectrometry (MS) seen as the most popular primary spectrometric technique has received increased interest in the last few decades allowing the on-line volatiles collection and characterization of pyrolysis end products, while carbon-13 nuclear magnetic resonance (NMR) techniques have allowed more detailed examination of the structure and composition of raw materials [3] and improved characterization of liquid and char products [4][5].

A case study on the fast pyrolysis of agricultural residues involving the use of <sup>13</sup>C labelled materials and mass spectral data from the Py-GC/MS technique has revealed important details on primary synergistic mechanisms existing between the main biocomponents of lignocellulose; thus confirming the origin of carbohydrates- and lignin-derived compounds within the bio-oil.

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## FAST PYROLYSIS OF DIFFERENTLY-TREATED OKRA (*Abelmoschus esculentus*) STALKS BY PY-GC/MSD

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Fast pyrolysis of lignocellulosics has been investigated under a variety of conditions and from several points of view, since by this straightforward technique it is possible to produce liquid biofuels and chemicals [1]. On the other hand, biomass pre-treatment technology plays an important role in many biorefinery processes based on lignocellulosics. According to an integrated forest biorefinery (IFBR) concept, one interesting approach, mainly for recovering valuable carbohydrates-derived material, is to apply hot-water extraction (“autohydrolysis”) (HWE) to fibrous biomass raw materials prior to pulping [2].

In general, compared to wood, non-wood feedstocks have somewhat lower contents of cellulose, hemicelluloses, and lignin, but may have higher contents of extractives, other organics, and inorganics. However, several non-wood feedstocks are excellent raw materials for the future because they are readily available, environmental friendly, and technologically suitable [3,4]. Besides utilizing the hot-water-treated non-wood materials for delignification, they might also be a potential feedstock for thermochemical conversion.

In this study, the fast pyrolysis of untreated ( $O_{ref}$ ) and hot-water-extracted (140 °C, 90 min) ( $O_{HWE}$ ) okra (*Abelmoschus esculentus*) stalks as well as the soda-anthraquinone(AQ)-cooked (15 % active alkali, AQ 0.1 %, 15 min) pulps of these raw materials ( $P_{ref}$  and  $P_{HWE}$ , respectively) was investigated by pyrolysis-gas chromatography with mass-selective detection (Py-GC/MSD). The main idea was to detect differences in the thermochemical behavior of these feedstocks with varying chemical composition for evaluating their suitability for pyrolysis. There is no comprehensive literature information available regarding the pyrolysis products of okra stalks.

In each case, two pyrolysis temperatures (500 °C and 700 °C) and two residence times (5 s and 20 s) were applied. Major GC-amenable pyrolysis products were classified into several compound groups (mainly furans, phenols, ketones, anhydro sugars, and carboxylic acids including their derivatives) and changes in the relative portions of these monomer-related fragments were determined under varying conditions. The formation of the main products was shown to be characteristically dependent on feedstock and reaction conditions. Examples of the similar “fingerprint” compounds derived typically from lignin and carbohydrates (cellulose and hemicelluloses) were furfural, guaiacol, isoeugenol, syringol, 4-allylsyringol, 1-hydroxy-2-propanone, 2-methyl-1-propanol, 1,3-cyclopentadione, 3-methyl-2-hydroxy-2-cyclopenten-1-one, 2,6-dimethyl-3-(methoxymethyl)-*p*-benzoquinone, and acetic acid.

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# INHIBITION OF CHAR FORMATION FROM CELLULOSE IN FAST PYROLYSIS WITH AROMATIC SUBSTANCES

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Pyrolysis is a future promising technology to convert biomass resources to bio-chemicals and bio-materials. However, the non-selective co-production of solid char with liquid and gaseous pyrolysis products makes the chemicals production difficult due to the energetically and economically costly purification step. For these reasons, improving of the product selectivity is a quite important issue for chemicals production with the pyrolysis-based technologies. This paper deals with the utilization of aromatic substances to control the formation of solid char from cellulose. We reported that aromatic substances stabilize levoglucosan and other low-molecular-weight glycosides against the thermal transglycosylation and dehydration to form furans and char/coke [1], both of which are commonly observed as the major initial reactions of carbohydrate pyrolysis. This unusual stabilization effect was explained by the inhibition of proton-donation, which acts as an acid catalyst to promote these reactions, through hydrogen bonding of carbohydrate OH groups to aromatic  $\pi$  electrons [1]. If this could apply to the pyrolysis of cellulose, char/coke formation from cellulose would be inhibited, and this improves the selectivity of the low-molecular-weight chemicals.

A cellulose sample (CEOLUS FD-F20) and various aromatic compounds were used for the pyrolysis experiments, which include hydrocarbon- [1,3,5-Triphenylbenzene (462°C), *p*-Quaterphenyl (516°C)], ether (-O-)- [1,3-Diphenoxybenzene (375°C)], amine (>N)- [4,4'-Bipyridyl (305°C), 9-Phenylacridine (404°C)], amide (-NHCO)- [6(5H)-Phenanthridinone (435°C)] and carbonyl (>C=O)-types [Benzophenone (305°C), Anthraquinone (381°C), 1,2-Benzanthraquinone (472°C)] (value in the parenthesis : boiling point). Pyrolysis was conducted under the slow and fast pyrolysis conditions. Slow pyrolysis was conducted by heating a mixture of cellulose and aromatic substance in a flask with a mantle heater. On the other hand, the mixture in a ceramic boat was pushed into a furnace tube which was preheated at 600°C and quickly heated under a nitrogen flow of 150mL/min (Fast pyrolysis).

The pyrolysis results were quite different depending on the heating condition; under the slow heating conditions, cellulose was converted to the solid carbonized substances as observed in the neat cellulose pyrolysis, whereas the solid char formation was completely inhibited with some aromatic substances under the fast pyrolysis conditions. The amine- and carbonyl-types having the polar substituents were especially effective. The boiling points > 400°C were also important for this char inhibition effect. Regardless of the chemical structures of the aromatic compounds, the major components of the volatile products was levoglucosan. The results are discussed as illustrated in Fig. 1, by considering the nature of cellulose crystalline structure. It is well-known that fast pyrolysis of cellulose forms the melt-phase of the intermediates for char formation, although the slow pyrolysis gives char with preserving the original shape. The temperature ranges where the cellulose pyrolysis occurs are also reported to vary depending on the slow and fast pyrolysis conditions, that is, 360-385 and 400-450°C, respectively [2]. Slow pyrolysis of cellulose would proceed with the activation from the inside of the crystalline cellulose (active cellulose) [3], and hence the aromatic substances could not access to the inside of cellulose. On the contrary, under the fast pyrolysis conditions, the depolymerization of cellulose quickly occurs at the higher temperatures of 400-450°C to form the liquid intermediates. Then, the coexisting aromatic compounds could effectively interact with the liquid intermediates. The observed requirement of the boiling point >400°C is consistent with this proposal, and the polar aromatic compounds would interact with the surface of cellulose crystallites more effectively, because the literature shows that the most of the surface has hydrophilic nature [4].

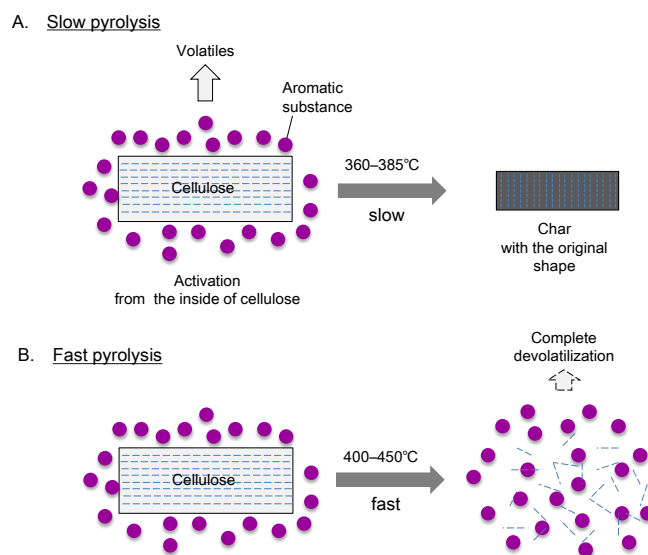


Fig. 1 Role of aromatic substance in cellulose pyrolysis.

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## Biofuels development by fast pyrolysis process from biomass in Korea

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In general, second generation biofuel produced from woody biomass is expected to be an effective avenue for reducing fossil fuel consumption and greenhouse gas (GHG) emissions in road transport. It is important that under the new Korean initiative, pilot scale studies evolve practices to produce next generation liquid biofuels. Whereas the first generation of biofuels is based on well established technologies, the development of processes. **The objective** of this study is to investigate fuel characteristics of bio-oil to obtain by a BFB reactor on 1b/d pilot scale unit for fast pyrolysis from biomass in Korea. **From the methods**, The conditions of pyrolysis (temperature: 500 °C, feed: 15kg/h) are chosen in order to enhance bio-oils production. This study was focused on a fuel characteristics of bio-oil from biomass by using fast pyrolysis to use transport fuels. Biomass fast pyrolysis is a novel and most effective method to convert biomass into liquid fuel with yields a high as 60% based on dry feed uses. In fast pyrolysis, bio-oil is produced by rapidly heating biomass to intermediate temperature (450 ~ 500 °C) in the absence of any external oxygen followed by rapid quenching of the resulting vapor. **In conclusions**, Bio-oil has poor properties due to the complexity of composition of bio-oil so as to use effectively. So we bio-oil fuel by fast pyrolysis investigated components of bio-oil in Korea. The bio-oil from biomass are different physiochemical properties from conventional fossil fuels.

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## AMMONIA AS CARRIER GAS IN FLUIDIZED-BED FAST PYROLYSIS AND ITS EFFECTS ON BIO-OIL YIELD AND PROPERTIES

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In this study, the effects of ammonia as carrier gas on the yield and composition of bio-oils were studied in a 1 kg/h bench-scale continuous bubbling fluidized bed. The ammonia was mixed with nitrogen in a static mixer before fed into the pyrolysis reactor, and the volume fraction of ammonia in the mixed gas was varied between 0 and 1. In addition, the influence of pyrolysis temperature on products distribution and liquid products properties were also examined. It was found that the liquid products (bio-oils) generated were apt to separate into two phases (with aqueous phase on the top and oil phase on the bottom) if the bio-oils were left standing for 30min, especially in the cases of ammonia volume fraction greater than 10%. However, the pH of bio-oils was improved from 2.18 (for the case without ammonia) to 10.61 (with 100% of ammonia). In addition, the content of phenolic compounds in the bio-oils was found increased while aldehydes and ketones decreased, some of which reacted to form pyrazines. The high heating value (HHV) of the bio-oil obtained was increased to 23.50 MJ/kg with 100% of ammonia used compared to 20.47 MJ/kg at the pure nitrogen atmosphere. Finally, the forming mechanism of nitrogen-contained compounds in bio-oil was studied with the help of various analytical instruments.

## FAST PYROLYSIS PROCESSING OF *MISCANTHUS X GIGANTEUS* USED IN PHYTOREMEDIATION FOR PRODUCTION OF FUELS AND CHEMICALS

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Biofuels are projected to be the fastest growing renewable sector in the world. Bioenergy can be produced from biofuels will come from very large integrated biorefineries, but until then there will be reliance on high grade drop-in fuels for addition to conventional fossil derived fuels. In addition, the increasing emphasis on biofuels will be accompanied by greater interest in renewable and sustainable chemicals.

This study addresses the application of biomass used in phytoremediation of contaminated soils for production of fuels and chemicals. Phytoremediation generates large quantities of contaminated biomass, for which fast pyrolysis can be considered as a suitable technology for production of fuels and value-added bulk chemicals. This technology offers the unique advantage of producing a liquid fuel (bio-oil) directly from biomass in high yield. Although much of the recent R&D activities in this area have been at a research level more companies are becoming interested in the potential of producing and using bio-oil in different applications for bioenergy and biorefineries.

Bio-oils from *Miscanthus x giganteus* used in phytoremediation process were produced using a 1 kg/h fast pyrolysis reactor to obtain a quantity of bio-oil comparable with existing industrial reactors. Biomass and pyrolysis products (bio-oils and chars) were analysed with the focus on the metal distribution and target elements include: lead (Pb), chromium (Cr), arsenic (As), zinc (Zn), cadmium (Cd), copper (Cu) and nickel (Ni). Bio-oil stability was measured using viscosity, water content, pH and heating value changes under specific conditions.

## Fast Pyrolysis of Bagasse and Groundnut Briquettes using Py-GC/MS and Py-FT-IR

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Lignocellulosic agro residues are potential renewable resources that can be utilized for the production of bio-fuels, platform chemicals and biopower. Annually, 140 billion tons of agro residues are generated globally, which is equivalent of 50 billion tons of fossil fuel oil. India alone generates 243 million tons of agro residues per year. Briquetting is a common practice to densify biomass in order to facilitate its easy transportation and processing. In India, biomass briquettes are either combusted alone or co-fired with coal in many large and community scale power generation facilities. While this is one of the solutions to utilize the large volume of agro residues generated in India, it may not be an optimum solution. The generation of bio-oil or upgraded biofuels from agro residues is a promising option to reduce our dependence on conventional petroleum-based fuels. Fast pyrolysis, which involves heating the biomass at medium temperatures (c.a. 500-600 °C) in inert atmosphere at short residence times (few to tens of seconds), is a promising technique to produce high yield of bio-oil that can be potentially upgraded to transportation biofuels. Biomass briquette is a complex feedstock in terms of composition. During the briquetting process, a number of additives such as fillers and binders are added to low density agro residues. For example, saw dust is a common additive whose composition is significant (c.a. 20-30%) in biomass briquettes. Therefore, this study is intended to evaluate the effect of heterogeneity/particle size of biomass briquette and fast pyrolysis temperature on bio-oil composition and time evolution of major pyrolysates using a combination of analytical techniques like pyrolysis-GC/MS and pyrolysis-FT-IR.

Bagasse and groundnut briquettes (obtained from Thermax Ltd.) were crushed and ground to three different sizes, viz. 0.25 mm, 0.71 mm and 1.40 mm. Proximate, elemental and higher heating value (HHV) analyses of biomass particles were performed using standard methods. Thermogravimetric analysis (TGA) of the biomass particles was performed at different heating rates (0-30 °C/min) in N<sub>2</sub> atmosphere (SDT Q600 T.A. Instruments). The variation of apparent activation energy (E<sub>a</sub>) and pre-exponential factor with conversion for all biomass particles was evaluated using integral isoconversional method of Vyazovkin. Fast pyrolysis experiments were carried out in Pyroprobe® 5200 pyrolyzer (C.D.S. Analytical) interfaced with GC/MS (Agilent Technologies) and FT-IR spectrometer (Agilent Cary 660). 300±20 µg and 8 mg of biomass was utilized for Py-GC/MS and Py-FT-IR experiments, respectively. The sample heating rate employed in Pyroprobe® was 10,000 °C/s.

While there was no significant effect of particle size on volatile matter, fixed carbon and ash content of the biomasses, the carbon, hydrogen and oxygen content varied with particle size, especially for bagasse briquettes. The HHVs of bagasse and groundnut briquette particles were 15.5 and 13.5 MJ/kg, respectively. The apparent activation energies of pyrolytic decomposition, evaluated by Vyazovkin's method, were 120-240 kJ/mol in the conversion range of 10-80 wt.%. Importantly, the order of variation of average E<sub>a</sub> (in kJ/mol) for bagasse and groundnut briquette particles followed the trend: bagasse - 1.4 mm (229) > 0.25mm (209) > 0.71 (175), groundnut - 0.25 mm (231) ≈ 0.71 mm (223) > 1.4 mm (169). These trends agree with the CHO composition of the feedstocks. The production of phenolic compounds and furan derivatives was unaffected by particle size, while the yields of mono- and polyaromatic hydrocarbons, cyclo-oxygenated species, anhydrosugars and char significantly varied with particle size. For example, the yield of aromatics decreased from 16.80% (0.25 mm) to 3.42% (1.40 mm) for bagasse briquette particles at 500 °C. Interesting trends in yields of various organic functional groups with particle sizes were also observed at higher fast pyrolysis temperatures (650 and 800 °C). Importantly, from Py-FT-IR analysis of the pyrolysates, it was inferred that the particle size does not affect the timescale of pyrolysis (or the maximum evolution of various organic compounds). The time taken for maximum production of various functional groups such as phenolics, aromatics, aliphatics, carbonyls and alcohols at 500 °C was 13±2 seconds. However, at fast pyrolysis temperatures of 650 and 800 °C, this time decreased to 10 and 7s, respectively. This study unravels, for the first time, the effects of particle size/composition of biomass briquettes on (a) apparent activation energies of thermal decomposition, (b) fast pyrolysis product distribution at different temperatures, and (c) typical reaction time involved in fast pyrolysis.

## Migration of AAEMs and chloride during biomass pyrolysis in an entrained flow reactor

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### Abstract:

The technologies for controlling multi-pollutants of NO<sub>x</sub> and mercury emitted from coal-fired flue gas have been paid more attentions. The combination technology of sorbent injection and flue gas conditioning has been considered as a promising mercury emission control technology. However, this technology is not applied widely due to the limitation of sorbent cost and flue gas conditioning. Because of the characteristics of low sulfur, low nitrogen and higher contents of AAEMs (Alkali and alkali earth metals, mainly K, Na, Ca and Mg) and chlorine bound in biomass, biomass reburning can form appropriate concentrations of AAEMs and chlorine in the flue gas and flyash, which is benefit to promote NO reduction and catalytic oxidation of vapor elemental mercury, and finally to achieve simultaneous control of NO<sub>x</sub> and mercury in conventional air pollution control devices (APCDs).

In this paper, several biomass including cotton stalk (CS), maize stalk (MS), rice husk (RH), sunflower stalks (SS), Wood Chips (WC) and wheat stalks (WS) was selected, and biomass pyrolysis characteristics was carried out in an entrained flow reactor. The biomass coke and flue gas components was collected by an inside sampling probe. The morphologic characteristics and surface functional groups of test samples were measured by scanning electron microscopy (SEM) and Fourier transform infra-red (FTIR) spectroscopy, respectively. The raw biomass and collected biomass coke were digested in a PTFE beaker with an acid mixture (HF, HCl, HClO<sub>4</sub> and HNO<sub>3</sub>), and the concentration of AAEMs and other elements characterized by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The chloride content was analyzed by using digital ion meter. The effects of biomass species, biomass feed rate, particle size, pyrolysis temperature, flue gas components and residence time on migration of AAEMs and chloride bound in biomass was analyzed. The migration mechanism was discussed based on the experimental result. The results indicated that biomass species, pyrolysis temperature and pyrolysis atmosphere have significant influences on migration of AAEMs and chloride, and the migration mechanism was also discussed.

**Key words:** biomass pyrolysis; alkali/alkaline earth metals (AAEMs); chlorine; migration

## IMPACT OF HOT WATER PRETREATMENT ON THE PYROLYSIS OF BIRCH AND SPRUCE WOOD

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Despite the great number of investigations biomass utilization for chemicals dropped far behind fossil raw materials in the last century. Biomass pretreatment is one of the bottle-necks for its preparation to thermochemical transformation products with high added value. Demand to consider the existing and future regulations as well as the movement to environmentally friendly technological processing arise the necessity to develop new technologies and methods. Hot water extraction (HWT) as a physical pretreatment method for preparing raw material to pyrolysis is not very broadly investigated. For this reason the aim of the work was to elucidate the impact of hot water treatment on the behavior of the remaining lignocellulosic part in the pyrolysis process.

Birch and spruce wood particles (fraction 0.2-0.6 mm) were extracted with hot water in the Parr 4554 7.5 l reactor and solid to liquid ratio 1:15 at a temperature range 150-210° for one hour with stirring. After that the samples were rapidly cooled down and depressurized. The obtained samples were washed, dried, compositional content of them was determined, and analyzed with Py-GC/MS.

As expected, lignocellulosic yield decreased with the raising of the HWT temperature and filtrate analysis showed simultaneous increase of the content of acids, aldehydes and lignin, but sugars and dry matter content rose up at 170°C for birch wood and up at 180°C for spruce and after that decreased because of autohydrolysis and succeeding decomposition.

Results of thermogravimetric analysis demonstrated the increase of the yield of solid carbonaceous residue. At 800°C the increase was from 14.5 and 13.1% to 22.9% and 22.7% for untreated birch and spruce wood, respectively, explained by the extraction of the hemicellulosic part. At the same time the temperature of the maximum of the main degradation (DTG) for birch wood practically did not change until HWT temperature 170°C with a following decrease, and for spruce wood growth was up to 180°C with following decrease.

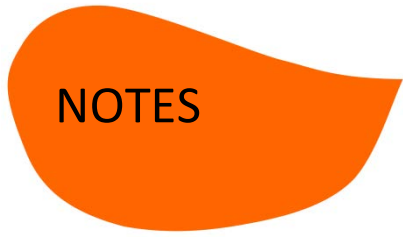
Analytical pyrolysis results showed that compared with untreated birch and spruce wood the amount of CO<sub>2</sub> and low molecular weight compounds in the volatile products decreased, but the impact of temperature was negligible. On the other hand, the amount of carbohydrates increased at HWT temperature 200°C and 190°C, correspondingly, but then started to decrease. At the same time the content of phenols and guaiacyl derivatives increased, but the amount of syringyl compounds decreased in the lignin compounds. Independently from wood species the increase of HWT temperature decreased the yield of cyclopentanes, acids and esters, but the yield of alcohols increased at 190°C. Regarding the yield of aldehydes and ketones, it started to decrease from 170°C for birch and 190°C for spruce. It must be mentioned that the yield of furans from spruce treatment temperature practically did not change, but for birch it went through a maximum at 170°C.

The highest HWT impact was on the yield of sugars, mainly levoglucosan. Its content increased 10 times for birch wood at 200°C and only 4 times for spruce wood at 210°C. Partly it can be assigned to the part of cellulose rising with the extraction of the hemicellulosic part, but mainly it give evidence of the cellulosic structure changes favorable to chain depolymerization. At the same time the amount of hemicellulose-origin sugar derivatives decreased. Extended HWT time to 1.5 and 2 hours for birch wood gave similar effect as temperature raising.

The Py-GC/MS analysis of extracted Klasson lignin showed that starting from HWT temperature above 150°C the amount of sugars increased.

The HWT is a good method for removing the hemicellulosic part of wood, but it does not give satisfactory enhancement for thermochemical conversion to sugars and anhydrosugars alone.





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ABSTRACTS

# **Biomass / Kinetics**

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**Oral presentations**

## RECENT ADVANCES IN REACTION MECHANISMS AND MULTI-SCALE MODELLING OF BIOMASS PYROLYSIS

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The reaction mechanisms and multi-scale modelling of biomass pyrolysis have been thoroughly reviewed in a recent publication by Anca-Couce in *Progress in Energy and Combustion Science* [1]. The recent advances in the understanding of the fundamental reaction pathways have been described, including quantum-mechanical calculations, and the description of pyrolysis as a two-step process, i.e., primary pyrolysis and secondary charring, the effect of the presence of an intermediate liquid compound, and the influence of inorganic species have been discussed. It has been emphasized the need to describe biomass pyrolysis as the sum of the contributions of its individual components, i.e., cellulose, hemicellulose and lignin. The determination of mass loss kinetics from thermo-gravimetric experiments has been analysed, and the product composition and heat of reaction that are experimentally obtained during pyrolysis have been presented, along with detailed schemes that can be used to predict them. Finally, it has been shown that a multi-scale consideration of pyrolysis on multiple levels - namely, on molecular, particle and reactor levels - is required to accurately describe biomass pyrolysis. Intra-particle phenomena and particle models have been discussed and the reactor level has been analysed. The review is concluded with a list of research focal points that will be important in future.

In this work, the previously described review is presented together with the recent efforts of the authors in order to further develop detailed reaction schemes and to incorporate them in a multi-scale description of biomass pyrolysis. Commonly employed reaction schemes for biomass pyrolysis, such as the single component competitive scheme, are not able to describe the complex reactions that take place in this process and have several limitations, e.g., compounds with very different properties are lumped in one category. Detailed reaction schemes are required to gain a more fundamental understanding of biomass pyrolysis that in turn would allow the development of more targeted applications. The most promising detailed pyrolysis reaction scheme published thus far is the one developed by Ranzi et al. [2] for lignocellulosic biomass, which was adapted by Anca-Couce et al. [3] in order to introduce secondary charring reactions. Biomass consists in this scheme of cellulose, hemicellulose and 3 types of lignin which independently decompose and the volatiles are represented by 20 species, including permanent gases and condensable species. It has been shown by the authors that the adaptation of this detailed reaction scheme is able to predict with good accuracy the product composition of biomass pyrolysis [3] and torrefaction [4] in a fixed bed reactor and mass loss in thermo-gravimetric experiments, without the presence of heat and mass transfer limitations [4]. Moreover, this detailed reaction scheme has been recently coupled with a single particle model, in order to describe in a multi-scale way the complex reactions and transport processes that take place during pyrolysis of a single biomass particle. The model is able to reproduce with good accuracy the experimental results that have been conducted with spruce pellets in a single particle reactor at different temperatures regarding mass loss, the temperature profiles including the exothermic bump in the centre of the particle at the end of the experiments, and the final yields of the pyrolysis products as well as the instantaneous release of the main species, such as H<sub>2</sub>O and CO<sub>2</sub>.

In summary, the use of detailed reaction schemes in a multi-scale approach is required in order to correctly describe biomass pyrolysis. Results of the application of an adapted pyrolysis scheme, which can predict mass loss evolution and product composition at different conditions, are presented in this work. Moreover, it is shown that a single particle model which is coupled with this detailed scheme is able to describe the mass loss, the temperature profiles and the product composition during single particle pyrolysis experiments, where chemical reactions take place together with transport phenomena.

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## The Kinetics of Cellulose Glycosidic Bond Cleavage

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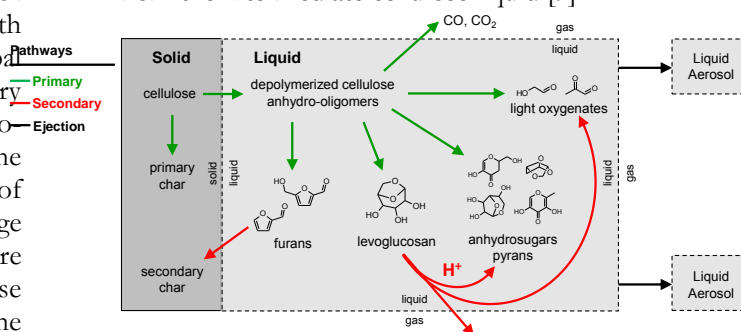
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Molecular understanding of the high temperature decomposition of cellulose remains one of the leading challenges for pyrolysis researchers, with significant questions remaining with regard to global polymer conversion kinetics as well as the elementary mechanisms to form volatile organic products (i.e. bio-oils). Despite decades of effort focusing on the development of lumped kinetic models, the range of models and associated kinetic parameters is large (activation energy,  $E_a$  of 10 to 63 kcal/mol) [1]. More recently, molecular characterization of cellulose pyrolysis products has put more focus on the elementary reactions of cellulose fragmentation [2,3]. Enhanced capability for quantifying complex mixtures such as bio-oils via new analytical detectors including the ‘Quantitative Carbon Detector’ or QCD enables simple compositional insight of pyrolysis products [4].

The difficulty in elucidating the chemistry of cellulose decomposition arises from validating proposed mechanisms developed by computational methods. Numerous reaction mechanisms of varying types (homolytic, heterolytic, or concerted) have been proposed for each class of products including furans, levoglucosan and pyrans [3,5,6]. However, for each of these mechanisms, the calculated energetic barriers cannot be verified by any existing experimental method (e.g. TGA), and it remains unclear which mechanisms are representative of the chemistry of cellulose decomposition.

To address the challenge of verifying calculated cellulose mechanisms, we have proposed the use of a new technique called ‘Thin-Film Pyrolysis’ or TFP, whereby cellulose films are prepared at micron-scale thickness [3,7]. At the conditions of thin films (~10  $\mu\text{m}$ ), a comparison of the relative rates of global reaction and heat transfer indicates that cellulose decomposes absent the artifacts of transport limitations. Thus, cellulose reacts until it produces a volatile product such as levoglucosan, furfural or glycolaldehyde. These volatile products will then evaporate before reacting further, thus constituting the green ‘primary’ pathways identified in Figure 1. Alternatively, for thicker samples of cellulose decomposition, volatile components will need to diffuse to the cellulose melt surface prior to evaporation, and reactions occurring during this transport process are referred to as ‘secondary reactions’ identified as red in Figure 1 [8]. Additionally, a third pathway to cellulose decomposition products

includes the spontaneous ejection of aerosols directly from the intermediate cellulose liquid [9].



**Fig. 1. Primary (green), secondary (red) and aerosol pathways of cellulose decomposition [3,8,9].**

Using Thin-Film Pyrolysis, we show that the primary reactions of Figure 1 can be evaluated for comparison with computed pathways, for which the apparent kinetic barriers have been predicted by density functional theory. Simulations by Car-Parrinello Molecular Dynamics (CPMD) have previously shown [3] that glycosidic cleavage can occur via homolytic fragmentation which propagates through the glucan ring producing either pyrans, furans or anhydrosugars. These mechanisms are compared directly with the kinetics of an alternative mechanism of chain hydrolysis to produce glucose, which undergo conventional carbohydrate mechanisms to furans and light oxygenates. The kinetics of cellulose decomposition are presented for varying temperatures, and rate expressions and measured apparent energy barriers are presented and compared with proposed mechanisms of cellulose decomposition. The results provide clear mechanistic conclusions of biopolymer chemistry above 400 °C giving a starting point for a complete molecular description of pyrolysis chemistry.

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## Experimental and kinetic study on pyrolysis of woody and non-woody biomasses

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The importance of pyrolysis in the overview of the biomass thermochemical conversion processes lies in its recognized flexibility with respect to the desired product addressing both the energy and non-energy sectors. When char is the desired product, slow pyrolysis conditions are required and high temperatures are preferred to better develop char characteristics useful for its further application as fuel or adsorbent even giving up high yields [1]. Several studies show the relevance of biomass chemical composition, besides the thermal conditions, in determining pyrolysis products distribution and characteristics [2]. Many efforts have been directed to characterize pyrolysis kinetic mechanisms in order to predict weight loss curves in inert atmosphere [3] and in some cases the whole spectrum of product yields, gas and composition [4]. Kinetic schemes have been developed consisting of sets of independent simultaneous reactions where biomass main components react independently so that the global thermal behaviour reflects the individual behaviour of the components, weighed by the composition. Nevertheless, if these models referring to cellulose, hemicellulose, lignin and in some cases extractives as main components give an acceptable representation of woody biomass composition, this is not true when high extractives and ash content biomass are considered. Moreover, the existence of cellulose-hemicellulose, cellulose-lignin and inorganic-organic matter interactions needs to be considered [5, 6]. In this work six biomasses have been selected and divided in two categories basing on their composition in terms of cellulose, hemicellulose, lignin, extractives and ashes: olive (OB) and kiwi branches (KB) representing woody biomass, pine bark (PB), wheat straw (WS), rice husks (RH) and cork (C) considered as non-woody biomass. Pyrolysis tests have been carried out up to 973 K and heating rate HR=7 K/min in a reactor capable to combine an effective control of sample thermal conditions and the possibility to obtain product amounts sufficient for off-line analysis [7]. Product yields and composition have been compared with the results of non-interacting model mixtures and numerical predictions. The model mixtures are computed by superimposing the data of isolated biomass components, while numerical predictions are performed by means of a kinetic tool developed in MATLAB using the Bio-PoliMi mechanism [4] and the Cantera reaction kinetics library [8]. As shown in Figure 1, there is a good agreement on the char yield between numerical and experimental data. On the contrary, the model is not able to predict the distribution between gas and liquid products underestimating the liquid yield in favour of gas yield mainly for not-woody biomasses.

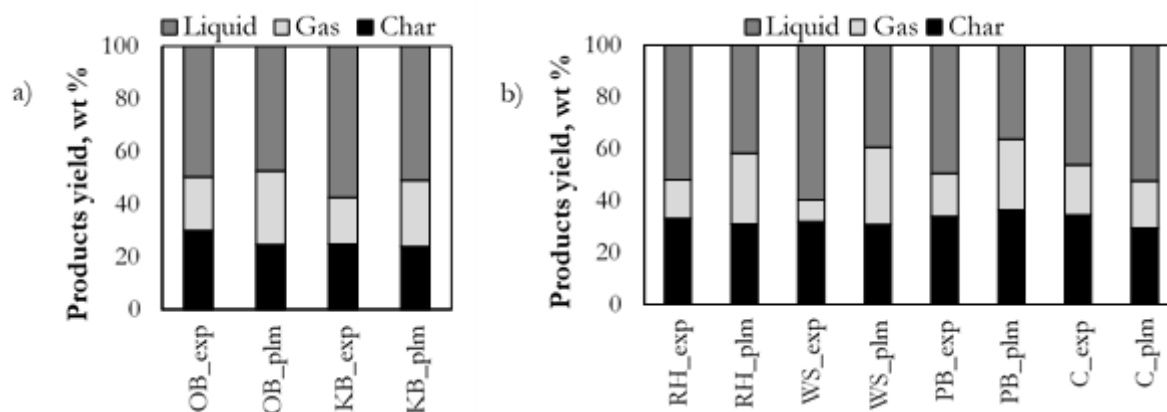


Figure 1. Yields of char, liquid and gas for woody (a) and non-woody (b) biomasses.

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# EVOLUTION OF CELLULOSE WITH DIFFERENT CRYSTALLIZATION MORPHOLOGY DURING PYROLYSIS BASED ON IN-SITU DIFFUSE REFLECTANCE FT-IR

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## ABSTRACT

Microcrystalline cellulose (cellulose I) was dissolved by the ionic liquid 1-butyl-3-methylimidazolium chloride. Cellulose II and amorphous cellulose were obtained through different regeneration methods [1] after detection of X-ray diffraction (XRD). In-situ diffuse reflectance FT-IR (DRIFT) was applied to observe the collapse of hydrogen bonding network in cellulose during pyrolysis and its impacts on the subsequent reactions in different crystal states with a heating rate of 5 °C/min from 120 °C to 450 °C. The diffuse reflection spectrums were analysed by two-dimensional perturbation-based correlation infrared spectroscopy (2D-PCIS). Simultaneous thermogravimetry and differential scanning calorimetry (TG-DSC) was also employed as a supplement to measure energy transformation. The results showed the inter hydrogen bonds starts to break up, forming free O(2)H and O(6)H at 150 °C. Intra hydrogen bonds showed different thermal stability in different samples, which breaks up at 210 °C, 270 °C and 300 °C for amorphous cellulose, cellulose I and cellulose II. Under the protection of hydrogen bonds, cross-linking reaction took place at the same temperature of 240 °C, while in different reaction rate for the three samples. Besides, results from 2D-PCIS revealed that the breakage of pyran ring was earlier than it of glycosidic bond, probably as a result of hydrogen bonding network. Text of the abstract here.

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## R-OH HYDROXYL CATALYSIS OF PYROLYSIS REACTIONS

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This paper discusses how R-OH hydroxyl species like water can catalyze pyrolytic decompositions, as shown with experimental measurements and computational chemistry. Bimolecular reactions are known to be important for pyrolysis. In classical chain-reaction theory, radicals augment the relatively slow, high-activation-energy reactions of homolytic decomposition through H-abstractions, beta-scission decompositions, and internal isomerizations. At temperatures where no radicals are present, concerted, pericyclic molecular decompositions are known to dominate, notably for dehydrohalogenation reactions like  $\text{CH}_2\text{CHF} = \text{C}_2\text{H}_4 + \text{HF}$ . Similar pericyclic dehydrations can become important, especially in biomass decomposition where OH groups are abundant. It is less recognized that R-OH groups can catalyze decompositions and isomerizations through pericyclic bimolecular reactions.

Recent papers by Seshadri and Westmoreland [1,2] used computational quantum chemistry to identify noncatalytic and catalytic routes non-radical, non-ionic routes that explain the experimental formation and destruction of levoglucosan from glucose, tying it mechanistically to the decomposition of cellulose to bio-oils. That work also found unimolecular and bimolecular pericyclic reactions involved in the interconversions of sugars from cyclic to linear forms and in generating five-membered rings. Pericyclic routes have been found independently and in parallel by other groups, but they did not identify the catalytic potential. Mayes and Broadbelt [3] computed a unimolecular concerted route from cellobiose to levoglucosan by dehydrating the C6 hydroxyl; Assary and Curtis [4] computed routes from cellobiose to levoglucosan by unimolecular and bimolecular pericyclic reactions; and Agarwal et al. [5] found cellobiose decomposition-reaction trajectories to levoglucosan by using VASP ab-initio molecular simulations. Subsequent Reactive Monte Carlo modelling by Zhou et al. [6] has supported the proposed dominance of these routes in the absence of solvents and of catalytic ions. Pericyclic routes also appear to occur in the pyrolysis of synthetic polymers like poly(hydroxyamide) [7] and fuel molecules like JP-10 (exo-tetrahydrodicyclopentadiene) [8,9]. However, the catalytic role of hydroxyl seems especially pertinent for pyrolysis of biopolymers.

The present paper examines the experimental and computational evidence for these hydroxyl-catalyzed pathways. TGA-DSC and flash-pyrolysis data are presented for pyrolysis of sugars, polymers, and small compounds, including product speciation by GC-MS and GCxGC-TOFMS. Likewise, pathways predicted by computational quantum chemistry are examined and discussed, including predictions of transition states, internal reaction-coordinate following, thermochemistry, and rate coefficients using Gaussian 09 [10], ChemRate [11], and our own codes.

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ABSTRACTS

# **Biomass / Kinetics**

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**Poster presentations**



## KINETIC MODEL OF THE PYROLYSIS OF BIOMASS-COAL BRIQUETTES

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The Steel industry is increasingly concerned about CO<sub>2</sub> emissions resulting from their use of fossil fuels, as a consequence the interest in renewable and sustainable energy sources is increasing. Coal and biomass blends are gaining increasing importance as a renewable energy source, since they lead to reductions in fossil fuel usage and contribute to the reduction of CO<sub>2</sub> emissions in the energy sector.

The study of the thermal decomposition of these blends is essential for assessing their applicability and for optimizing the pyrolysis process with a view to scaling up in cokemaking. Thermogravimetric analysis is the most common technique used to evaluate thermal decomposition and perform kinetic studies. A large number of research papers have dealt with thermal decomposition kinetics of coal and biomass with the aim of obtaining kinetic parameters that will serve to predict their behaviour during thermal treatment. Some studies use Coats Redfern model to evaluate kinetic parameters based on experiments carried out at various heating rates and provide reliable estimates of the kinetic parameters.

In this work two coals, sawdust and coal tar were selected to prepare four blends. Thermogravimetric analyses at heating rate of 10 °C/min and up to 1000 °C were carried out with the blends and their components. The experimental decomposition profiles of the blends were compared with the calculated data taking into account the amount of each component in the blend. No interaction was found when comparing the experimental and calculated decomposition profiles of the blends. Coats Redfern model was used to obtain the activation energies and the pre exponential factors of the raw materials and the blends. The thermal decomposition profiles calculated using the kinetic parameters were in good agreement with the experimental results in all cases. In addition the thermal decomposition profiles of the blends were successfully predicted from the prediction of the thermal decomposition of the raw materials.

Keywords: lignocellulosic biomass, coal, pyrolysis, Coat Redfern.

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## Combustion Characteristics and Kinetic Analysis of Hydrothermally Derived and Pyrolytic Carbon Materials

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More energy will be required for the growing population around the world, especially as living standards improve [1]. To produce bio-carbon materials, the use of expensive fossil-based precursors contribute to high costs, along with high temperature treatment processing [2]. Hence, hydrothermal carbonization (HTC) of biomass is expected to play an important role in low-cost synthesis of carbon materials [3]. In this study, carbon samples, containing hydrothermally derived carbon material from corn starch (HTC-S), wood and barbeque charcoals, were analysed by non-isothermal TGA methods to calculate the mass loss kinetics of the thermal decomposition with linear temperature program in air at different heating rates (5, 10, 15, 20, 30 °C min<sup>-1</sup>). Different reaction regions were observed from the derivative thermogravimetric (DTG) curves due to the thermal degradation of the carbon skeleton. After the evaporation of absorbed water, the more initial mass loss of HTC-S occurred in lower temperature regions than that observed in the other charcoals, which was caused by abundant cellulose and lignin contents contained in charcoals. To gain a detailed insight of the carbon structures, three carbon materials were characterized by SEM, EDX, and Elemental Analysis. Based on correlation coefficients of different reaction models and the coefficient of variations of the activation energy (E) values obtained, the TG and DTG curves of HTC-S were analysed to derive the best suitable reaction order ( $n=3/2$ ) by fitting the Coat-Redfern equation [4] under five different heating rates. The initial E of HTC-S (calculated from  $n=1.5$  order) reaction model was about 72 kJ mol<sup>-1</sup>, which indicated that HTC carbon materials' potential as a combustible material. More importantly, the change of DTG curves of HTC-S under different heating rates agreed with the model calculation, demonstrating the relationship between the constant heating rate and DTG.

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## KINETIC MODELS FOR THE PYROLYSIS OF BIOMASS FUEL IN A DROP TUBE FURNACE.

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The partial substitution of coal by carbon-neutral fuels such as biomasses is a promising way to reduce the environmental impact of coal utilization. Biomasses can supply around 14% of the world's energy consumption [1]. Co-firing coal and biomass is an option for converting biomass into power generation. In such a context, the operating parameters of the large size plants have to be optimized with models able to simulate biomass devolatilization and combustion which are the main thermochemical processes involved.

High particle heating rate (approximately  $10^4$ - $10^5$  °C s<sup>-1</sup>) has to be achieved in order to characterize solid fuels under conditions similar to those taking place in actual power plant furnaces. Drop tube furnace (DTF) is an appropriate tool for the investigation of pulverized fuel pyrolysis and combustion [2]

The aim of the present contribution is to propose new procedures for the characterization of the pyrolysis of solid biomass under a pulverized form. Both experimental investigations and modelling are conducted. Woody biomass pyrolysis is investigated on the one hand in a DTF (fast pyrolysis) and on the other hand in a thermogravimetric analyser (slow pyrolysis) both under N<sub>2</sub> and CO<sub>2</sub> atmosphere.

The woody biomass is prepared from beech. It is crushed and sieved in the range 200-280 μm. DTF experiments are conducted under in the temperature range 600°C-1000°C using a total gas (N<sub>2</sub> or CO<sub>2</sub>) flow rate equal to 840 SLPH. The pulverized fuel is injected through a water-cooled injection probe in a tubular reactor (interior diameter equal to 70mm) with a uniform mass flow rate equal to 17 g h<sup>-1</sup>. The position of the sample probe is adjustable. It allows quenching the char at different drop distances (from 7cm to 70cm). The corresponding residence time of the solid fuel in the reaction zone of the DTF is in the range 120ms-870ms. The yield of volatile products is obtained by a perlite tracer method. On the other hand, the thermogravimetric analysis (TGA) is carried out using a TA Q600 device. Small masses (10 mg) of biomass are placed in an alumina crucible and heated up to 900 °C at different heating rates (5, 10 and 20 °C min<sup>-1</sup>) under N<sub>2</sub> and CO<sub>2</sub> atmosphere with a flow of 100 mL min<sup>-1</sup>.

The maximal volatile yield is about 93 % (dry ash free). The final extent of the thermal degradation of woody biomass appears to be independent of the furnace set point temperature in the range of 600 to 1000°C. Thermogravimetric experiments show that the decomposition occurs at temperatures lower than 1000 °C. The maximum devolatilization yield reaches 76% (dry ash free) in TGA.

Two models are proposed for the simulation of the biomass devolatilization under high heating rate. First, a single reaction model is used, which allows extracting kinetic parameters directly from the DTF experiments. Secondly, an Independent Parallel Reaction model [3] is tested, which allows extracting kinetic parameters for the thermal decomposition of cellulose, hemicellulose and lignin under slow heating rate i.e. considering TGA experiments. Then the IPR model and the corresponding kinetic parameters are used in the case of DTF i.e. under high heating rate. The results of the two approaches are compared and discussed.

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## SIGNIFICANCE OF THE ACTIVATION ENERGY AND ITS IMPLICATIONS FOR BIOMASS PYROLYSIS KINETICS

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Many efforts have been made in rationalizing the pyrolysis kinetics of lignocellulosic materials and concerns have been raised as gross disparities in solid state reaction kinetics were pointed out<sup>[1]</sup>. This is linked to the fact that the ‘exact’ mechanism of biomass pyrolysis is still unknown. In addition to that, the selection of an appropriate model development approach for modelling the pyrolysis of biomass present a real challenge as many methods have been developed <sup>[2]</sup>. Although, both mathematical <sup>[3]</sup> and experimental <sup>[4]</sup> methods have allowed permitted to make considerable progress to be made in kinetics, the separate use of these methods has often led to opposite conclusions rather than complementary. More recent views on kinetic study recommends ~~to~~ combination of different approaches to rationalize the analysis of solid-state and to permit the development of more accurate models. On a few recent occasions, researchers have combined the powerful isoconversional analysis with a model-fitting <sup>[5]</sup> or a DAEM method <sup>[6]</sup> to determine apparent activation energies and select the most suitable kinetic model or improve the modelling performance of this latter.

In this study, the Friedman’s isoconversional method has been adopted to determine the dependency of apparent activation energies ( $E_{\alpha}$ -dependency) on pyrolysis conversion by means of an automated and rigorous methodology based on a series of past recommendations <sup>[7, 8]</sup>. This procedure has led to the determination of  $E_{\alpha}$  with confidence intervals for the *Radiata pinus* biomass free of extractives and three of its substructures, previously isolated using wet chemistry methods.  $E_{\alpha}$ -dependency values for extracted pine wood, holocellulose and  $\alpha$ -cellulose were found to be in good agreement with the literature, while those for lignin, 169.9 to 319.3 kJ/mol were higher than the unique values usually reported for the pseudocomponent ascribed as lignin (46 kJ/mol <sup>[9]</sup> - 167 kJ/mol <sup>[10]</sup>) and model compounds (93 kJ/mol <sup>[11]</sup>).

Based on the new range of  $E_{\alpha}$  values, a biomass pyrolysis kinetic scheme assuming three parallel reactions (degradations of holocellulose and lignin, and a global synergistic reaction) has been developed to describe the complex process of biomass pyrolysis.

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# Biomass pyrolytic polygeneration: Evolution of Bamboo Char Structure

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Biomass pyrolytic polygeneration technology is that the gas, liquid and char products from biomass pyrolysis are all used by downstream consumer. Hence, compared with fast pyrolysis technology for bio-oil and carbonization for charcoal, this technology has a relative good performance on economic income. Char product has a significant contribution on the economic income since it has a widely utilization like solid fuel, biochar and adsorbent. To deeply understand the mechanism of char formation during biomass pyrolysis and well predict the char property during pyrolysis, bamboo was pyrolyzed in the range of temperature from 250 °C to 950 °C and these chars from different temperature were characterized by FTIR, FT-Raman, XRD and N<sub>2</sub> adsorption. (2) The char formation process can be divided into three stages. During the degradation stage (250–450 °C), the raw biomass is converted to a network-like structure in which the basic node is the fusing aromatic with 1 to 2 aromatic rings, connected by functional groups containing methyl, methylene, and oxygen. During the reforming stage (450–650 °C), cleavage of the functional groups containing methyl, methylene, and oxygen occurs, and the size of fused aromatics increases from 1 to 2 rings to 3 to 5 rings. The final stage, condensation (> 650 °C), leads to further enlargement of the fused aromatic structure up to  $\geq 6$  rings, due to dehydrogenation and cleavage of ether bonds.

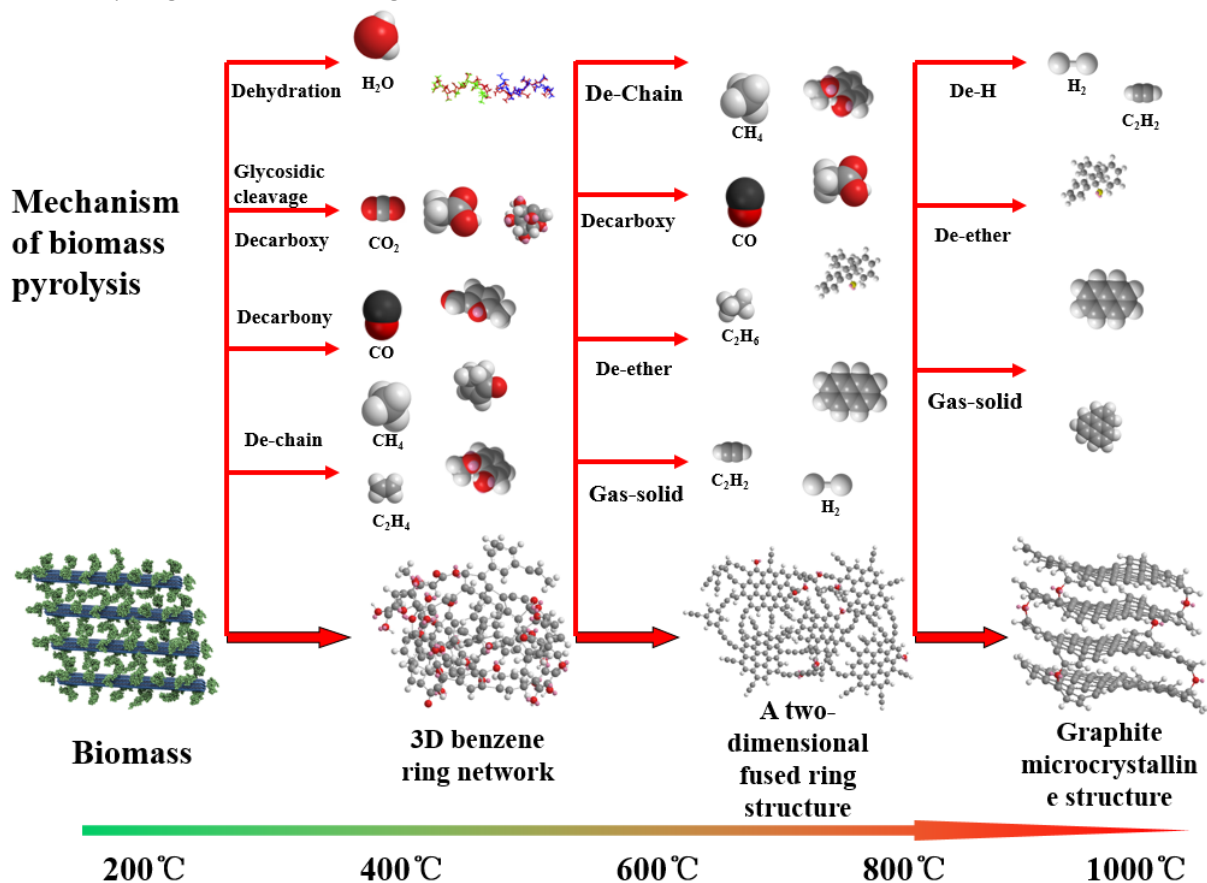


Figure The Mechanism of biomass pyrolytic polygeneration

# GAS-PHASE REACTION MECHANISMS OF LEVOGLUCOSAN AS THE INTERMEDIATE OF BIOMASS GASIFICATION

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Gasification is a promising future technology for power generation and the production of synthetic petroleum and other chemicals via the Fischer-Tropsch (FT) process. However, tar generation, which causes coking and clogging of the pipeline from gasifier and deactivation of the FT catalyst, is a challenging issue to be solved. Understanding of the chemistry involved in biomass gasification would be very helpful for exploiting the tar- and coke-free clean gasification systems. This paper deals with the molecular mechanisms for the pyrolytic conversion of the gaseous levoglucosan (1,6-anhydro- $\beta$ -D-glucopyranose, LG), the important intermediate in biomass gasification, as studied in the temperature range of 500-700°C at residence times of 0.11-0.45s with a two-stage tubular reactor. The experimental results were also discussed with the results of density functional theory (DFT) calculation with Gaussian 09 conducted at the level of M06-2x/6-311+G(d,p)//M06-2x/6-31+G(d,p).

Levoglucosan is pyrolyzed differently in the gas and molten phases; molten LG decomposed (polymerized) at  $>250^{\circ}\text{C}$ , while the decomposition of the gaseous LG started at  $500^{\circ}\text{C}$  and gave only fragmentation products (mainly C1 and C2 aldehydes/ketones and noncondensable gases) without the formation of any furans and coke [1]. From the following kinetic investigation,  $-\ln [\text{LG}]$  was not linearly proportional to the residence time, and the deviation became greater at the higher temperatures of 650-700°C. The Arrhenius plot could not be explained with one single straight line [activation energy ( $E_a$ ): 35.1 kcal/mol, A:  $2.03 \times 10^9$  (550-600°C) and  $E_a$ : 16.7 kcal/mol, A:  $3.03 \times 10^5$  (600-700°C)].

To evaluate the homolysis and heterolysis pathways, bond dissociation energies (BDEs) of the C–C and C–O bonds in LG and  $E_a$  values of possible heterolysis reactions were calculated by the DFT method. As a result, even the weakest bond (C<sub>6</sub>–O<sub>1</sub> bond) was found to have a relatively high BDE of 71.8 kcal/mol. On the contrary, cyclic Grob reaction involving the C<sub>3</sub>-OH and C<sub>6</sub>-O exhibited relatively low  $E_a$  of 57.4 kcal/mol (Fig. 1), although the other cyclic Grob reactions had much larger  $E_a$  of 87.1 and 91.2 kcal/mol. The  $E_a$  values of the possible dehydration reactions also exhibited the high  $E_a$  values of 72.7–80.7 kcal/mol. Interestingly, the product (a vinyl ether) from the cyclic Grob reaction was found to have very weak bond (BDE : 51.1 kcal/mol), which could be cleaved at  $500^{\circ}\text{C}$  (the onset temperature of gaseous LG decomposition). The following reactions from the resulting radicals reasonably explained the formation of acrolein and glyoxal. These products accounted for 36.8 mol% of the products obtained at  $500^{\circ}\text{C}$ , which was reduced to 18.0 mol% at  $600^{\circ}\text{C}$ . These experimental data support the involvement of the cyclic Grob reaction. The  $E_a$  values, which became greater from 16.7 (600-700°C) to 35.1 kcal/mol (550-600°C) by lowering the pyrolysis temperature, is also consistent with this conclusion.

At a higher temperature of  $600^{\circ}\text{C}$ , methylated LG and C2/C3 model compounds (propylene glycol and ethylene glycol), both of which do not have any structural elements allowing for cyclic Grob reactions, also decomposed effectively. Along with the relatively low  $E_a$  (16.7 kcal/mol, 600-700°C), these results suggest the radical chain reactions prevailing at such high temperatures than  $600^{\circ}\text{C}$ . The radical chain pathways were investigated starting from various C- and O-centered radicals obtained from LG by using the DFT calculation. It is also considered that the radical p-orbital and the  $\sigma$  orbital of the C–X bond that is cleaved must lie in the same plain for the  $\beta$ -scission reactions proceeding. From the C-centered radicals, dehydration reactions via the intermediates with C=O groups could occur to give intermediates with comparatively low BDE bonds, which results in the fragmentation to hydrocarbon gas-rich gases such as ethylene/acetylene. On the other hand, from the O-centered radicals, syngas (CO and H<sub>2</sub>) could be formed via the aldose-type intermediates, which are selectively fragmented to CO and H<sub>2</sub>.

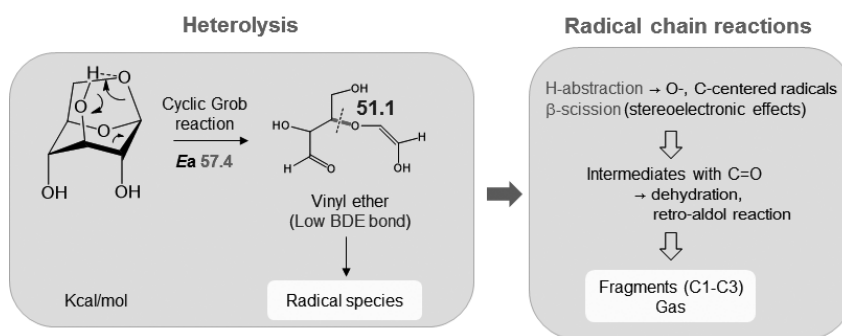


Fig. 1 Proposed pathways for pyrolysis of gaseous LG.

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## Pyrolysis and combustion kinetic study of hydrothermally carbonized glucose-graphene oxide hybrids

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Carbon based materials are widely studied for their functions in many fields owing to their remarkable thermal, electronic, and structural features. A serious drawback of the carbon based materials is their oxidation above 350 °C, which limits their use in high-temperature environments. A number of studies have been conducted on the effects of various inhibitors, protective coatings, and hetero atom dopant. Considering multi- advantages of graphene in the flame retardant property [1] and active radical scavenger [2] in polymer composite materials, we used hydrothermally carbonized glucose-graphene oxide hybrids (C/C hybrids) as matter model to evaluate graphene on the effect of thermostability and/or oxidation resistance. The pyrolysis and combustion process were studied using nitrogen and synthetic air as carrier gases at different operating conditions on a STA analyzer. It shown the graphene can increase thermostability of the carbon based materials dramatically. Different kinetics models were tested to correlate the experimental results. The kinetics parameters, that is, the pre-exponential factor, the activation energy, and the reactor order were also obtained. Also, a room temperature electron paramagnetic resonance (EPR) behaviours C/C hybrids with various graphene ratio were performed. We attempted to reveal the mechanism from the differences of EPR intensity, g-value, and radical concentrations.

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## FIRST PRINCIPLES BASED KINETIC MODEL FOR BIOMASS FAST PYROLYSIS: CYCLIC MODEL COMPOUNDS

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Lignocellulosic biomass contain a variety of 5 and 6 membered ring structures. Detailed kinetic modelling of biomass fast pyrolysis thus requires fundamental understanding of the pyrolysis of compounds like cyclohexane, methyl cyclohexane and cyclopentane. Therefore a kinetic model is being developed to predict the pyrolysis chemistry of these three model compounds. Thermodynamic data and most rate coefficients are determined with the Group Additivity method [1] with parameters derived from first principle calculations. The set of elementary reactions for intermolecular and intramolecular addition, hydrogen abstraction, recombination is generated via automatic network generation [2]. It is augmented by (a) eight reactions, for which the kinetics are taken from experimental measurements, (b) several special reactions directly calculated at the CBS-QB3 level of theory, and (c) a sub-mechanism for molecular growth chemistry including formation of polycyclic aromatic hydrocarbons taken from Wang et al. [3]. This model (referred to as GA model henceforth) so far has been validated against two experimental data sets probing different operation conditions: 1. flow tube experiments (LCT) at 1.7 bar cyclohexane, 630 – 800 °C and a space time of approximately 0.4 s, and 2. flow tube experiments (Hefei) at 0.8 mbar cyclohexane, 780 – 1250 °C and a space time of 5 ms [4]. The GA model predicts the experimental data generally reasonably well and performs overall better than five models found in the literature for cyclohexane pyrolysis (fig 1): Ranzi [5], CSM [3], Nancy [6], JetSurF [7] and Hefei [4]. Rate and sensitivity analysis results will be presented to explain the differences between the various models.

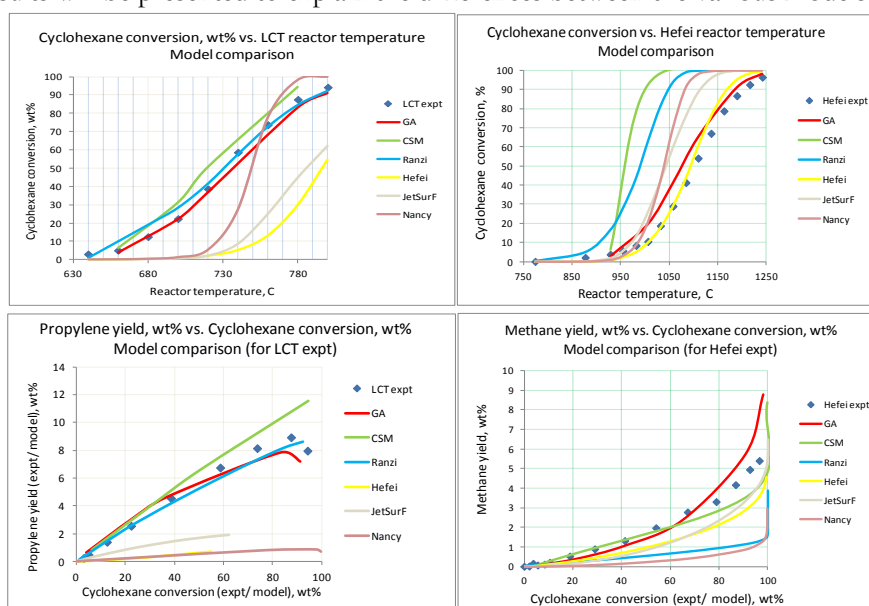


Figure 1: Comparison between experimental data and predictions with six different kinetic models

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# EXPERIMENTAL TESTS AND NUMERICAL MODELING OF BIOMASS PYROLYSIS IN A VERTICAL- TUBE REACTOR

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Recycling of carbonaceous waste materials and production of syngas *via* thermal gasification of biomass are viable routes to increase carbon efficiency, and reduce reliance on fossil fuels[1]. Experimental and numerical investigation of chemical kinetics [1], heat and mass transfers in fluidized [3] and fixed bed gasifiers [2] have attracted much interests. Due mainly to the complexity of the combined chemistry and heat and mass transfer within gasifier, these phenomena have been modeled in one- [2] and two-dimensional approaches[4]. Moreover, because of the computational limits, transport properties have been generally obtained thanks to phenomenological models or empirical relations [2].

In the present study, a 3D multiphysics model coupling fluid flow, multi - mode heat transfer (convection, conduction and radiation) to the kinetics of pyrolysis has been developed for a reacting system consisting of a packed bed of biomass (wood chips with a moisture of 10%) particles subject to heating in an electric furnace. The reaction consists of an endothermic decomposition of the feedstock into volatiles species, tars(assumed to be hydrocarbon as  $\text{CH}_{1.522}\text{O}_{0.0228}$ )[2].

Numerical model involves many heat transport parameters such as Nusselt number, effective conductivities, and radiative properties and also mass transport properties namely the permeability, specific surface, and Dupuit-Forchheimer coefficient according to the extension of Darcy's law. It was also important to evaluate the composition of the biomass, the moisture of the sample, and the kinetic of the chemical reactions. Information related to heat and mass effective transport properties were obtained from computed CFD on representative volume obtained from X-ray micro-tomography. To evaluate the thermal behavior of the biomass several analyzing techniques have been used as Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC). Studies about proximate and elementary analyses and determination of sorption and desorption isotherms of samples were also done to characterize this biomass.

In order to validate numerical results, some experimental tests will be realized at laboratory scale in a vertical and tubular electric furnace. The packed bed, positioned at the center of the furnace, has a porosity ranging from 0.61 to 0.74 and biomass particles mean diameter is about 1mm.

During the experimental tests both the temperature and the kinetic of the pyrolysis reaction but also the nature and the amount of produced gas will be measured.

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## EVALUATION OF THE BEHAVIOR OF COLOMBIAN BIOMASS UNDER CONDITIONS OF PYROLYSIS AND GASIFICATION OF BIOCHAR: A KINETIC APPROACH

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### Abstract

The thermal and kinetic study of three agroindustrial biomass pyrolysis from Colombia: Sugarcane bagasse, rice husks and palm kernel shell; and steam gasification biochar prepared by fast pyrolysis of biomass into a fluidized bed reactor, was developed into a thermogravimetric analyzer (TGA). In the case of pyrolysis, the results obtained in non-isothermal conditions four heating rates and environmental N<sub>2</sub>, allows to identify the stages of degradation of biomass indicating different reactivities, which was attributed to the different contents of cellulose, hemicellulose and lignin of these. A model-free method is used to obtain the activation energy and pre-exponential factor, obtaining the variation of reaction rate with temperature for the conversion of 10 to 80%, fluctuations activation energies corroborated that pyrolysis of biomass is a complex reaction involving parallel reactions, competitive and consecutive. The biochar steam gasification process was analyzed isothermally at 800, 850 and 900 ° C. With the approach of the kinetic parameters using the modified volumetric model (MVRM) was found that biochar from pyrolysis of rice husk has the higher reaction rate and this increases to a greater extent, compared to the other samples biochar, with temperature variation. The catalytic effect of ash on the gasification process was evaluated by a comparison of the reactivity of each biochar with the mineral composition of the raw material source, however, it was not possible to establish a direct relationship between the reactivity and composition mineralogical, because the rice husks contains the largest amount of non-catalytic species but the biochar had the highest reactivity during the gasification process. The study is complemented by monitoring gaseous species during the two thermochemical conversion processes.

## LEVOGLUCOSAN FORMATION FROM CELLULOSE: PYROLYSIS MECHANISM IN THE PRESENCE OF RADICAL-FORMING SPECIES

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Levoglucosan is an anhydrosugar known to be one of the main products of polysaccharides pyrolysis. The reaction mechanisms leading to its formation have remained an active research field for decades, but a definitive conclusion still needs to be reached. In the course of the years, many hypotheses have been formulated. One of the first models described levoglucosan formation via a concerted displacement mechanism [1]. However, this pathway implicated a dependence of the yield of the anhydrosugar from the nature and geometry of the glycosidic bond in polysaccharides, which has not been observed [2]. Ionic mechanism was proposed by observing a dependence of the levoglucosan yield by the presence of inorganic salts [3], but the role of these species has not been fully understood yet. Radical mechanism [4, 5], which is more suitable in a high-temperature system, has also been proposed, but lacks strong experimental evidences.

Real-time measurement of the system properties during the pyrolysis is not easy, since the reactions are almost instantaneous. The most widely used strategy is based therefore upon the comparative analysis of the products mixtures arising from performing the pyrolysis in different experimental conditions, mainly obtained by varying the furnace temperature and/or the gas pressure.

A less adopted strategy is based upon the co-pyrolysis of polysaccharides with radical scavenging species. If the formation of levoglucosan proceeds via a radical mechanism, interactions in the reaction system can take place, and then a difference in the composition of the pyrolysis products will be observed. Very few examples of this strategy can be found in the literature [6], and its potential still needs to be explored.

Our work aims to test the effect of the presence of a radical-interacting species on the pyrolysis mechanism of cellulose. Pyrolysis products will be identified by GC/MS analysis. Two different species are considered: a radical scavenger and a radical initiator. In the first case, if a radical is formed during the cellulose pyrolysis, it will be consumed by the scavenger, and a loss in the peak height of levoglucosan will be observed. In the second case, an interaction between the radical intermediate of cellulose and the radical product of the initiator could take place. As a result, not only the peak height of levoglucosan would diminish, but different pyrolysis products could be detected by the GC/MS system.

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## DENSIFIED MICROALGAE AS A PRECURSOR FOR SYN-GAS PRODUCTION

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### Abstract

As fossil fuels are depleting the search for alternative sources of energy is gaining more and more importance, especially if methodologies are low-cost, easily implementable and environmental friendly. Regarding the sources, their abundance and availability, decentralization, ease to extract and handle and heating value are very precious features. Moreover, the possibility of taking profit from residues (such as biomass) is very appealing since it allows to face a disposal problem at the same time.

The use of biomass materials to produce syn-gas via gasification processes is well documented [1]. For this task, the biomass used have to satisfy some requirements (such as high carbon content, low moisture, adequate elemental composition poor in corroding elements) which involves that previous processing of the precursors is often mandatory. One pretreatment that has recently gained prominence is hydrocarbonization (HTC), or wet pyrolysis which can increase the heating value of biomass, regardless of the moisture content of the starting material, which is already a standing out advantage. This technique can, for example, take profit from humid materials such as orange or tomato peels, sludge or algae.

If the algae derive from photosynthetic growing systems, then the process becomes even more interesting, because the origin of the carbon to be gasified has been fixed from environmental CO<sub>2</sub>, which can offer a way to:

- a) Capture of CO<sub>2</sub>, helping to mitigate the greenhouse effect.
- b) Use of the corresponding C for energy production.

This work investigates the use of microalgae hydrochars as precursors for syngas production, by means of air and steam gasification processes. In the first place, HTC test were made in order to define the optimal operating conditions (temperature, dwell time and ratio biomass/water). Tests were made in a 0.15 L stainless steel autoclave (Berghof). Secondly, hydrochars were subjected to gasification (bench scale installation) and the production of gases was followed by gas chromatography (Konic). These processes were performed at 850 °C, using environmental air (100 mL/min) and steam (0.3 g/min).

It was found that efficiency is improved by using temperatures above 200 °C, residence times of 10 h, and very high loads of biomass (20:100 g biomass:water), so these conditions were selected for subsequent gasification. In these processes, it was clear that the quantity of CO and H<sub>2</sub> greatly improved in the case of steam gasification, which was mainly associated to the participation of water gas and water gas shift reactions. H<sub>2</sub> molar proportions up 60% were achieved, which is competitive with the results obtained from steam gasification of other traditional lignocellulosic materials [2].

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## COMPARATIVE KINEMATIC STUDY OF PRE AND NON-PRE-TREATED VINEYARD WOODY RESIDUES.

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The interest in production of renewable energy carriers such as bio-oil and gas, and charred solid products for soil remediation or as feedstock for advanced materials transformation from pyrolysis of lignocellulosic biomass has increased in the last decade. Nowadays the rational use of natural resources and energy efficiency play a remarkable role in the design and development of new technologies and equipment for biomass transformation. Thereof, it is important to understand the behaviour of biomass under thermochemical conversions, for instance pyrolysis. Knowledge of the kinetics of the feedstock material is important in the design of a new pyrolysis reactor for instance. A well designed reactor would reduce the resources input for operation and yield high quality products. Another equally relevant consideration is the pre-treatment of the feedstock material to be transformed. In this work, a comparative kinematic study was carried out for the same feedstock (vineyard woody residues) under two scenarios. The first scenario is a non-pre-treatment case, the second one is the evaluation of the effects of washing the vineyard wood on kinematic parameters. Applying the Flynn-Wall and Vyazovkin for non-isothermal data yielded average values of activation energy of 147.3 and 148.1 kJ/mol respectively for the non-pre-treatment scenario. New data from the application of different kinematic models, apart from the two previously mentioned, will be compared in both scenarios. The obtained kinematic parameters and energy consumption for the pre-treatment of the feedstock are useful founding pillars in future designing of highly efficient pyrolysis reactors that comply both real world constraints and environmental concerns.

## EXPERIMENTAL STUDY ON THE INITIAL THERMAL DECOMPOSITION OF RESORCINOL

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Lignin, a major component of woody biomass, consists of characteristic p-hydroxy phenyl units, which often contain one or two methoxy substituents in ortho position to the hydroxyl group. Therefore, substituted phenols and phenyl ethers are good model compounds to understand lignin chemistry. Indeed, molecules like guaiacol, hydroquinone and catechol have been studied in the past for this reason. In particular catechol is widely considered a model compound for low-ranked coal, lignin and biomass tars. A common pattern in the pyrolysis chemistry of phenylethers is that decomposition starts with O-CH<sub>3</sub> bond scission. On the other hand, phenol, catechol and hydroquinone mainly decompose via a molecular CO elimination channel. Interestingly, resorcinol, the 1,3- dihydroxybenzene isomer of catechol and hydroquinone, has so far received little attention and the question arises if CO elimination is again the favoured reaction pathway. Since resorcinol is a solid it is questioned whether the fast pyrolysis of solid resorcinol yields different products than resorcinol decomposition in the gas phase.

To address those issues, resorcinol pyrolysis has been studied in a newly constructed micro-pyrolysis reactor setup. It consists of a commercial two-stage isothermal pyrolysis reactor, which is connected to a comprehensive analysis section. Latter consists of two parts: 1. a two dimensional gas chromatography (GC×GC) coupled with a flame ionization detector (FID) and a time-off-flight mass spectrometer (TOF-MS) is used to simultaneously identify and quantify large molecules, and 2. a specially designed multi-column GC system coupled with a pulse discharge detector (PDD) and two thermal conductivity detector (TCD) is employed to detect permanent gases and light components.

For the study of solid to gas transformation at fast pyrolysis conditions, small amounts of resorcinol were placed in a small inert cup, which is dropped into the hot region causing rapid heating of the sample. A He carrier gas flow swipes the vapours directly into the GC. The effluents are cryo-trapped and then injected into the columns. In these experiments, the second reactor was not used. Pyrolysis at high temperatures (e. g. 800°C) yielded a large number of products ranging from CH<sub>4</sub> to large PAH. Furthermore, a substantial fraction of resorcinol was converted to char. Even at 500°C several pyrolysis products such as phenol were observed, while the experiments showed that resorcinol vaporized cleanly and completely at 350°C.

In a second set of experiments, the first reactor was coupled with the second reactor in series. The first reactor was kept at a low temperature (between 250°C to 280°C) to vaporize resorcinol, and the vapour was swept into the heated second reactor. Reaction products were observed at temperatures between 800°C to 850°C. A preliminary interpretation of the data leads to the conclusion that at around 800°C only CO<sub>2</sub>, cyclopentadiene and pyrolysis product of latter product are detected. If confirmed, this means that resorcinol decomposes in the gas phase in a distinctly different way than its dihydroxy benzene isomers.

### Acknowledgments

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## ENHANCED THERMAL SEGREGATION OF LIGNIN AND CELLULOSE DECOMPOSITION PRODUCTS: AN ANALYTICAL STUDY OF TIME AND TEMPERATURE EFFECTS

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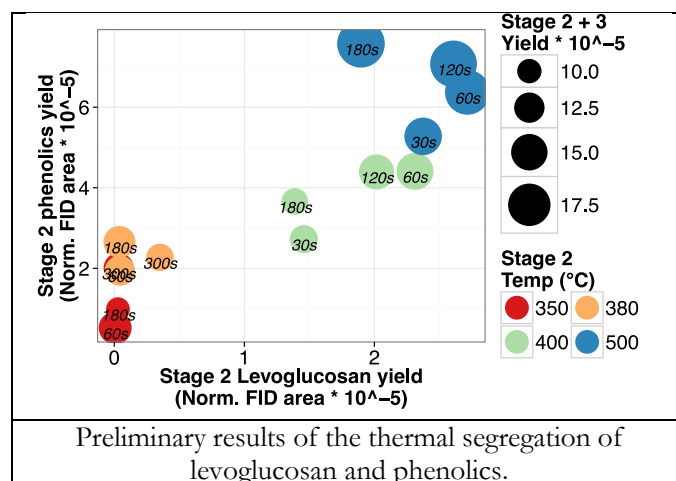
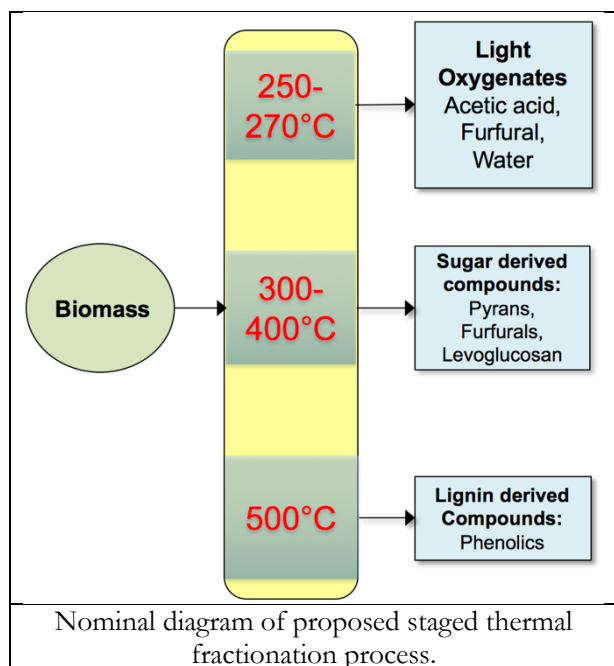
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The difficulty in processing and upgrading fast pyrolysis products prompts the need for investigation into alternative methods of thermochemical biomass deconstruction. Staged thermal fractionation has been proposed as a method to avoid problems of quality and reactivity of fast pyrolysis bio-oil [1-3]. Using successively increasing thermal treatment regimes to target the degradation of individual biopolymers can yield enriched product streams for more facile and stable catalytic upgrading and/or separation processes.

In this work we use analytical pyrolysis to evaluate the effects of time and temperature on the segregation of the degradation products of biomass treated with successive thermal fractionation. A relatively large quantity of oak biomass was torrefied at temperatures below 270°C in a gram-scale reactor to remove hemicellulose while leaving lignin and cellulose unconverted. The remaining solid was then divided and exposed to discrete successive thermal treatments in a CDS Analytical 5250T pyroprobe coupled to a Shimadzu QP-2010+ GC/MS-FID. The detected compounds were lumped into catalytically relevant functional groups for analysis.

Intermediate torrefaction temperatures of 350°C, 380°C, and 400°C were chosen for exploration. From these results, torrefaction of this enriched solid at 380°C for 3 minutes was found to result in good segregation of lignin- and cellulose-derived products, but the total carbon yield was lower than single stage fast pyrolysis of the same solid. This analytical investigation demonstrates that it may be possible to deliver higher-purity product streams to downstream catalytic reactors than current pyrolysis technologies allow, leading to increased total process carbon and hydrogen efficiency.



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## UPGRADING OF RICE STRAW AND LEUCAENA BY DEGRADATIVE SOLVENT EXTRACTION USING 1-METHYLNAPHTHALENE AND KEROSENE AT 350 °C

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We have recently presented a method that we call “Degradative solvent extraction” to utilize biomass waste effectively [1]. The method, which treats the low grade carbonaceous material in a non-polar solvent at around 350 °C, dewater, selectively deoxygenate the raw materials, and separates the sample into three fractions: Soluble, Deposit, and Residue. The smallest molecular weight fraction, Soluble, is free from water and mineral matter and its unique properties, carbon content as high as 82%, peak molecular weight of ca. 300, etc., are almost independent of raw material [1]. One of the difficulties of the method is using expensive 1-Methylnaphthalene as a solvent. In this work, the possibility to use kerosene as a solvent was examined. Rice straw (RS) and Leucaena (LC) were subjected to a degradative solvent extraction method by using 1-methylnaphthalene (1-MN) and kerosene (WS3060) as solvents. It was found that the carbon-based yields of the Soluble fraction were as large as 67.6-70.7% and 43.7-47.5% when using 1-MN and WS3060, respectively. Fig. 1 shows the weight basis yield (%wt, d.a.f.) of the products for RS and LC using 1-MN and WS3060 as solvents. The elemental compositions of Soluble fraction were C = 78.9 – 84.7 wt%, H = 6.1 – 8.8 wt%, and O = 7.0 – 13.9wt%. These results showed that WS3060 can be used a solvent for upgrading biomass by the degradative solvent extraction method. Detailed characterization of the solid fractions showed potential utilization of the fractions as high quality solid fuels or precursors of chemicals and carbon materials.

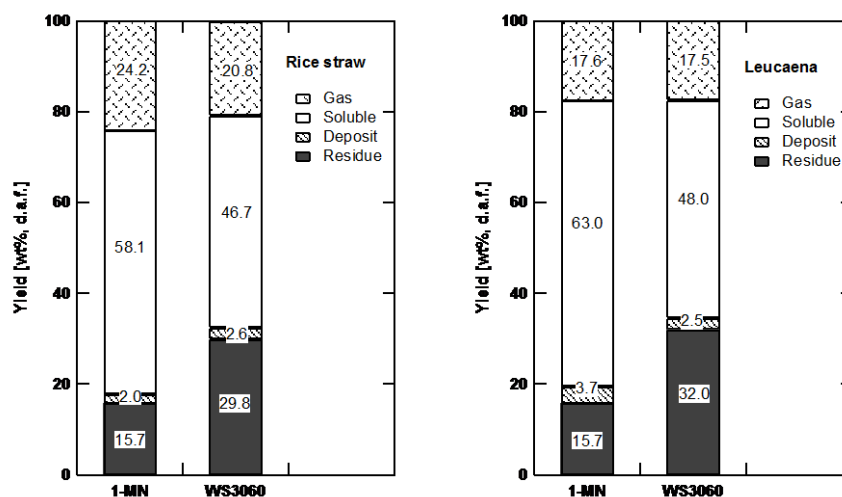


Fig. 1 Weight basis yields (wt%, d.a.f.) of the products from RS and LC using 1-MN and WS3060 as solvents.

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## CELLULOSE, XYLAN AND LIGNIN INTERACTIONS DURING PYROLYSIS OF LIGNOCELLULOSIC BIOMASS

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**ABSTRACTION:** During pyrolysis of biomass, different components decompose at different rates and within distinct temperature ranges. The difference in reactivity between the three basic components (cellulose, hemicellulose and lignin) makes pyrolysis complex. The aim of this study sets out to establish the relative contributions of the two phenomena (reactions between biomass components and effect of biomass structure on these reactions) during biomass pyrolysis by comparing the pyrolysis behaviour observed during pyrolysis of synthetic biomass samples (prepared from cellulose, xylan and lignin) and actual lignocellulosic biomass. Therefore, this study firstly pyrolysed three components independently and then studied the pyrolysis behaviour of synthetic samples and lignocellulosic biomass. The experiments were performed in a TGA and in a wire mesh reactor (WMR), which provides segregation between particles and therefore data can be interpreted as representing single particle behaviour. The data obtained are used to link the decomposition of cellulose, hemicellulose and lignin and the possible interactions within lignocellulose.

### PROCEDURE

Commercial microgranular powder cellulose, xylan to represent hemicellulose, and lignin were used in this work. Four composite pellets (cellulose/xylan, cellulose/lignin, xylan/lignin and cellulose/xylan/lignin) were prepared by mixing fine cellulose, xylan and lignin in equal proportion. All samples were pressed and then crushed into 106-150  $\mu\text{m}$  size. The above samples were pyrolysed in TGA and WMR. Their corresponding product distribution were compared with predicted yields based on the behaviour of single components. Three original feedstocks, pine, spruce and oak, were also studied in this work. The full compositional analysis of the three original feedstocks was performed using protocols developed by NREL [1] and modified by Ray et al [2]. Similarly, the product distributions of the three feedstocks were compared with those calculated using composition analyses of the biomasses and individual component pyrolysis behaviour. Experiments in WMR have been carried out at 0.5 and 1000  $^{\circ}\text{C s}^{-1}$ , to a peak temperature ranging from 300 to 500  $^{\circ}\text{C}$  in He, with a holding time at the peak temperature of up to 15 s. In TG, the samples were pyrolyzed in  $\text{N}_2$  at 0.5  $^{\circ}\text{C s}^{-1}$ , to a peak temperature ranging from 300 to 500  $^{\circ}\text{C}$ .

### RESULTS AND CONCLUSION

Xylan and lignin contributed most char yield and were affected significantly by heating rate, while cellulose mainly produced condensibles and less affected by heating rate. The maximum rate of weight loss of cellulose and lignin occurred at 350-425  $^{\circ}\text{C}$ , which increased the possibility of interaction. At 300  $^{\circ}\text{C}$ , experimental product distribution fitted well with predicted one for physical mixtures in TG and WMR, which means interaction was not found when the pyrolysis of cellulose did not begin. At higher pyrolysis temperature in slow heating rate by TG, more char were obtained for physical mixtures containing cellulose. At higher heating rate in WMR, more char and less tar were also found for physical mixtures including cellulose, except for cellulose/lignin. The results indicates that the pyrolysis of cellulose played an important role in biomass interaction. Comparatively, different with synthetic samples, less char and more tar were obtained for lignocellulosic biomass at higher temperature at both heating rate. This may be due to the different microscopic architecture of biomass compared with synthetic samples. The lack of local porosity of physical samples increased the possibility of repolymerisation reactions leading to gas and char formation, which was proved by SEM. For lignocellulosic biomass, the crossing-linking reactions of xylan or lignin was minimized by intermediate products of cellulose. The multicellular porous structure of lignocellulosic biomass made escape of intermediate product easier [3].

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ABSTRACTS

# **Biomass / Reactors**

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**Oral presentations**

## PYROLYSIS OF WOOD IN A LARGE-SCALE MECHANICALLY FLUIDIZED REACTOR

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To maximize the yield of organic liquids from biomass pyrolysis, the biomass heating rate should be maximized and the vapor residence time inside the reactor minimized. Using fluidized beds to perform this type of fast pyrolysis yields products that are highly diluted by fluidization gases, resulting in higher capital and operating costs. Large pyrolytic auger reactors avoid product dilution but cannot achieve high heating rates; they also require mixing of the biomass with a hot solid carrier such as sand. Furthermore, with both auger and fluidized bed reactors, the product char is contaminated with the inert bed material or solid carrier.

This research presents a novel large mechanically fluidized reactor that can operate under fast pyrolysis conditions without the limitations of auger or fluidized bed reactors. The unit can process 50 to 100 kg/hr of biomass. The biomass feeder, pyrolysis reactor and product recovery trains are very compact. The whole plant is set up on a 2.3 m x 6 m trailer that can be moved easily from site to site. Induction heating of the pyrolysis reactor confers 3 main advantages: (1) compactness of the reactor because of very high transfer rates; (2) ease of unit control thus reducing manpower requirements; (3) rapid preheating and cooling meaning that the unit is productive for about 7 hours of a typical 8-hour shift. The power consumption of the mixer motor is greatly reduced thanks to aeration of the reactor by the produced vapours and gases.

Uncontaminated char is continuously withdrawn and cooled. Stripping of product vapours is integrated within the char extraction screw to maintain high bio-oil yields and obtain a dry, high-quality char product.

Hot organic gases and vapours exiting the reactor first flow through a high temperature electrostatic precipitator (ESP) to remove dry, entrained fine char particles. An electrostatic precipitator is more compact and easier to operate than hot filters. The hot, solids-free vapours and gases are then cooled in a condensing train that integrates an electrostatic demister to provide a valuable, dry bio-oil. The remaining gases are presently sent to a flare system, but could be burned to recover their energy. The use of a mechanically fluidized reactor means that there is no dilution of the product vapours by a carrier or fluidization gas, which allows for a very compact and efficient condensation train.

Pyrolysis was performed in the mechanically fluidized reactor with wood. Products yields and compositions were similar to those obtained with a fluidized bed equipped with a fractional condensation system.

## Catalytic upgrading of pine wood pyrolysis vapors in a downer reactor: Preliminary results with zeolite

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Fast pyrolysis oil cannot be utilized as a transportation fuel as it is, due to its very high content of oxygen (usually around 40 wt. %), which makes it immiscible with hydrocarbons and determines a high tendency to polymerize. For such reasons, pyrolysis oil is currently upgraded by means of hydro-deoxygenation, where reaction with H<sub>2</sub> is utilized to take out oxygen in the form of H<sub>2</sub>O molecules. Despite being very effective, hydro-deoxygenation needs pure H<sub>2</sub> and it is quite expensive, thus driving the conversion of biomass into fuels out of economy.

Catalytic upgrading of pyrolysis vapors (CUPV) can potentially eliminate the need for hydro-deoxygenation. Catalysts are utilized in order to reduce the oxygen content in the pyrolysis vapors prior condensation. In the literature, a number of tests are reported, where several kinds of catalysts have been screened. Most tests have been conducted in fixed beds, where the catalyst gets progressively de-activated by coke formation: pyrolysis vapors thus flow through a bed whose characteristics change over time.

In the present study, CUPV was carried out by means of a downer reactor. In such unit both catalyst and pyrolysis vapors are fed from the top and they flow co-currently to the bottom. Through such original approach, vapors always contact fresh catalyst, which is continuously supplied by a screw conveyor. Low solid holdup can be obtained and back-mixing is reduced, owing to the co-current gravity-driven flow. As a result, it is possible to obtain a much clearer picture on how the catalyst work. Moreover, from the technological point of view, the results obtained with the downer could be utilized for the design of a riser. Both reactors are indeed conceptually similar (co-current flow, low catalyst holdup), with the downer being easier to implement at laboratory scale.

A bench-scale system (biomass throughput: 100 g/h) for fast pyrolysis, followed by a downer, was built (Fig. 1). Zeolite was utilized as catalyst. Very low values of catalyst holdup, in the order 10<sup>-5</sup>÷10<sup>-4</sup>, were achieved. The ratio between the rates of catalyst and biomass varied between 1.4 and 8.3. In this way, it was possible to investigate the effect of increasing amounts of fresh catalyst with a constant vapor residence time in the downer of around 1 s.

The liquid products were obtained as a two-phase stream, with an organic-rich heavy phase on the bottom (oil) and an aqueous-rich light phase on the top. Results show that oil with an oxygen concentration around 25% on dry basis can be obtained, compared to 36.6 % of the thermal oil. The quality of the oil, in terms of de-oxygenation efficiency, does not depend on the catalyst flow rate in a significant way. Similarly, it was observed that, apart from an initial increase, the yield of organics in the heavy oil is mostly constant (around 15 wt. %). On the other hand, increasing amounts of catalyst result in lower and lower yields of organics in the light aqueous phase.

A possible interpretation of the results is that the catalyst intensively cracks the sugars from the cellulosic fraction of biomass into coke and water, while lignin is reacted to a minor extent.

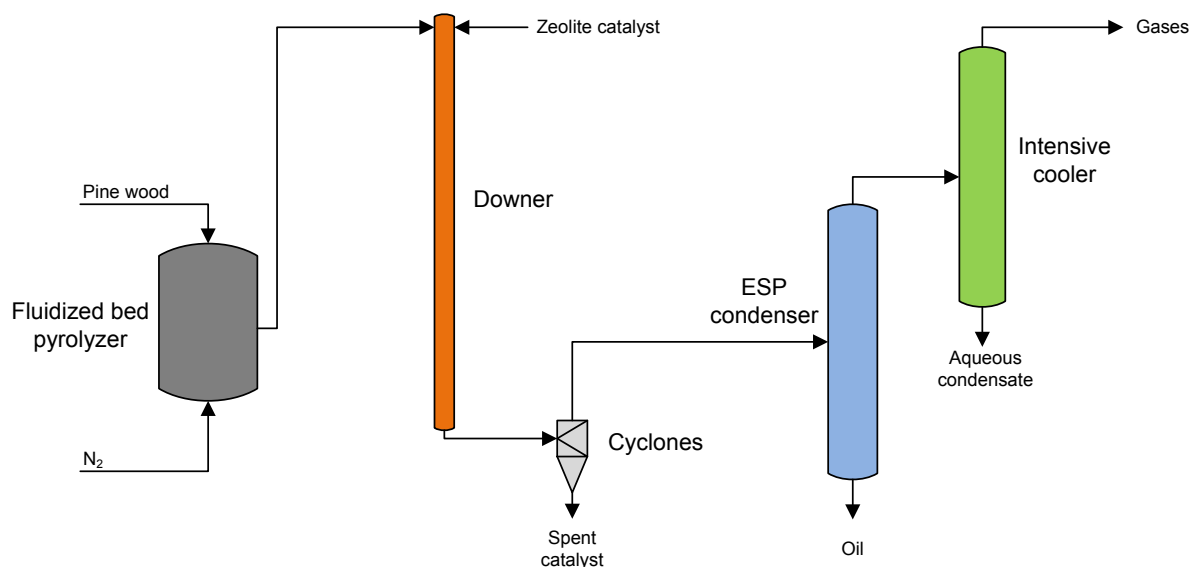


Figure 1 – Schematic flowsheet of the experimental setup.

# PYRENA PYROLYSIS EQUIPMENT FOR NEW APPROACHES IN CIRCULATING FLUIDISED BED CATALYTIC PYROLYSIS FOR BETTER BIO-OIL AS A PRECURSOR FOR FUELS AND CHEMICALS

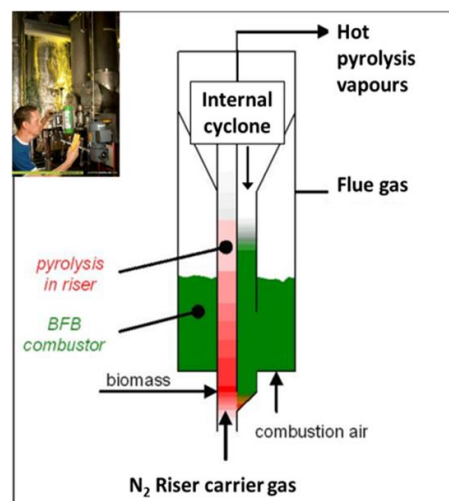
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PYRENA is a novel integrated system that features ONE reactor in which fast pyrolysis, gasification and combustion can be combined. PYRENA is suitable for (catalytic) fast pyrolysis and offers several benefits over existing state-of-the-art fast pyrolysis reactors such as continuous catalyst recycling, combination of in-situ and ex-situ catalysis, combination of pyrolysis, gasification and combustion in one heat-integrated system. Especially the flexibility regarding the use of catalysts is an attractive option, because it offers a route (via in-situ and ex-situ catalysis) to a better bio-oil that probably requires less downstream upgrading when compared to analogous pyrolysis systems. Better bio-oil means a fast pyrolysis bio-oil that is more stable, less acidic and relatively low in oxygen. These characteristics enable the use of this bio-oil as a good precursor for a drop-in co-feed in existing oil-refineries for the production of transportation fuels. Alternatively, the enhanced fast pyrolysis oil quality opens up several possibilities for extracting value added chemicals such as sugars, furanics and phenols.

PYRENA consists of a bubbling fluidised bed reactor vessel, in the center of which an internal riser reactor is located for the pyrolysis, see the figure. Biomass is fed to the riser reactor at a maximum feed rate of 5 kg/hr and pyrolysed at 400 – 600°C. The required heat is provided by hot sand or catalyst that circulates from the surrounding bubbling bed into the riser. The sand is heated via the combustion or gasification of the pyrolysis char that is transported from the riser reactor via an internal cyclone. The hot pyrolysis vapours are quickly quenched and recovered via direct or fractionated condensation. The PYRENA system is roughly comparable to a circulating fluidised bed (CFB) system. A major difference is the integration; most state-of-the-art CFB reactors use an external reactor for combustion of the char and heating of the sand.



PYRENA is deployed in a current Dutch national CatchBio – Catalytic Pyrolysis project to produce bio-oil samples for the project consortium and to test catalysts. The CatchBio project deals with the application of catalysis in dedicated pyrolysis reactors aiming at improving the quality of the produced oil. Existing knowledge on catalytic pyrolysis serves as a starting point to study and optimize the catalyst in continuous reactors at a scale of 0.1 – 5 kg biomass per hour. Finding the best reactor configuration for catalytic pyrolysis is an integral part of the work. One of the target applications of the oil is a refinery co-feed. The main result of the project will be the identification of the best catalyst–technologies combinations for which a techno-economical evaluation and environmental assessment will be performed. PYRENA is a promising candidate.

PYRENA has successfully participated in a recent international round robin test on fast pyrolysis [1]. PYRENA bio-oil from poplar and wheat straw was nicely comparable with other state-of-the-art pyrolysis reactors. The PYRENA set-up has been modelled in a coarse techno-economic evaluation, aimed at a scale of 300 kt/yr of dry biomass intake. Currently, PYRENA is used to study the effect of the environmentally benign mineral olivine as a mild, cheap and easily regenerable cracking catalyst on the fast pyrolysis of softwood.

This research has been performed within the framework of the CatchBio program. The authors gratefully acknowledge the support of the Smart Mix Program of the Netherlands Ministry of Economic Affairs and the Netherlands Ministry of Education, Culture and Science.

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## DESIGN OF A GAS-SOLID VORTEX REACTOR DEMONSTRATION UNIT FOR THE FAST PYROLYSIS OF LIGNOCELLULOSIC BIOMASS

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Fast pyrolysis of lignocellulosic biomass is regarded as one of key potential technologies for the production of chemicals, fuels and energy. Ideally, fast pyrolysis is carried out at conditions that allow high interfacial heat transfer, precise temperature control and short residence times of the pyrolysis vapors ( $\ll 1$  s). The latter implies also rapid cooling of the pyrolysis vapors and efficient removal of char<sup>1</sup>. Several reactor configurations have been developed during the last decades, and technologies were scaled up to demonstration and industrial plant scale: static and circulating fluidized beds, rotating cone, ablative and auger reactors. With the currently established reactor technologies it has not been possible to reconcile the actual and required operation conditions, particularly the accurate control of the reaction temperature and the minimization of the residence time of the pyrolysis vapors. Here we present the design of a demonstration unit for fast pyrolysis based on a novel reactor technology which addresses those issues by carrying out fast pyrolysis in a centrifugal field. By establishing centrifugal forces that exceed gravity multiple times a dense and uniform bed of particles can be formed, in which gas-solid slip velocities are three-to-five times those of conventional fluidized beds<sup>2</sup>. Larger gas-solid slip velocities lead to the intensification of interfacial transfer of mass, energy and momentum and to the reduction of the gas-to-solid space time ratio.

The entire setup can be divided in five sections: Gas-Solid Vortex Reactor (GSVR), solids feeding, carrier gas conditioning, char separation and bio-oil condensation. The center piece of the demonstration unit is the GSVR, which consists of two concentric cylinders. As can be seen in Figure 1 the carrier gas is distributed around the annulus and enters the inner cylinder via eight rectangular inlet slots of 1 mm width positioned at a  $10^\circ$  angle with respect to the tangent. Biomass is fed into the inner cylinder, next to the inner wall, via a circular conduit of 10 mm diameter positioned at an  $20^\circ$  angle with respect to the horizontal plane. The axial length of the reactor is 15 mm and the diameter of the inner chamber is 80 mm. Momentum is transferred from the gas to the particles, causing them to rotate in the chamber and generating a large centrifugal force. Mass and energy balances on the GSVR showed that the biomass mass flow rates, which can be processed, range from  $1.4 \times 10^{-4}$  to  $1.4 \times 10^{-3}$  kg s<sup>-1</sup>. The corresponding gas (N<sub>2</sub>) mass flow rates and inlet temperatures are  $5.0 \times 10^{-3}$ – $1.0 \times 10^{-2}$  kg s<sup>-1</sup> and 800–923 K. At the aforementioned operation conditions, heat transfer coefficients of 300–450 W m<sup>-2</sup>K<sup>-1</sup>, *i.e.*, three to five times those of conventional fluidized beds, can be reached<sup>2</sup>. A mathematical model of the reactor, which incorporates intra-pellet heat transfer, was developed and used to assess the effects of solids and gas flow rates, moisture content and pellet size on the yields of bio-oil, gas and char.

The solids feeding section consists of a combination of a gravimetric feeder, equipped with twin screws, and an “*in-house*” developed injector screw. The carrier gas conditioning section consists of a 100 kg liquid N<sub>2</sub> dewar, which is connected to an electric vaporizer and two packed bed heat exchangers. The heat exchangers are connected in series and they are indirectly heated by electric heating modules. Downstream of the GSVR, char is separated by means of a high throughput cyclone connected in series with a high efficiency cyclone. The pyrolysis vapors enter tangentially into a double tube heat exchanger integrated with an electrostatic precipitator. The heat exchanger is folded in a double U form which allows collecting two fractions of bio-oil. Cold flow and reactive Computational Fluid Dynamic (CFD) studies<sup>2</sup> have shown the suitability of the GSVR for biomass fast pyrolysis. The first results obtained with this demonstration unit will be discussed, demonstrating the concept and illustrating its process intensification capabilities.

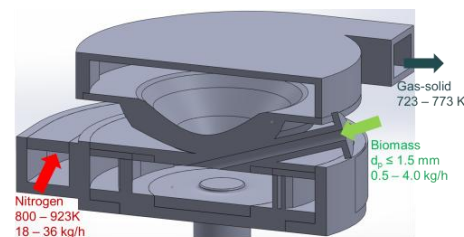


Figure 1. Gas-Solid Vortex Reactor schematics

### Acknowledgments

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## THERMO-CATALYTIC REFORMING PROCESS (TCR®) SCALE UP FROM PILOT PLANT TO DEMO-SCALE

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In Germany more than 7500 anaerobic digestion plants generate about 60 million tons of digestate residues every year. This wide potential of residues from biogas plants can be converted into valuable storable products to contribute present energy challenges (e.g.: biochar, hydrogen, liquid fuels). For the conversion of such feedstocks, Fraunhofer UMSICHT developed the Thermo-Catalytic Reforming (TCR®) unit for power generation and biofuel production. The technology can be used for power and heat production by the utilisation of the TCR® products (oil and gas) on a dual-fuel engine. Additionally, the produced biochar can be energetically used (e.g. by gasification). Furthermore the produced oil and biochar are storable and therefore useable for balancing energy supply.

Started from lab-scale (TCR®-2 kg/h) unit over a demo-scale (TCR®-30 kg/h) plant, the TCR® technology is looking forward to industrial scale of a 300 kg/h plant.

Aim of the work was the upscaling validation of the pilot plant to a demo-scale. It was of great interest to transfer and demonstrate the high quality of the products (oil, gas and char) from a 2 kg/h to a 30kg/h plant.

Operation parameters like residence time, temperature and heating rate of the TCR® process were transferred from the 2 kg/h lab-scale to the 30 kg/h demo-scale plant and serve as a basis for further scale-up for industrial applications.

Ultimate and proximate analyses of the pyrolysis products were carried out. In addition, further analysis of bio-oil by GC-MS was performed to validate the successful scale-up.

Several test runs with digestate showed that operation parameters from the lab-scale plant were successfully transferred to demo-scale. The chemical analysis demonstrated the high quality and similarity of the products. The gas contained a high amount of hydrogen (about 40 vol. %) with a lower heating value of 13-14 MJ/kg. Results from the bio-oil analytics showed a low total acid number (2 mg KOH/g), low viscosity (10 mm<sup>2</sup>/s) and a lower heating value of 35 MJ/kg as well as a low water content (2 wt. %) and oxygen content (about 9%). Bio-oil composition by GC-MS showed condensed aromatic hydrocarbons as main compounds, while lower amount both of oxygenated compounds (e.g. phenols) and N-compounds (e.g. indoles) have been detected. Furthermore, no significant differences between oils collected from the two different plants have been observed.

The TCR® oil was found miscible with bio- and fossil fuels representing therefore an attractive prospect for engine applications.

The presentation will highlight the potentials and chances of the Thermo-Catalytic Reforming to contribute present energy challenges, by showing some of the most recent achieved accomplishments. Within the scope of the conference, the focus will be on possible industrial application of pyrolysis technology in an energy context.

## THERMO-CHEMICAL MODEL OF A SCREW PYROLYSIS REACTOR

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Among the thermochemical processes, pyrolysis has an unexplored potential to convert low-rank materials into more valuable solid, liquid and gaseous fuels. Furthermore, pyrolysis may aim at producing building blocks for chemical and other high quality products. While fast pyrolysis in fluidized bed appears the most suitable option to process woody materials, intermediate pyrolysis adopting screw reactors seems to be the right solution for low-grade biogenic feedstocks. The definition of low-grade feedstock includes a wide spectrum of materials, such as agricultural and animal residues, as well as municipal organic waste and sewage sludge, which share some common features like chemical and physical heterogeneity.

In order to overcome the problems linked to the energy exploitation of the aforementioned materials, the Karlsruhe Institute of Technology developed a novel screw reactor, the STYX, with integrated hot gas filtration [1]. The feedstock is transported by the screw along the through reactor. Within each single pitch, depending on the granular properties, the material may undergo mixing. The process heat is provided indirectly through the vessel walls and optionally through the shaft of the screw. The feed is heated and the drying process takes place. When the pyrolysis temperature is reached, the three main components of the lignocellulosic materials start to decompose into a wide range of volatile substances. After the first solid decomposition, the pyrolysis vapours undergo further reactions: homogeneous (in the gas-phase) and heterogeneous (on the filter surface). The vapours may be distinguished into condensable organics, water and non-condensable gases. During the decomposition process, a carbonaceous residue is retained in the solid phase, forming the pyrolysis char, which is a biomass substitute in co-firing coal power plants [2].

In order to reduce the experimental effort, the design and optimization require reactor modelling based on the physical and chemical mechanisms taking place during the process. The simulation of pyrolysis of low-rank biogenic feedstocks in a screw reactor with integrated hot gas filtration describes the transport and the thermal mechanisms, as well as the conversion process, in terms of design parameters of the reactor, i.e. geometry of the vessel and of the screw, and operational parameters such as the temperature profile of the reactor, residence time and throughput. For the reactor model, two approaches will be presented. On the one hand, the reactor is described by a cascade of perfectly mixed modules adopting the so-called penetration model, which results in an average temperature and conversion degree with the solid medium; the other approach describes the granular solid as a fixed bed with underlying temperature and conversion profiles. The differences will be highlighted. The thermal and chemical mechanisms, i.e. heat transfer from wall-to-solids, etc. as well as drying and primary and secondary kinetics of pyrolysis are described adopting basic models from the literature.

In this work, the mathematical model of the screw pyrolysis reactor is presented in details taking into account the residence time behaviour of the solids, the heat transfer within the granular solid and with the gases and the chemical kinetic mechanisms. The results are presented as function of the position along the reactor. Temperature, gas composition and conversion profiles are reported for exemplary cases and compared with experimental data gained at STYX reactor. The validation is presented for inert material, with and without drying, as well as for the pyrolysis of beech wood. To conclude, the ongoing work for the description of the secondary gas-phase homogeneous reactions and for the heterogeneous reactions on the filter surfaces is described.

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## A flexible three-stage thermochemical conversion process TSTC Process

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After having delivered and tested a first industrial-scale (12,000 tpy) prototype of its proprietary “*intermediate pyrolysis*” technology (HALOCLEAN<sup>®</sup>), Sea Marconi started a major review of several engineering and process aspects of the plant, leading to a completely reengineering of its technology, that led to a brand new patented solution for the thermochemical conversion of biomass into bioenergy or bio-products.

A first 100-kg/h pilot-scale prototype has been successfully delivered and is currently under thorough testing at Sea Marconi premises in Lorraine (France) within the framework of the LORVER project ([www.lorver.org](http://www.lorver.org)).

This new solution represents the synthesis of the experience made after several years of work on pyrolysis plants, involving an accurate fault analysis of Sea Marconi own solutions and alternatives available on the market, with the aim of reaching the reliability required by industrial level applications and allowing a straightforward scale-up to higher throughputs.

It is designed as a three-stage gasification system, sometimes referred as *pyro-gasification*, where pyrolysis, (partial) oxidation and gasification occur in three different reaction zones properly interconnected. While the main technical feature (recirculating hot steel spheres) of the previous Sea Marconi’s solution is preserved, together with the corresponding advantages, such as flexibility, all the shortcomings of the former technology have been avoided by design.

Partial oxidation of pyrolysis char supplies process energy to pyrolysis through the recirculation of heated steel spheres. Steel balls also enhance the pyrolysis process, providing mixing and milling effects of the organic matter being thermally treated. Gasification of tars and char occur into two separate reaction zones. Reforming of pyrolysis tars can be catalytic or not, preserving the same reactor. Finally, downstream producer gas is properly cooled and cleaned with a revolutionary dry cooler that allows the recovery of high-temperature heat from the gas stream, with benefits for the overall energy balance (DEVELTAR).

The plant is designed in a way that process and product flexibility can be easily attained. Feed rate can be largely varied within nominal maximum throughput, process temperatures can be modified separately among the three reaction zones, and even product distribution can be modified according to applications: for instance, part of the char can be extracted before partial oxidation upon request, while the tar gasification module can be disabled to implement a pyrolysis process.

From the engineering perspective all the technical critical issues were properly addressed: spheres do not exit the hot zone of the plant, allowing for a simple sphere recirculation scheme. Separation of different atmospheres for different reaction zones is intrinsically provided by design, not by complex sealing systems. Relative motion of mechanical parts is completely avoided along the spheres loop, circumventing potential jams, wear, abrasion and corrosion.

Finally, the plant is delivered in a containerized modular fashion that makes logistic and installation straightforward tasks, minimizing the required civil engineering activities before erection.



ABSTRACTS

# **Biomass / Reactors**

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**Poster presentations**

## FLUIDIZED BED PYROLYSIS OF OLIVE KERNEL BIOMASS IN A THERMOGRAVIMETRIC REACTOR

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The thermal decomposition of difficult biomass materials is an area of applied pyrolysis that has been extensively studied but is not fully understood. There is a definite lack of data linking the minutiae of decomposition mechanisms (such as the use of milligram-scale TGA) versus realistic pilot-scale measurements where mass conversion rates are challenging to measure. This research presents a series of experiments utilising a Thermogravimetric Fluidized Bed Reactor (TGFBR) developed to enable on-line monitoring of mass variation with reaction time and comparing this to a commercially available TGA apparatus, to show the effects of particle size, fluidization conditions and diffusion under isothermal and non-isothermal conditions. Typical sample sizes were 40g per run.

The apparatus used rapid heating and uniform bed temperature conditions over a range of fluidizing gas flowrates along with effective suppression of the external diffusion. In total 5 size grades of biomass were studied, ranging from 300 to 1400  $\mu\text{m}$ , plus an 'as received' sample of <4000  $\mu\text{m}$ . Application of the TGFBR to olive kernel biomass demonstrated fluidized pyrolysis to have a higher conversion rate at 660 °C, where the reaction was complete in 15 seconds for larger particle size (<4000  $\mu\text{m}$ ), whilst the pyrolysis was faster for the small particles studied – completing in around 10 seconds for the smaller grades studied.

The pyrolysis in the TGFBR at a pre-set temperature was analysed by using the isothermal kinetic approach, resulting in an activation energy of around 65 KJ/mole. The reaction was further found to be aligned to the two-dimensional diffusion model expressed by  $G(x) = x + (1-x) \ln(1-x)$ . A non-isothermal condition was then used to determine the activation energy of the biomass pyrolysis via TGA, where the activation energy was found to be approximately 97 KJ/mole, potentially as an effect of external diffusion in the TGA, however the reaction mechanism was the same. The TGA results for the olive kernel showed two main peaks of weight loss, the lower temperature peak correlated with the decomposition of hemicellulose whilst the upper temperature peak correlated mainly with a stage of cellulose decomposition. Lignin thermal decomposition was observed to occur throughout the temperature ranges studied.

The effect of particle size on the conversion of the biomass was investigated at temperatures of 300, 400, 500, 600 and 660°C in the TGFBR. The conversion rate was observed to increase with decreasing the particle size at high temperatures, whilst at lower temperatures (300 to 400°C) the rate was not strongly dependent on temperature. This suggests an inhibition due to lower internal diffusion. The conversion increased with temperature, however it showed no significant increase above 600 °C. There was no significant effect of particle size on pyrolysis found in the laboratory TGA experiment at a controlled heating rate of 20 °C/min.

## Guayule (*Parthenium argentatum*) pyrolysis biorefining – Production of hydrocarbons from guayule via tail-gas reactive pyrolysis

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Guayule (*Parthenium argentatum*) is a woody desert shrub cultivated in the southwestern United States as a source of natural rubber, organic resins, and high energy biofuel feedstock from crop residues. Some 20,000 kg ha<sup>-1</sup> yr<sup>-1</sup> of biomass is reported to be yielded from guayule cultivation and the acreage devoted to guayule is expected to grow due to renewed interest in guayule to replace imported Hevea rubber. We used guayule bagasse, the residual biomass after latex extraction, and guayule leaves as feedstock in a pyrolysis process that employs a reactive gas environment to formulate special intermediate bio-oil products. Our procedure allows for use of conventional hydro-treating with conventional noble metal catalysts and a simple distillation process to synthesize hydrocarbon (drop-in) fuels and chemicals. The analysis of the composite mixture of hydro-treated products from the bagasse shows that compositions containing up to 66% naphtha with the greatest fraction falling within the C8–C10 range could be synthesized, with most of the remainder (34%) in the diesel range (C12–C22) and trace amounts of larger hydrocarbons, up to C37. The product met several ASTM standards for drop-in fuels, but the sulfur content (primarily due to latex extraction additives) was relatively high at around 200 – 300 ppm, indicating the need for hydro-desulfurization to meet gasoline specifications. The composition of the guayule leaves is different from that of the bagasse, with the main differences being lower resin content, higher ash, and higher nitrogen content resulting from plant proteins. However, the combined effects of the leaves' composition and the tail gas reactive pyrolysis process creates a complex mechanism that results in a number of fuel and commodity or fine chemical compounds that can potentially be isolated or synthesized upon mild upgrading.

## EXPERIMENTAL COMPARISON OF FAST AND INTERMEDIATE PYROLYSIS AT PILOT SCALE

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In recent years, the concept of intermediate pyrolysis has been developed. It applies similar reactor temperatures as fast pyrolysis, but at a lower heating rate and longer vapour residence time at reactor temperature. Many biomasses have been investigated in either processes, but there exists little concerted effort on comparing intermediate and fast pyrolysis directly with the same type of biomass. Pilot plants with a scale of 10 kg h<sup>-1</sup> of biomass input are under operation at the Karlsruhe Institute of Technology that realize both intermediate pyrolysis (the ‘STYX’ plant [1]) and fast pyrolysis (the ‘Python’ plant [2]). Both reactors utilize auger technology to transport the biomass. In the case of fast pyrolysis, a preheated heat carrier is added in order to achieve the required heating rate. These two plants have been used to convert the same four types of biomass feedstock ranging from nearly ash-free woody biomass to ash-rich wheat straw. Additionally, a lab-scale fluidized bed reactor was used as ‘reference’ technology for fast pyrolysis with the same four biomasses. All experiments were performed with the same biomass particle size. Three of the investigated biomasses were obtained from a round robin test organized by the IEA Task 34 to compare fast pyrolysis oil quality of different technologies.

It was found that intermediate pyrolysis produces significantly less liquid products than the fast pyrolysis process for all four investigated biomasses (see Figure 1). The product distribution is shifted towards solid and gaseous products instead. Interestingly, there are some differences of how the bio-oil yield varies with the type of biomass. On the one hand, both processes produce the lowest amount of liquid products with the feedstock containing the most ash (wheat straw and a blend containing wheat straw). On the other hand, fast pyrolysis achieved the highest bio-oil yield with beech wood while intermediate pyrolysis achieved the highest oil yield with poplar wood although it contains more ash than the beech wood.

Both processes produce two condensates, one organic condensate (including some water) and one aqueous phase (containing some organics). The amount of aqueous condensate produced by fast pyrolysis did not vary significantly within the different types of biomass. Contrarily, the less aqueous condensate was obtained from intermediate pyrolysis the more ash the feedstock contained. This surprising observation might be an effect of water saturation and/ or different polarities in the bio-oil.

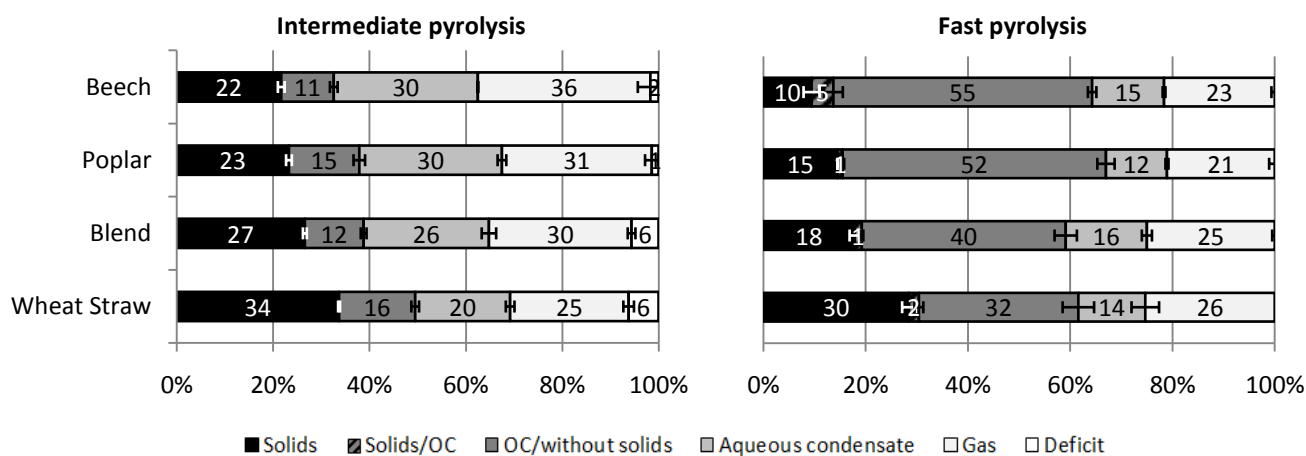


Figure 1: Mass yield of different product fractions after intermediate and fast pyrolysis (as received basis)

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## PROCESS SIMULATION OF THE CHEMICAL LOOPING PROCESS FOR HYDROGEN PRODUCTION USING HEAVY FRACTION OF BIO-OIL AND CARBON EMISSION ANALYSIS

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Fast pyrolysis bio-oil is a renewable liquid fuel readily stored and transported with higher energy density, however, its poor physical and chemical properties severely restrict its large-scale application as a transportation fuel. Bio-oil must be further upgraded through quality modification processes, among which low-temperature hydrogenation process of the light fraction of bio-oil (LFB) shows more promising potential [1]. Nevertheless, the heavy fraction of bio-oil (HFB) accounting for about 38% or more of bio-oil is difficult to upgrade itself to bio-fuel or chemicals. As a high-carbon energy carrier, HFB can be used as feedstock for hydrogen generation [2], which may contribute to achieve self-sufficiency in hydrogen gases required by the hydrogenation process of LFB.

Currently, most of hydrogen gases have been produced from fossil fuels such as natural gas, coal and fossil oil by means of centralized coal gasification and steam methane reforming followed with water gas shift and purification and separation processes. However, the processes aforementioned are more expensive in investment and energy-intensive releasing large amounts of CO<sub>2</sub> leading to global climate warming [3-4]. The chemical-looping process for hydrogen generation (CLHG) is an upgrading integration combining the traditional steam-iron process with the novel chemical looping combustion process, which shows noticeable potential to produce high purity hydrogen gases with inherent capture of CO<sub>2</sub>. HFB, a renewable energy carrier, is nearly free of sulphur and ash which can alleviate the environmental problems as an alternative to fossil fuels utilized for CLHG. To date, there have been few researches on CLHG using bio-oil or HFB as feedstock [5], especially on the overall process.

The main subject of this study is to reasonably evaluate CLHG process performance utilizing HFB as feedstock and iron oxide as oxygen carrier (OC) circulating among three reactors from the viewpoint of whole system, which is based on the reactor and process simulation by means of ASPEN PLUS software. The two-stage fluidized bed reactor is adopted to simulate the fuel reactor (FR) in order to fully convert HFB fuel into CO<sub>2</sub> and H<sub>2</sub>O considering thermodynamic equilibrium constraints. The key parameters for reactors are discussed including the mole ratio of Fe<sub>2</sub>O<sub>3</sub> in fresh OC to carbon in HFB, conversion ratio of OC and steam, the mass ratio of inert support to OC, the reactor temperature and pressure, etc. Subsequent process simulation performed on the basis of the reactor parameters obtained is conducted to evaluate the overall performance of HFB CLHG process. The simulation data of FR show that the two-stage fluidized bed reactor can completely convert HFB. And process simulation results indicate that this process is feasible and has a thermal efficiency (HHV) about 75% for energy conversion from HFB to hydrogen under conservative presupposition. With the concentrated CO<sub>2</sub> sequestration, the HFB CLHG process becomes a carbon negative process.

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## PLASMA/CATALYST DEVELOPMENT TO PRODUCE HIGH QUALITY SYNGAS FROM BIOMASS

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Biomass gasification is considered a promising technology in order to develop a sustainable energy system and to decrease our current dependence on fossil fuels. Thus, biomass is converted into a syngas stream which can be combusted for power and heat generation but also used as raw material for production of fuels and chemicals. The main drawback of biomass gasification and its implementation at large scale is the formation of tar compounds together with the product syngas. Tar is defined as a complex mixture of condensable hydrocarbons with molecular weight higher than benzene and causes several operational problems in process equipment as well as in turbines and engines used in applications of the produced fuel gas. In addition, the presence of, tar makes the syngas problematic for applications such as the Fischer-Tropsch process for chemical production where syngas tar leads to serious coke deposition over the catalyst. The main objective of this study is to develop a catalyst with plasma that can be used to produce a high quality syngas from biomass.

Several nickel-based catalysts including 10 wt.% and 20 wt.% nickel loading with different supports such as alumina, silica and zeolite were prepared and investigated for their suitability in the production of hydrogen and syngas from the two-stage pyrolysis-gasification of wood pellets. The catalyst samples were calcined at 750°C for 3 hours. The calcined catalysts were also treated using non-thermal plasma, discharge power 40W for 40 min to investigate the effect of plasma on the catalyst efficiency and stability (Figure 1).

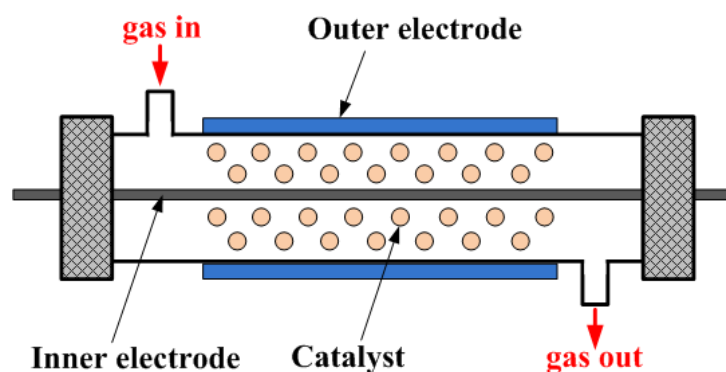


Figure 1 Plasma-catalysis configuration: single-stage system

All experiments were carried out at a pyrolysis temperature of 500°C and gasification temperature of 750°C in the presence of steam using a 1:2 ratio of catalyst to biomass.

The gaseous products were analysed using packed column gas chromatography (GC) for hydrocarbon gases and permanent gases. Reacted catalysts were characterised using a variety of methods, including, temperature programmed oxidation (TPO) analysis, scanning electron microscopy and transmission electron microscopy.

The results showed that plasma has a beneficial effect. Plasma treated catalysts showed higher syngas yield and carbon conversion, and lower carbon deposition compared to not treated catalysts.

## CATALYTIC AND NON-CATALYTIC BIOMASS PYROLYSIS PROCESS IN A CONTINUOUS SCREW REACTOR

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In the pyrolysis process, biomass is decomposed into solid, liquid and gaseous products, which can be used as fuels and/or source of chemicals. Most of the literature about biomass pyrolysis is focused on bio-oils production and optimization. However in practice it is rather difficult to make use of bio-oils, since they are a complex mixture of products with rather low higher heating value (HHV), high oxygen and water contents and are corrosive. Therefore from a practical point of view it is much easier to make use of pyrolysis gases than of liquids. Profit can be made of pyrolysis gases since they can be used as gaseous fuel, synthesis gas or source of hydrogen.

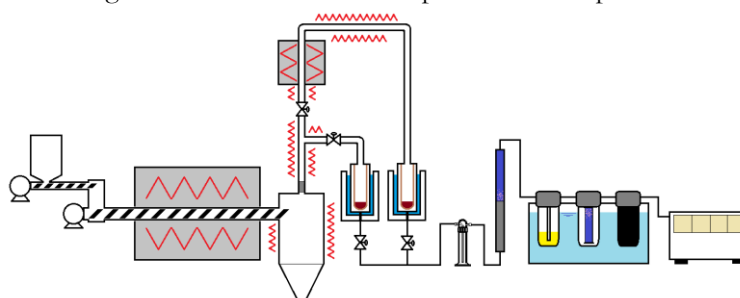
Therefore the objective of this work was to optimize the pyrolysis process in order to promote the production of high value gases together with a solid (charcoal or biocoque) useful as reducing agent in metallurgical applications, and this implies minimizing the production of liquids. In order to obtain high gas yields and a solid useful as biocoque, high pyrolysis temperatures and low heating rates are required. This work has been carried out operating in such conditions and with a practical approach, using a laboratory scale continuous pyrolysis plant which resembles a potential industrial plant.

The sample pyrolyzed was a woody biomass waste sample (pine tree) coming from forest activities carried out in the north of Spain. The pyrolysis plant (Figure 1) consists of two reactors connected in series. Firstly biomass pyrolysis takes place in the screw reactor with feeding rates around 90 g h<sup>-1</sup>, at high temperatures ( $\geq 750$  °C) and with different residence times. The solid (charcoal) leaving the reactor is collected in a closed bin and the vapours are driven to a tubular reactor, where they are treated either with or without catalyst. The vapours are then separated into the bio-oils which are trapped in a condensation system and the gases which are finally cleaned (activated carbon and silica gel double column and isopropyl alcohol, silica gel and mechanic particles filters) and analyzed in a micro-GC connected to the plant.

Different operating conditions and different Ni-containing catalysts have been tested. The detailed composition of the initial sample, as well as of the solid, liquid and gaseous products obtained in the experiments, will be presented.

The use of catalysts is decisive for optimizing pyrolysis gases. On the one hand higher gas yields and lower total liquid yields are obtained. The liquids obtained when high temperatures and low heating rates are used, as in this study, are a mixture of aqueous and organic products; the latter are very much decreased when appropriate catalysts are used. On the other hand the gas composition is also influenced by the catalysts. The Ni-based catalysts used in this study, promote H<sub>2</sub> production while CO and CH<sub>4</sub> are decreased, and so a high value gas for H<sub>2</sub> production or for Fischer-Tropsch synthesis is obtained.

Figure 1. Flow sheet of the experimental setup used





## PRODUCTION OF PYROLYSIS OILS FROM BROWN ALGAE USING AN AUGER-TYPE CONTINUOUS PYROLYSIS REACTOR

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The pyrolysis of marine biomass including micro- and macroalgae has been suggested for the production of sustainable petroleum-like liquid fuels [1]. Compared with the lignocellulose or other cellulosic biomass, the absence of lignin is predicted to facilitate the use of marine biomass for the production of liquid fuels. Although the macroalgae have been suggested to be the feedstocks of liquid fuel production, the high content of moisture and inorganic elements increased the production of bio-char and the continuous pyrolysis process using the fluidization bed became impossible [1]. In this study, we suggest the production of macroalgae-based pyrolysis oils using an Auger-type continuous pyrolysis reactor instead of fluidization-bed reactors which has been used for the pyrolysis of lignocellulose. The Auger-type pyrolysis reactor was designed and manufactured in our lab. *S. Japonica*, a brown algae obtained in the south seashore of Korea, was used as a feedstock following the grinding to the fine powder. The process conditions including, the pyrolysis temperature, the feeding rate, the size of algae particles, the pretreatment method, and the flow rate of carrier gas, were studied and the effects of these variables were discussed. As listed in Table 1, the Auger-type continuous pyrolysis reactor produced 10.45 – 22.69% of oil. The production of bio-char was large with the yield of 41.15 – 74.88% because of the presence of minerals [1]. The highest yield of oil was 22.69%, and the optimization of process conditions will be discussed. The possible strategy to improve the quantity and quality of macroalgae-based pyrolysis oils will be also discussed.

Table 1. Representative results of continuous pyrolysis of *S. Japonica* using an Auger-type continuous pyrolysis reactor.

|         | Yield (%) |       |       |
|---------|-----------|-------|-------|
|         | Oil       | Char  | Gas   |
| Entry 1 | 22.69     | 41.15 | 36.16 |
| Entry 2 | 17.16     | 45.52 | 36.82 |
| Entry 3 | 16.42     | 58.21 | 25.37 |
| Entry 4 | 10.45     | 74.88 | 14.68 |

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## TECHNO-ECONOMIC ANALYSIS OF DECENTRAL CHP CONCEPTS BASED ON PYROLYSIS

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Pyrolysis of low-rank agricultural residues, such as shrub cuttings, digestate, chicken manure, etc., is an attractive process opportunity for the production of heat and power (CHP) in decentral system units and for the recycling of valuable products. The aforementioned raw materials present technical and economic issues, which are high inorganic content and low energy density in addition to potentially high storage and logistic costs. As result, few technologies are suitable for the handling and exploitation of such feedstocks. Specifically, screw reactors are able to convert a wide spectrum of materials with flexibility. With this purposes, the Karlsruhe Institute of Technology developed the STYX, a through screw reactor with integrated hot gas filtration, to produce particle-free vapours which can be burnt or liquefied in following process steps. Fuel flexibility and heat requirements have been investigated with various materials [1, 2].

This paper reports the techno-economic evaluation of different pyrolysis/CHP integration concepts of a scaled-up reactor under the actual energy market constrains.

On the basis of the experimental results in bench scale (capacity of 2 kg h<sup>-1</sup> to 4 kg h<sup>-1</sup> depending on the feed), a pyrolysis reactor component has been developed for the thermodynamic software EBSILON® Professional. The pyrolysis products yields and properties were introduced for different reactor temperatures and for two feedstocks, namely beech wood as reference case and chicken manure.

Under well-defined process constrains, i.e. thermal capacity of 500 kW and autothermal pyrolysis operation, two different flow schemes were developed and compared in terms of heat and power production. In the first option, the plant is equipped with a condensation unit to recover the liquid and to utilise it in a CHP motor; the second option foresees the direct combustion of the vapours to produce electricity in an externally fired micro gas turbine (see Fig. 1).

The results of the thermodynamic models enabled the description of the main plant items. Based on the internal knowledge and scale-up correlations, the investment costs were derived. Different energy scenarios under the German legislation were evaluated to develop variable process costs and benefits. Finally, the results of the techno-economic analysis were expressed in terms of required char price for the long term profitability of the process. Sensitivity analyses indicate the most promising applications for the technology.

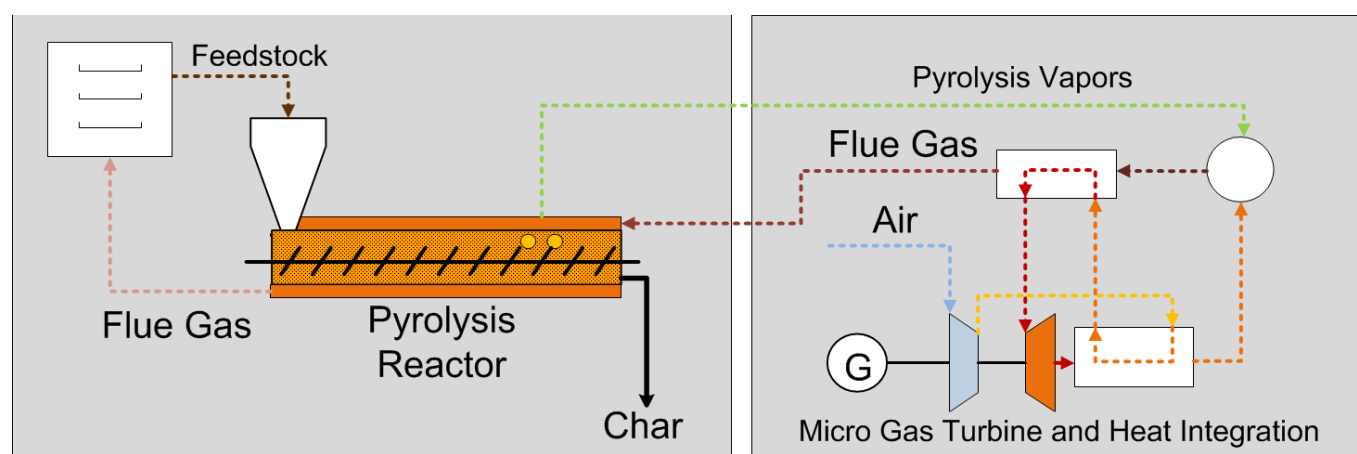


Fig. 1: Pyrolysis CHP Configuration with externally fired micro gas turbine

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## **STUDY OF THE IMPACT OF BIOMASS COMPOSITION ON SYNGAS QUALITY IN A BUBBLING FLUIDIZED BED REACTOR THROUGH MODELING AND SIMULATION**

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The recent growing concern on safeguarding the environment from the harmful effect of global warming caused by the release of large quantities of anthropogenic CO<sub>2</sub> into the environment mainly from fossil fuels utilisation for energy production has triggered a renewed interest in the use of renewable energy resources. Amongst the renewable resources, biomass has unique characteristics. Like fossil fuels, it comprises of mainly organic carbon and hydrogen and can therefore be used for the production of carbon based chemicals and fuels to replace those presently being produced from fossil fuels. Hence, biomass seems to be the only renewable resources which can compete with fossil fuels (in terms of applications) for the production of energy as well as other value added products.

On the other hand, biomass is an abundant renewable energy resource and more evenly distributed than fossil fuels. It is regarded as being CO<sub>2</sub> neutral as the CO<sub>2</sub> it absorbed during the growth phase is released back into the atmosphere when it is consumed making it a better energy resource than fossil fuels in terms of environmental impact. There are several technologies used for the conversion of biomass into value added products. These technologies are grouped into: biochemical, thermochemical and chemical conversion. For the thermochemical conversion of biomass, heat is used to extract the energy contained in the biomass material. This can be achieved by combustion, pyrolysis or gasification.

Pyrolysis and gasification are regarded as more advanced technologies compared to combustion as they are used to produce liquid or gaseous fuel from any given biomass material. Gasification helps to generate syngas which is a valuable product as they can be used either directly or treated to produce more advanced fuels and chemicals. Unlike coal and natural gas, there is a wide variation in the composition of biomass material. Studies have shown that even biomass materials of the same specie grown in different environments vary widely in composition. This is a major challenge as it impact directly on the composition of the syngas generated during its gasification.

Thus, it is worthwhile to investigate the effect of these variations in composition on the quality of syngas generated during gasification operation. This research will investigate the impact of biomass composition on the composition of syngas generated during gasification operation. The study will be carried out using modeling and simulation using Aspen Plus. The different biomass materials will be modeled using the proximate and ultimate analysis data from the various biomass characterisations in the literature. Some of the non-food woody biomass to be considered in this analysis include: redwood, pine wood, oak etc. The reaction mechanism and kinetics for the pyrolysis and gasification process will be obtained from the literature. The model will be validated using experimental data from the literature.

This study forms part of our planned detailed research on technical and economic assessment of different biomass resources as feedstock for pyrolysis and gasification.

## STOCHASTIC REACTOR MODELLING FOR BIOMASS PYROLYSIS

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Biomass gains increasing popularity as an alternative to fossil fuels, as it enables a sustainable way for heat and power generation as well as secondary fuel production. Biocarbon for example, the carbonaceous solid product from biomass pyrolysis (and gasification) may be able to replace fossil carbon carriers in a number of industrial applications.

The first steps in all thermochemical conversion processes are drying and devolatilization, resulting in the release of water vapour and gases of low molecular weight. Secondary gas phase reactions and char oxidation further alter the product composition, the latter being especially important for the prediction of biocarbon yields from pyrolysis.

Modelling thermochemical biomass conversion involves both the description of transport of energy, mass and momentum as well as modelling the complex chemical kinetics that occur during the process. Transport phenomena are typically modelled using a numerical analysis such as CFD. This may however be a very time-consuming process.

The present work focuses on an alternative, more CPU efficient approach, to model biomass pyrolysis, using the LOGEsoft gasification module. [1] Transport phenomena are handled by the software. It is a zero-dimensional model that describes the state variables as probability density functions. The reactor is divided into a certain number of cells. These contain a number of particle packages each, which in turn are composed of a certain amount of solid matter, pore gas and bulk gas. The particle packages mix with each other and exchange heat and mass. The conservation equations are solved to determine the species composition, particle size, porosity and temperature of both the bulk gas and solid matter. The reactor may be modelled as a series of partially stirred reactors, but also as a plug flow reactor, tracking a particle within a single cell. The gasification module is also capable of solving a detailed chemical mechanism to describe the gas phase reactions. A subroutine is developed and implemented in the software that accounts for heterogeneous reactions between the char surface and the gas phase.

In order to validate the applicability of the stochastic reactor approach for biomass pyrolysis, a study is carried out comparing the predicted product gas composition obtained from experimental work by Qin et al. [2] with both the stochastic reactor and a CFD model [3]. In the experiments, previously conducted at the Technical University of Denmark, beechwood particles undergo rapid heating in a drop tube reactor with different reactor atmospheres of nitrogen, steam and air [2].

In the proposed model, a simple one-component and one-step devolatilization reaction is used to describe the biomass decomposition into CO, CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub> and char. The model also takes drying into account. The gas species further react according to five global gas phase reactions. The kinetic-/diffusion-limited rate model (proposed by [4]) is implemented to determine the surface reaction rate. The gas phase composition obtained from the stochastic model is compared with the experimental results and the product composition predicted in the CFD model. As the same kinetic scheme and kinetic constants as in the numerical approach as used, the performance of both approaches to model transport phenomena can be compared.

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## Pyrolysis-gasification of sawdust for high H<sub>2</sub>/CO-ratio syngas through chemical looping process in a dual fluidized bed system

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### ABSTRACT

Pyrolysis-gasification to produce syngas is one of technologies for the production of transportation fuels and chemicals[1-3]. Currently, the stoichiometric ratio of H<sub>2</sub>/CO in the syngas is essential for these conversions to the target products, for example, 2:1 for methanol and 3:1 for SNG, but the H<sub>2</sub>/CO ratio could just be enhanced by the shift reaction in the process, which makes the facilities complicated[4,5].

In this context, pyrolysis-gasification through chemical looping process in a dual fluidized bed system was proposed to increase the H<sub>2</sub>/CO ratio and to simplify the process. The system offered two separate fluidized bed reactors: a fast fluidized bed used as the fuel reactor for the biomass pyrolysis and hydrogen production, while a bubbling fluidized bed used as the air reactor for the char combustion. Besides, the fuel reactor was separated into two different zones: the lower zone was for the biomass pyrolysis and the higher zone was for the hydrogen production and the gas conditioning. Natural hematite was used as bed material and oxygen carrier to achieve the chemical looping circulation in the system (Fig.1).

The experiments for this process of sawdust were conducted in the dual fluidized bed system, regarding the influences of different fuel reactor temperatures, steam-to-biomass (S/B) ratios and steam preheating temperatures. The optimum H<sub>2</sub>/CO ratio (2.45 mol mol<sup>-1</sup>) in the syngas was screened from the following operating condition: the fuel reactor temperature of 820 °C, the S/B ratio of 1.00 kg kg<sup>-1</sup> and the steam preheating temperature of 500 °C. Overall, the experiments carried out in the present work suggest that high H<sub>2</sub>/CO-ratio syngas production was promising and further investigations were necessary.

**Key words:** High H<sub>2</sub>/CO-ratio syngas; Pyrolysis-gasification; Chemical looping; A dual fluidized bed system; Sawdust

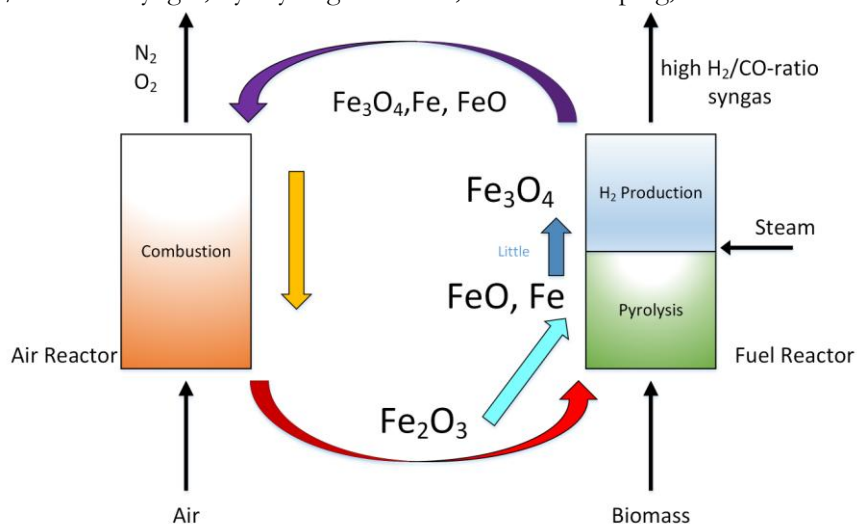


Fig. 1 Pyrolysis-gasification through chemical looping process in a dual fluidized bed system (natural hematite is used as the oxygen carrier)

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ABSTRACTS

# **Biomass / Slow pyrolysis**

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**Oral presentations**

## STUDY ON THE EFFECTS OF USING A CARBON DIOXIDE ATMOSPHERE ON THE PROPERTIES OF VINE SHOOTS-DERIVED BIOCHAR

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Producing biochar from vine shoots, a residual lignocellulosic biomass from vine pruning, could be a way to manage this waste and generate environmental and agronomic benefits. Among the different thermochemical processes, slow pyrolysis can retain the feedstock carbon in stable biochar with high value-added as a soil-applied carbon sequestering agent [1]. It is well known that the pyrolysis process parameters and the feedstock nature require continuing research because of their influence on the physicochemical properties of the produced biochar. One of these parameters to study in depth is the type of pyrolysis atmosphere. In terms of energy efficiency, recycling CO<sub>2</sub> from residual flue gases into the pyrolysis process may be economically beneficial. In addition, CO<sub>2</sub> can replace the use of an expensive N<sub>2</sub> environment leading to important cost savings. However, research is needed to analyse the effects of modifying the inert environment N<sub>2</sub> to CO<sub>2</sub> on the pyrolysis products' distribution, especially on the biochar yield and properties. In addition, working under moderate pressure (1 MPa and above) can result in higher biochar and fixed-carbon yields with respect to conventional atmospheric carbonisation, as reported in recent studies [2].

For all the reasons above-mentioned, the specific aim of this study is to investigate the effects of using a different atmosphere (100% N<sub>2</sub> and 100% CO<sub>2</sub>) at two levels of absolute pressure (i.e., 0.1 and 1.1 MPa) on biochar yield and properties. The analysed response variables were char and fixed-carbon yields ( $y_{char}$  and  $y_{FC}$ , respectively), fixed-carbon content, molar H:C and O:C ratios as well as BET specific surface areas ( $S_{BET}$ ) of produced biochars.

Pyrolysis experiments under both CO<sub>2</sub> and N<sub>2</sub> environments were conducted using a fixed-bed batch type reactor that was operated at 600 °C, as optimal pyrolysis peak temperature based in previous studies [2]. The residence time for the vapour fraction was kept constant at a value of 3 min. The raw vine shoots were ground in a shallow way to save energy on size reduction pre-treatments. The resulting particle size was between 0.85 and 10 mm, and about 400 g of feedstock was used per test.

From analysing the obtained results, several observations can be made:

- As expected, due to the peak temperature value employed in the pyrolysis process,  $y_{FC}$  values (0.22-0.29) as well as H:C and O:C ratios (below 0.4 and 0.2, respectively) indicated high C sequestration potential [3] for all of the produced biochars.
- The results also show that using CO<sub>2</sub> instead of N<sub>2</sub> at 0.1 MPa leads to an increase in the fixed-carbon content (from 66 to 83 wt. %) and a decrease in H:C and O:C molar ratios.
- With regard to the pressure effect, a clear increase in both the  $y_{char}$  and  $y_{FC}$  yields and a decrease in H:C and O:C molar ratios were observed when pressure was raised from atmospheric to 1.1 MPa for both environments.

In other words, it seems that some interaction effect between pyrolysis atmosphere and pressure can exist. Pilon and Lavoie [4] suggested that the secondary pyrolysis reactions could be inhibited under CO<sub>2</sub> environment at atmospheric pressure. In fact, liquid yield increased (from 38 to 42 wt. %) at the expense of char (from 33 to 26 wt. %) for the atmospheric experiments performed here under N<sub>2</sub> and CO<sub>2</sub>, respectively. In addition, this inhibition has also been observed in the gas composition, decreasing the lower heating value due to a minor production of CH<sub>4</sub> and H<sub>2</sub> [5]. However, the inhibition of secondary charring reactions was not observed when pyrolysis was performed under CO<sub>2</sub> at 1.1 MPa (both  $y_{char}$  and  $y_{FC}$  yields increased). More interestingly, the pyrolysis under these conditions also led to a market increase in the BET specific surface area (196.5 m<sup>2</sup> g<sup>-1</sup>) of the produced biochar. This increase in porosity could be explained by an enhanced conversion of carbon through the Boudouard reaction.

According to the mentioned and highlighted results, using CO<sub>2</sub> as pyrolysis atmosphere appears to be a very promising alternative to produce more stable and porous biochars from vine shoots.

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## EFFECT OF TORREFACTION ON PROPERTIES AND PYROLYSIS BEHAVIORS OF WOOD AND BARK

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Torrefaction is a promising thermal treatment technique for improving properties of biomass fuels. In the present work, Norwegian spruce stem wood and bark were torrefied at two temperatures (225 °C and 275 °C) and holding times (30 and 60 min). The grindability of the torrefied biomass was evaluated by determining energy requirement for grinding, and the particle size distribution and micro structure were compared with untreated wood and bark. An increase in the torrefaction temperature gave the strongest effect on grindability of the torrefied product among the studied parameters. For the stem wood, the specific energy required for grinding torrefied material decreased significantly with increasing torrefaction temperatures. The grinding energy of torrefied stem wood was reduced from 236 kWh/t to 59 kWh/t when torrefied at 275 °C with 60 minutes holding time. In addition, with increasing torrefaction temperature and holding time, the percentage of fine stem wood particles ( $d < 300 \mu\text{m}$ ) in the particle size distribution after grinding increased considerably. The energy used for grinding untreated bark was 39 kWh/t and is significantly smaller than that for grinding stem wood. The torrefaction treatment has less pronounced effect on grindability of the bark. The higher heating value of torrefied stem wood and bark increased with increase in torrefaction temperature. The pyrolysis behaviours of the untreated stem wood, bark and torrefied products were examined in detail by using TG-MS technique. The different mass loss rate profiles of the untreated samples indicate the differences in the physical and chemical properties of stem wood and bark of the same species. The decomposition of bark started at a lower temperature and the maximum rate of decomposition is considerably smaller, taking place at a lower temperature than in case of the stem wood. The torrefaction treatment at 225°C significantly modifies pyrolysis behaviours of the bark, while the torrefaction treatment at this temperature caused less pronounced effects on pyrolysis behaviours of the stem wood. After torrefaction at 225°C the decomposition of the bark and wood starts at very similar temperatures. The evolution profiles of the volatile products have been recorded by the mass spectrometer to gain a better understanding of the differences in the decomposition behaviour of untreated and torrefied wood and bark. The TG-MS results revealed that increase in torrefaction temperature had most evident effects on pyrolysis behaviours of the wood and bark. It is mainly attributed to change of structure of the wood and bark during torrefaction treatment.



## FAST TORREFACTION VERSUS CLASSIC TORREFACTION: COMPARISON OF THE PRODUCTS ON A PILOT SCALE CONTINUOUS REACTOR

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Biomass torrefaction – also called mild pyrolysis – is a thermochemical treatment driven at low temperature (200-300°C), at atmospheric pressure and in an inert atmosphere, to produce a homogeneous solid. This torrefied solid has a higher energy content, is more hydrophobic, is easier to grind and fluidize than the raw biomass. These modifications of the biomass make it more suitable to the gasification process, particularly in an entrained flow reactor for instance.

In most studies, the torrefaction is carried out at low temperature and long residence time. To the authors' knowledge, the solid and volatile products obtained after fast torrefaction – i.e. at higher temperature and shorter residence time – has not been studied.

The aim of this study is to compare the solid and volatile products of fast torrefaction (350°C) to those of classic torrefaction (300°C) of ash tree.

These torrefaction experiments were carried out on a continuous vibrating bed reactor called Vibrato. The biomass is electrically heated in five zones placed along the tube. The incondensable species are quantified online by micro GC. The condensable species are recovered separately in a three-step condensation system. The condensable species are then analysed with a GC MS, and 71 molecules are calibrated. Besides, the water content of the condensable species is determined by Karl Fischer volumetric titration. The ultimate analysis, the lower heating value and grinding energy measurement of the torrefied solids are performed.

For the same anhydrous weight loss, mass balance are slightly similar as torrefaction if classic or fast. Although the torrefied biomass yield is constant at 70 wt%, the incondensable and condensable species yields vary depending on the temperature and residence time. Additionally, the lower heating value of the torrefied solid slightly varies. Besides, the composition of the condensable species, based on the GC MS quantification, varies significantly. Around 20 molecules are identified and quantified in the torrefaction condensable species. Regardless of the operating conditions, water, acetic acid, 2 propanone, 1 hydroxy, glycolaldehyde dimer, methanol remain the major condensable species. The kind of torrefaction has a strong influence on torrefied solid grindability.

## TORREFACTION OF VARIOUS WOODY AND AGRICULTURAL BIOMASSES AND OF THEIR EXTRACTED CELLULOSE, HEMICELLULOSE AND LIGNIN THROUGH TGA-GCMS

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Nowadays, there is an increasing awareness on the importance of biomass waste as a renewable source of energy, materials and chemicals. In this context, the European project MOBILE FLIP aims at developing and demonstrating mobile conversion processes suitable with various underexploited agro- and forest based biomass resources in order to produce energy carriers, materials and chemicals. One of these processes is torrefaction, a mild thermal treatment, occurring typically between 200 and 300°C during a few tens of minutes in a default-oxygen atmosphere. The solid product obtained has properties closer to coal in terms of heating value, carbon content, hydrophobicity, grindability as well as flowability, and thus is suitable as fuel for combustion, co-combustion or gasification. During torrefaction, condensable coproducts are released, that can damage the installation but that may also be source of “green” chemicals. It is therefore crucial to characterize them to optimize the torrefaction process and design industrial units.

Up to now, only few works have been focused on characterizing and modelling both solid and condensable species during torrefaction versus operating conditions and feedstock type [1]. The biomass macromolecular constituents, namely cellulose, hemicellulose and lignin, are determining properties to predict biomass behaviour during torrefaction [2]. However, torrefaction tests on constituents are rare [1, 2] and always based on commercial constituents, which have been shown not to be representative of the original biomass tested, with the destruction of some groups and a decrease in the degree of polymerization. Our study proposes a breakthrough in the field with the first torrefaction tests on constituents extracted by optimized procedures from various woody and agricultural biomasses, namely one softwood, one hardwood, one straw and one herbaceous crop. These procedures enabled to get constituents closer to native biomass, since groups like acetyl in hemicelluloses are preserved and a higher degree of polymerization is kept. These experiments aim at characterizing solid and condensable species yields versus time and temperature and thus supplying the data necessary for further modelling.

The experimental set-up was composed of a thermogravimetric analyser (TGA) coupled with a gas chromatography mass spectrometer device (GCMS). An original system of 16 heated loops allowed sampling of volatile species released during torrefaction at different temperatures and then the storage of the samples before analysis in GCMS. Thanks to this device, kinetics of condensable species formation could be derived through one single dynamic experiment, together with mass loss. The tests were carried out on the different biomasses and their constituents.

The results showed that the traditionally used commercial constituents of biomass behaved differently from the extracted constituents of each biomass, both in terms of mass loss kinetics (see example of hemicellulose and xylan in Figure 1) and of volatiles produced. For instance, acetic acid was not present in a significant quantity during xylan torrefaction due to the removal of acetyl groups, while this species was found to be produced in large quantity, similar to that of the whole biomass, during hemicellulose torrefaction.

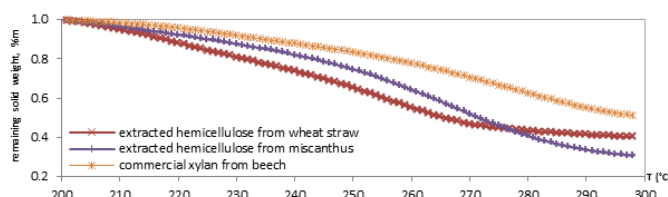


Figure 1. Remaining solid with in function of the temperature for non-isothermal torrefaction experiments in a TGA at 3°C/min for extracted hemicelluloses from wheat straw, miscanthus and commercial xylan from beech

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## CONTAMINANT ISSUES IN PRODUCTION OF BIOCHAR

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Biochar are pyrolysis solids intended for soil application. Before biochar is used for soil improvements, it must be ensured that it will neither cause negative effects on plants or the broader ecosystem, nor exceed legislated contaminant concentrations. At the UK Biochar Research Centre (UKBRC) a study of all relevant types of contaminants, potentially toxic elements (PTEs), polycyclic aromatic hydrocarbons (PAHs) and volatile organic compounds (VOC), was conducted on various sets of biochars from various different production conditions, feedstocks and three different pyrolysis units (around 100 biochars in total).

Little attention has been paid to VOCs in biochar in the literature so far. These inhomogeneous species are degradation products from the thermochemical conversion process and mostly end up in the pyrolysis liquid fraction. However, due to cold spots in the pyrolysis unit the amount of VOCs that end up in biochar can increase significantly. VOCs can be highly phytotoxic, but post-treatment can mediate the toxicity. PAHs are also formed during pyrolysis but behave differently to VOCs due to their higher boiling points. While production conditions such as carrier gas flow or the choice of feedstock mainly showed to influence the concentration of naphthalene in biochar, irregularities during production resulted in elevated concentrations of higher molecular weight PAHs.

In contrast to these organic contaminants, PTEs can neither be formed nor destroyed which means their presence in biochar is predominantly determined by the feedstock. However, significant levels of Cr, Fe and Ni can be introduced into biochar during production due to chromium-nickel-steel-furnaces. Biomass of little economic value, so-called marginal biomass, such as plants from phytoremediation, demolition wood or food waste digestate, are often contaminated with PTEs but also contain high concentrations of nutrients which both partly evaporate during pyrolysis. Overall, marginal biomass showed to be a suitable feedstocks for biochar production.

In conclusion, this elaborate study enables us to provide recommendations on the production of safe biochar. Formation of VOC and PAHs cannot be prevented but their presence in biochar from retention and deposition of organics can be minimized. Feedstock selection must be done appropriately to avoid high levels of PTEs in biochar.

## COKE/CHAR AND OTHER PRODUCTS FORMATION BEHAVIORS IN PYROLYSIS OF TEN SOFTWOOD/HARDWOOD SPECIES

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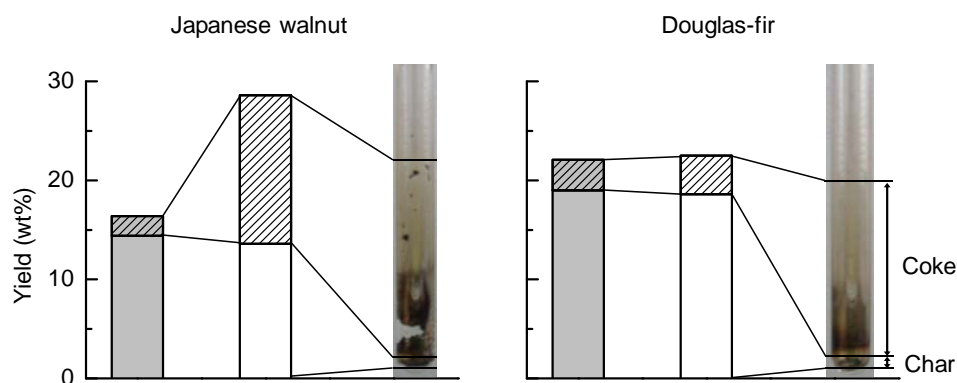
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Hardwood and softwood are different in their chemical compositions of hemicellulose and lignin. Xylan is the major composition of hardwood hemicellulose, while glucomannan contributes more in softwood. Softwood lignin composes of guaiacyl (G)-unit almost exclusively, whereas hardwood lignin includes both guaiacyl- and syringyl (S)-units. These variations in chemical composition would lead to the different pyrolysis behaviors for hardwood and softwood.

In our previous study [1], we compared the pyrolysis behaviors of Japanese beech (a hardwood) and Japanese cedar (a softwood) in a closed ampoule reactor under  $N_2/600^\circ C/40\text{--}600$  s. A striking difference was observed in the reactivity of char for gasification, which was much greater in beech than cedar. As for the tar composition from lignin, the S-derived products from beech were observed only at the short pyrolysis times, while the G-derived products survived. These differences would arise from the different chemical compositions of beech and cedar.

In order to confirm these points for various hardwood and softwood species, we conducted the pyrolysis of 4 additional hardwoods (Japanese zelkova, Japanese walnut, Japanese ash, and Japanese birch) and 4 additional softwoods (Western red cedar, Japanese cypress, Japanese larch, and Douglas-fir) under the conditions of  $N_2/600^\circ C/40\text{--}600$  s. The influences of inorganic metals in wood samples were also studied by using demineralized samples. As a result, two types of char were obtained, namely primary char and coke (Fig. 1). By extending the pyrolysis time from 120 to 600 s, primary char yields from the hardwoods decreased, whereas those from the softwoods were quite stable. Accordingly, the primary char fractions from the hardwoods were more reactive for the formation of volatile products, which resulted in the lower primary char yields at 600 s (9.4–14.4wt%) from hardwoods than those (19–23.8wt%) from softwoods. The demineralization pretreatment enhanced the formation of tar and the following conversion from tar to gas, which is probably originated from the enhanced formation of wood polysaccharides-derived tar including levoglucosan. Such positive effects of demineralization on the gas formation were more pronounced in pyrolysis of softwoods. On the contrary, demineralization substantially enhanced the coke formation from hardwoods at 600 s [2–4wt% (original) to 7.2–15wt% (demineralized)], although these yields were almost comparable from softwoods [1.9–3.1wt% (original) and 3–5wt% (demineralized)] (Fig. 1).

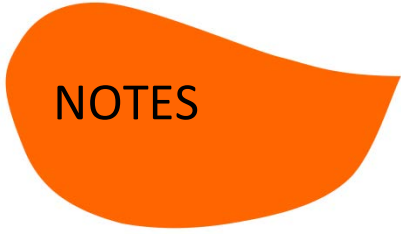
As for the GC-MS-detectable tar components from lignin, the S-derived products from all of the hardwoods tested were significant at 40 s, while almost completely disappeared at 80 s. Accordingly, the tar components became similar for all hardwood and softwood species at 80–600 s, although this makes the total yields from hardwoods much lower than those from softwoods.



**Fig. 1.** Yield of primary char and coke, and pictures of the ampoule reactors after pyrolysis of Japanese walnut and douglas-fir ( $N_2/600^\circ C/600s$ ). Grey, original wood; white, deionized wood.

### References

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# NOTES

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ABSTRACTS

# **Biomass / Slow pyrolysis**

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**Poster presentations**

## SLOW PYROLYSIS OF CHILEAN OAK: CHARACTERIZATION OF VOLATILE EMISSIONS AND BIO-OIL BY GC/MS

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The increase of energy consumption as consequence of economic expansion of global population, demands that renewable energies must be widely explored in order to assure sustainable development of human race. In addition, the reduction of fossil fuels resources, the rise of atmospheric carbon dioxide levels and gradually emerging consciousness about environmental degradation, has promoted novel strategies for sustainable production of fuels, mainly from renewable sources. Among them, biomass poses an adequate availability for large scale sustainable production of liquid fuels, contributes to about 12% of world primary energy supply and is also claimed as the only renewable substitute of organic petroleum. Biomass pyrolysis (*thermal degradation of biomass by heat in the absence of oxygen, which results in the production of charcoal (solid), bio-oil (liquid), and fuel gas products*) offers a convenient way to obtain liquid fuels and it becomes an essential area for research and development of new processes.

Several studies have been performed to identify interesting biomass pyrolysis derivatives that could be used as bio-oils directly or as raw materials for chemical industry. However, not all biomass species have been analyzed deeply. Therefore, the main goal of this article is to analyze chemical composition of gaseous and liquids products obtained from slow pyrolysis of Chilean native oak modifying heating ramp rate and nitrogen gas flow.

Biomass samples of Chilean Native Oak (*Nothofagus obliqua*) were obtained from a single tree, donated by Miraflores Angol Ltd. at Angol, IX Región, Chile. Samples were subjected to size reduction by sawing, chipping, grinding and sieving to achieve a granulometry lower than 2 mm. Biomass were characterized using the following standard methods: Humidity (UNE-EN 14774); Ash Content (UNE-EN 14775) and Calorific Value (UNE-EN 14918). Elemental and Proximate analysis were conducted in accordance with UNE-EN 15104 and ASTM D 3172-73(84) standard methods, respectively.

Pyrolysis experiments (at 623 K) were conducted in a cylindrical glass reactor (CGR) using 3 mg of biomass. Heat ramp rate and N<sub>2</sub> flow were modified from: 10 to 30 K·min<sup>-1</sup> and 60 to 120 cm<sup>3</sup>·min<sup>-1</sup>, respectively. Gaseous samples collected every 30 minutes at CGR exit (using a gas tight syringe), were injected to a Shimadzu Gas Chromatograph (GC2014) to analyze stream chemical composition. Bio-oils were obtained by condensation of vapors using a closed flask (10 cm<sup>3</sup>) at 273K. Taking into consideration the several species identified on bio-oils, a solvent fractionation method was used here. Bio-oil was diluted in a ratio of 1/1000 in seven solvents (methanol, acetone, dichloromethane, hexane, n-pentane, cyclohexane and toluene). Diluted samples were analyzed by Gas Chromatography/Mass Spectrophotometry (GC/MS) in order to identify chemical species, using a Shimadzu QP2010-plus equipment. Non-condensable gases were analyzed by Gas Chromatography. The pyrolysis product fractions were quantified gravimetrically and gaseous fraction was calculated by difference. Products distribution (bio-oil, gas and bio-char) for Oak biomass was 37%, 28.5% and 34.04%. More than 200 compounds were registered by GC/MS analysis, mainly aldehydes; anhydrosugars; furan derivatives; phenolic compounds and carboxylic acids, acetic acid and ketones. A high water content was observed in bio-oil samples, in accordance with other studies. Table 3 shown bio-oil composition results.

Table 1. Relative composition (%) of bio-oil obtained by Oak pyrolysis at 623 K

| Alcohols | Aldehydes | Anhydro sugars | Carboxylic acids | Esters | Ethers | Furan derivatives | Hydro carbons | Ketones | Phenol derivatives (lignins) | Pyran derivatives | Water | Oxo-compounds | n-i* |
|----------|-----------|----------------|------------------|--------|--------|-------------------|---------------|---------|------------------------------|-------------------|-------|---------------|------|
| 1,05     | 2,84      | 1,85           | 17,19            | 1,24   | 0,06   | 6,03              | 1,77          | 11,74   | 5,21                         | 1,10              | 43,5  | 2,23          | 4,19 |

\*non-identified

## CHARACTERIZATION OF THE LIQUID BY-PRODUCTS OBTAINED DURING TORREFACTION OF TYPICAL HUNGARIAN BIOMASS WASTE MATERIALS

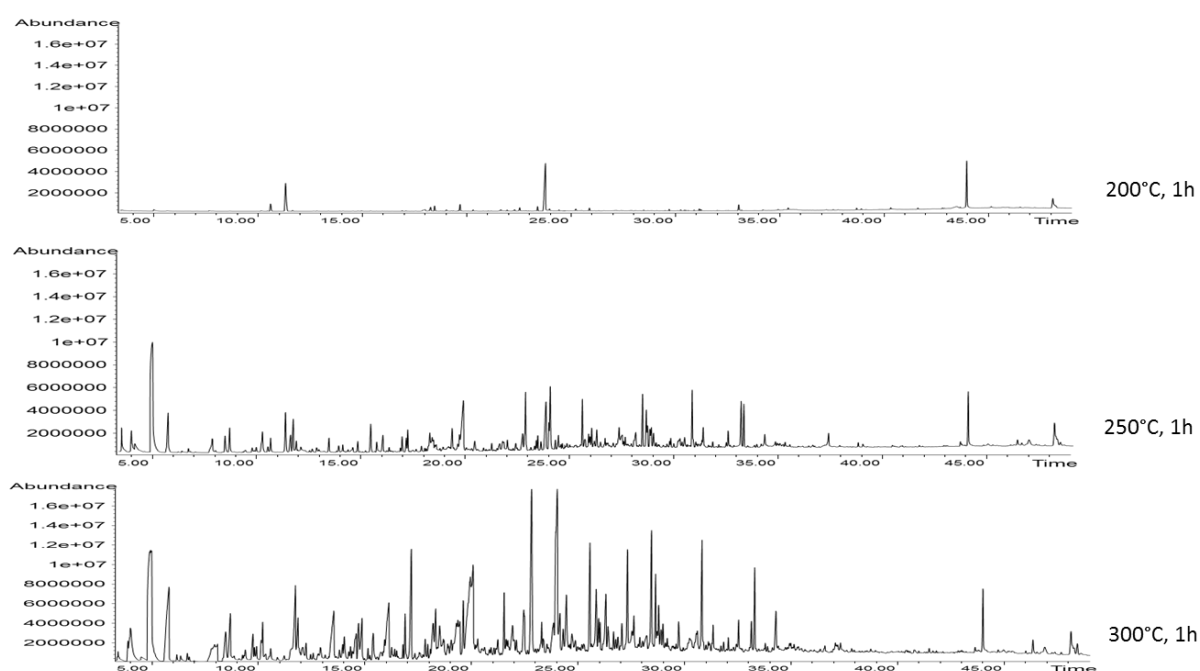
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The utilization of biomass in energetic processes has several disadvantages due to its high oxygen content, low calorific value, hydrophilic nature and high moisture content. Furthermore, the agricultural production of biomass involves high logistics and transportation costs due to the low energy density of biomass. These disadvantages can be reduced by the torrefaction pretreatment, which is a mild thermal pretreatment between 200 and 300°C for the conversion of biomass in an inert atmosphere. The purpose of the pretreatment from a chemical point of view is the removal of water and the acidic groups of hemicelluloses or the whole hemicellulose fraction with minor degradation of cellulose and lignin in the biomass. During the process water and a part of the volatiles are released, causing a decrease in mass, but an increase in the energy density; this way reducing the storing and transportation costs. Although the torrefied solid is the main torrefaction product, the characterization of the liquid fraction is also important in order to find the most suitable way to utilize the main by-product of the process.

In this work, the torrefaction liquid by-products of three typical Hungarian biomass materials, namely wheat straw, rape straw and black locust wood were studied. Five different torrefaction temperatures were applied: 200, 225, 250, 275 and 300°C with one hour isothermal period. Gas chromatography-mass spectrometry (GC/MS) and gas chromatography with flame ionization detector (GC-FID) techniques were used to provide both qualitative and quantitative results of the analysis of these by-products from torrefaction experiments. The yield of torrefaction products depends on the temperature and the nature of the biomass. By increasing the temperature, the mass of the solid material decreases, while the liquid yield increases. The liquid by-product is a mixture of various chemical compounds including acids, guaiacols, syringols, phenols, etc., forming as a result of the evaporation of extractable materials and the partial fragmentation of lignin, cellulose and hemicellulose during the mild pyrolysis. Increasing the temperature of the process increases the number of the components in the liquid product.



Pyrograms of rape straw liquid by-products (GC/MS)



## EVALUATION OF LIGNIN HYDROUS PYROLYSIS RESIDUES TO PRODUCE BIOCOKES AFTER CARBONIZATION

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The substitution of coking coals with biomass materials is receiving a lot of attention in recent years due to the simultaneous reduction in material costs and non-renewable carbon emissions in the carbonization process. Past research has suggested that hydrothermal carbonization (or hydrous pyrolysis) of biomass can produce residues with properties similar to those of cokes derived from coal [1]. However, this assumption was only based on the cold mechanical strength (i.e. tensile) of the cokes obtained. Furthermore, the coke yield obtained from biomass is limited by the different extents of degradation and concentrations of the main biomass constituents hemicellulose, cellulose and lignin. Indeed, the biomass constituent lignin produces higher char yields than cellulose and hemicellulose since it is the only one that possesses aromatic structures. Moreover, lignin is produced in vast quantities as a by-product in the pulp and paper industry, mainly as Kraft lignin, and will also be obtained as a waste product in future bio-refineries. Therefore, the aim of this work is to determine whether the residues obtained after hydrous pyrolysis of Kraft lignin can be transformed into a biological coke or biocoke after carbonization.

Residues were obtained after hydrous pyrolysis of a Kraft pine lignin using a wide range of reaction conditions (temperature, water content and residence time) and the residues were characterized through high-temperature rheometry, solid-state <sup>13</sup>C nuclear magnetic resonance (NMR), thermal gravimetric analysis (TGA) and field emission scanning electron microscopy with X-ray dispersive energy detector (FSEM-EDX). The results indicated that an increase in reaction temperature, an increase in residence time or a decrease in water content reduces the amount of fluid material in the residue. The hydrous pyrolysis conditions studied were not able to increase the maturation of lignin, i.e. shift the maximum fluidity to higher temperatures, but reduced the amount of mineral matter in the material. On the other hand, the residues obtained at high temperatures (> 300°C) presented good mechanical strength and porosity. The residue produced by hydrous pyrolysis at 350°C for 6 hours using 20 ml of water was chosen to carry out carbonization tests at 1000°C in a 80 g sole heated oven. The strength of the biocoke was assessed by the Ragan and Marsh method [2] and reactivity to CO<sub>2</sub> of the resulting biocoke was determined by the ECE-INCAR test [3]. Although the resistance to abrasion is not negatively affected, the reactivity of the biocoke is high compared to that of a prime coking coal used as a comparison. The results obtained were explained considering the surface area as determined by CO<sub>2</sub> adsorption and the composition of the inorganic matter determined by means of X-ray fluorescence (XRF).

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# THERMOGRAVIMETRIC ANALYSIS, COMPOSITION AND PORE DEVELOPMENT DURING PYROLYSIS OF COCONUT CORE

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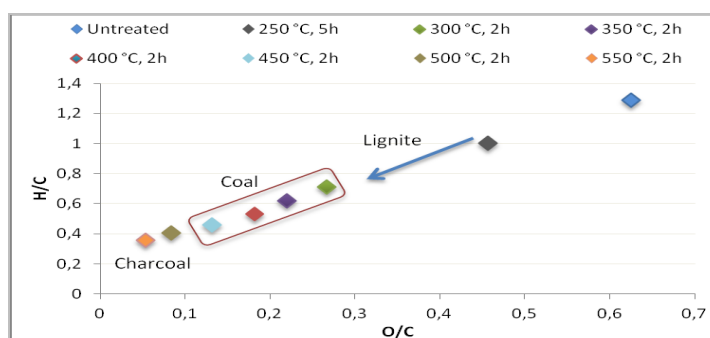
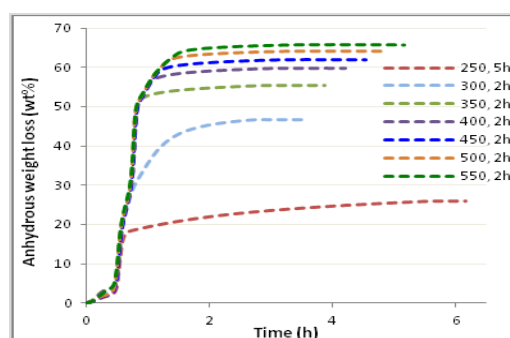
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## I. ABSTRACT

Presently, the coconut core or coconut endocarp *Acrocomia aculeata* variety present in the central-eastern region of South America, is an agro-industrial waste. A major feature of this biomass, is the high calorific value (HHV) of approximately 19,3 MJ/kg [1], which enable enormous potential of industrialization of coconut fruit in biorefinery to obtaining fuels, materials and chemicals, which justify a thorough study.

In this work, clean and dry particles of coconut core between 0.2 and 0.63 mm of size, were thermally decomposed at different temperatures (250 °C, 300 °C, 350 °C, 400 °C, 450 °C, 500 °C, 550 °C) in a nitrogen atmosphere. From the thermogravimetric curves, the most important weight loss was observed between 250 and 350 °C (Fig. 1). The change of the elemental composition after treatment, together with the untreated samples, was determined using an organic elemental analyzer (Thermo Scientific). From the evolution of the atomic ratio H/C as function of the atomic ratio O/C it can be seen that elementary composition changes to lignite [2, 3] under the treatment at 250 °C and towards a characteristic coal and charcoal at higher temperatures (Fig. 2).



**Fig. 1** Anhydrous weight loss (wt%) of coconut core. **Fig. 2** Van Krevelen plot for the treated and untreated coconut.

The specific surface of all samples was evaluated by adsorption of nitrogen using BET method at 77 K in a surface characterization analyzer (Micromeritics). The specific surface, increases with the treatment intensity, with a particular increase above 500 °C (Table 1).

**Table 1.** Surface area BET results.

|                                      | Untreated | 250 °C, 1h | 300 °C, 2h | 350 °C, 2h | 400 °C, 2h | 450 °C, 2h | 500 °C, 2h | 550 °C, 2h |
|--------------------------------------|-----------|------------|------------|------------|------------|------------|------------|------------|
| <b>Average BET (m<sup>2</sup>/g)</b> | 0.4       | 0.4        | 0.4        | 0.5        | 0.5        | 5.8        | 44.8       | 202.3      |

From the observation of coconut outer section with an environmental scanning electron microscope (ESEM), we registered for the first time the evolution of the pore structure with the treated temperature.

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## PREPARATION OF HIGH SURFACE AREA-ACTIVATED CHAR FROM BIO-CHAR BY KOH ACTIVATION AND ITS APPLICATION IN PHENOL ADSORPTION

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This study investigated the KOH activation of bio-char obtained from fast pyrolysis of different kinds of biomasses for adding its value as a phenol adsorbent. Bio-char derived from yellow poplar (YPC) and from Japanese red pine (JPC) were subjected to KOH activation at 700°C for 2 hr under N<sub>2</sub> inert condition with different ratios of 0, 2, and 4 (KOH/bio-char = w/w). Each activated char was referred to as its kind of biomass followed by the ratio such as YP0, YP2, YP4, etc. The phenol adsorption test was carried out up to 20 hr to reach an equilibrium state under various phenol concentrations in the range of 25-200 ppm.

The yield of activated char was 78.8 wt% for YP0 and 91.9 wt% for JP0 and it decreased to 40.5 wt% and 44.5 wt%, respectively, with the addition of KOH ratio of 4. The elemental composition also changed in the presence of KOH. The carbon ratio increased from 77.6 % and 81.9 % to 90.4 % and 90.1 % for YP and JP, respectively, while the hydrogen and oxygen ratio decreased. The surface morphology of each sample was determined by Scanning electron microscope (SEM) and Energy dispersive x-ray spectroscopy (EDS) analysis. From the SEM images, structural collapse and roughened surface of char were observed for YP4 and JP4. In addition, the major elemental composition of char surface changed by activation, specifically, the composition ratio of metals such as Mg, Al, K, and Ca decreased whereas that of carbon increased with the addition of KOH. Meanwhile, the surface area and pore distribution of char was largely influenced by KOH activation. The BET surface area of YP4 and JP4 were 1908 m<sup>2</sup>/g and 2711 m<sup>2</sup>/g, which increased by a factor of 205 and 102 times compared to YPC and JPC, respectively and even higher than that of commercial activated char (AC). Total pore volume also increased, but interestingly, micropore was produced most when the KOH ratio was 2.

In the phenol adsorption test, it was observed that the removal efficiency of phenol by activated char was significantly enhanced as KOH ratio increased. Also, both YP4 and JP4 were superior in adsorption capacity to AC in the following order : JP4>YP4>AC. The 96% of phenol was removed from 50 ppm of phenol solution, which has been measured as a concentration in effluents, by using activated char with KOH ratio of 4.

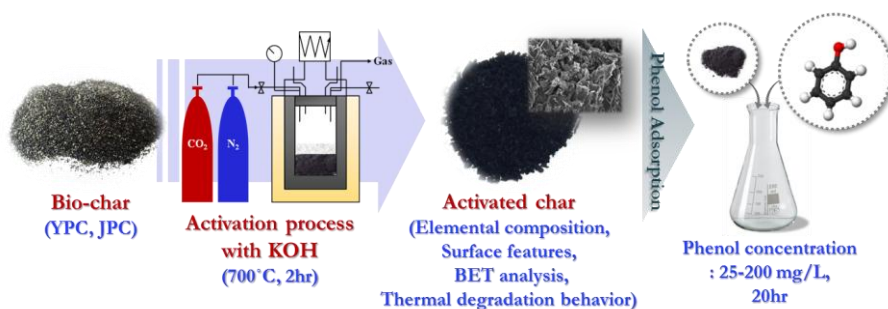


Figure 1. Overall process of activated char preparation and phenol adsorption

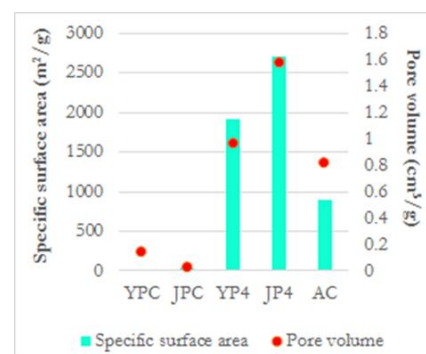


Figure 2. Comparison of specific surface area and pore volume of bio-char, KOH activated char, and commercial activated char

## TORREFACTION AS A PRE-TREATMENT FOR FLASH PYROLYSIS: A CHAIN ANALYSIS

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Flash pyrolysis oil from biomass is an attractive energy carrier because of its high volumetric energy density and its potential as a drop-in fuel in refineries. However, pyrolysis oil offers a number of challenges with respect to its quality. In comparison to fossil oil it has a low pH, a high oxygen content and a lower calorific value. To increase the oil quality, torrefaction could be applied as a pre-treatment for the flash pyrolysis process. Bio-oil from torrefied biomass was shown by a number of authors to have a higher quality than bio-oil from virgin biomass [1] [2] [3]. Furthermore, torrefaction also significantly improves the grindability of the feedstock. A good feedstock grindability is especially interesting for flash pyrolysis reactors, because these reactors require a feedstock with small particle size (< 2 mm). However, there is a price to be paid for this higher oil quality: an extra pre-treatment step, as well as severely lower oil yields from the flash pyrolysis process. The purpose of this work is to calculate the energy efficiency of the whole chain of torrefaction as a pre-treatment step for the production of bio-oil via flash pyrolysis.

To compare the different chains, the boundaries for the chain analysis are set equal. At the start of each chain, fresh biomass to be dried and ground is used, and at the end of each chain, the produced bio-oil is compared based on yield, heating value and quality (quality is expressed as oxygen content). In addition to literature data, experimental data was used from flash pyrolysis experiments in a range of 450-550°C with woody biomass (a softwood stream, European spruce, and a hardwood stream, ash, both virgin as well as torrefied variants) performed at the laboratory of Thermal Engineering of the University of Twente (UT). The obtained oil as well as the raw material were subjected to proximate and ultimate analyses to determine the heating value and oxygen content. Torrefaction experiments, with torrefaction temperatures ranging from 250-300°C, were performed both at the UT as well as at a torrefaction pilot plant of a Dutch research centre.

The chain with a torrefaction pre-treatment before pyrolysis is compared with a chain without torrefaction. For comparison reasons the latter chain with only pyrolysis is extended with an HDO (hydrodeoxygenation) post-treatment to upgrade the bio-oil to the same oxygen content as for the first chain. Energy costs of the production of hydrogen for this post-treatment were taken into account.

Experimental flash pyrolysis results show that oil yields from torrefied material went down with approximately 10-40% compared to oil yields from virgin material, depending on torrefaction severity. Heating values of the oil increased with 5-20%, and oxygen content lowered with 10-20%. The softwood stream yielded slightly better results than the hardwood stream. It is noted that the pyrolysis experiments with torrefied biomass have been carried out at the same pyrolysis conditions, while one could expect that the optimum operating window could be different. More experimental research is required on this point.

When assuming a decrease in grinding energy of 85% [4], the energy efficiency to products (char, oil, gas) went up from 58% for the pyrolysis with HDO post-treatment chain, to 68% for the torrefaction/pyrolysis chain. These results were obtained for softwood, a torrefaction temperature of 280°C and residence time of 45 minutes, and a pyrolysis temperature of 525°.

Concluding: from an energy perspective, a torrefaction pre-treatment before flash pyrolysis has a positive impact on the bio-oil chain's energy efficiency, especially when the increase in oil quality in the form of oxygen decrease is taken into account. Further improvement of the energy efficiency of the torrefaction/pyrolysis chain can be expected by experimental investigation of the interaction of the two processes.

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## Exothermal phenomena during torrefaction of wood chips

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Torrefaction is a mild thermal treatment performed at temperature in-between 200 and 300°C under neutral atmosphere. It induces some transformations into the material, resulting in improved features as a solid biofuel: hydrophobicity, higher energy content, increased grindability, improved flowability of resulting powders. This work is focused on exothermal phenomena which could occur during wood torrefaction. These phenomena could be a major issue for industrial process, leading to thermal runaway into the furnace. Exothermicity has been already reported in the literature [1]. It has been mainly put into evidence during torrefaction of massive wood pieces, typically with dimensions of several centimeters. Due to the rather weak thermal conductivity of wood, such geometry is unfavourable for the transfer and discharge of the heat produced at the heart of the piece. Similarly, a bed of wood chips could be an unfavourable configuration. Furthermore, industrial processes will probably not work under strictly neutral conditions, as leaks can not be avoided in large vessels and sweeping with huge flows of pure nitrogen is too expensive. The presence of a few percent of oxygen into the gas could promote exothermal reactions.

The objective of this work is to characterize exothermicity in wood chips exposed to temperature ranging between 240 and 300°C. Torrefaction tests have been performed with either hardwood chips (ash) or softwood chips (douglas), in neutral conditions or in the presence of a few percents of oxygen. Temperature into some wood chips has been recorded during the test. The table 1 gives an overview of the results obtained under neutral conditions. The excess of temperature indicated here ( $\Delta T_{\max}$ ) is defined as the maximal difference between the temperature into wood chips and the furnace temperature.

Exothermicity has been put into evidence in almost all the experiments, but the extent of the excess of temperature depends on the nature of wood (see table 1): it is more pronounced with ash wood than with douglas. The presence of oxygen into the gas impacts significantly the results, for oxygen contents as low as 2%v. The excess of temperature in such conditions can exceed 100°C.

| Temperature | Ash wood  |                   | Douglas   |                   |
|-------------|-----------|-------------------|-----------|-------------------|
|             | Mass loss | $\Delta T_{\max}$ | Mass loss | $\Delta T_{\max}$ |
| 240 °C      | 11%       | 12.6°C            | 5%        | 3.2               |
| 260°C       | 24%       | 33.9°C            | 8%        | 3.6°C             |
| 280°C       | 35%       | 53.1°C            | 19%       | 7.2°C             |
| 300°C       | -         | -                 | 33%       | 12.5°C            |

Table 1 – Torrefaction tests under neutral conditions: mass loss and temperature excess into the wood chips, for ash or douglas wood respectively. Temperature indicated here is the furnace temperature.

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## OPTIMISATION OF TORREFACTION AND PYROLYSIS OF INVASIVE ALIEN PLANTS FOR ENERGY APPLICATIONS

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In order to manage and control invasive alien plants (IAPs) prevalent in Africa, thermochemical conversion through torrefaction and slow pyrolysis was considered for energy applications. Two IAP biomasses, *Lantana camara* (LC) and *Mimosa pigra* (MP) characterised by high hemicelluloses and lignin content respectively, were used. For each of the processes, a separate optimisation study was conducted using central composite design (Statistica software version 12). The studied process variables were maximum temperature (200-300 °C for torrefaction and ≤ 625 °C for pyrolysis); hold time at maximum temperature (HT, ≤ 80 min) and heating rate (HR, ≤ 20 °C min<sup>-1</sup>). A thermogravimetric analyser (TG) was used to analyse the char yield evolution while the higher heating value (HHV) of the generated char was determined with a bomb calorimeter (Cal2k Eco Calorimeter, 2013). The formation of some characteristic volatiles was monitored by coupling TG with a Mass Spectrometer (MS).

Table 1: Influence of an increase of the process variables on the char yield and HHV

|            | Process        | Temperature (°C) | Hold time (min) | Heating rate (°C min <sup>-1</sup> ) |
|------------|----------------|------------------|-----------------|--------------------------------------|
| Char Yield | Torrefaction   | ---              | ---             | +                                    |
|            | Slow Pyrolysis | ---              | -               | -                                    |
| Char HHV   | Torrefaction   | +++              | +++             | Max at 10.5 (LC) and 20(MP)          |
|            | Slow Pyrolysis | +++              | +               | no trend                             |

---, +++ and Max indicate statistical trend (95% confidence interval); - and + are observed trends not detected by statistical analysis

Temperature majorly influenced the char yields and HHV for both processes (Table 1). The mass yield decreased with increasing temperature, while HHV values increased up to 25 and 31 MJ kg<sup>-1</sup> for torrefaction and pyrolysis, respectively. During torrefaction, for instance at 280 °C, LC recorded the higher conversion (differences up to 14 wt. %) than MP due to higher hemicelluloses content, resulting in enhanced char HHV (25 MJ kg<sup>-1</sup> for LC compared with 22 MJ kg<sup>-1</sup> for MP). Under pyrolysis, MP gave higher char yields with increased HHV (up to 31 MJ kg<sup>-1</sup>) due to higher lignin content leading to better energy yield (EnY). At 550 °C (HT of 15 min and HR of 4 °C min<sup>-1</sup>), MP char recorded an EnY of 53% compared with 47% for LC char.

During torrefaction, HT statistically impacted on mass yields and char HHV, with char yields decreasing as HT was prolonged, ultimately resulting into increased HHV. Under slow pyrolysis, the influence of HT was not statistically detected, though similar trends like those of torrefaction were observed. Due to the higher degrees of conversion during the heating stage of slow pyrolysis, the impact from HT was less influential on the product quantity and quality. For example, during a HT of around 50 min, decreases of LC char at a rate of 0.25 and 0.007 % min<sup>-1</sup> were observed at 280 and 440 °C respectively. The associated increases in HHV were of 2.7 MJ kg<sup>-1</sup> at 280 °C, and 0.27 MJ kg<sup>-1</sup> at 440 °C. Concerning the influence of HR, scarcely documented under torrefaction, it is interesting to note that different trends were obtained for both processes. As expected under pyrolysis, elevated HR yielded reduced char, while torrefaction gave an opposite trend. HR statistically impacted char HHV for torrefaction with an optimum HR at 10.5 and 20 °C min<sup>-1</sup> for LC and MP respectively, while no trend could be observed for slow pyrolysis (Table 1). Slow pyrolysis of biomass is majorly influenced by the conversion of cellulose, while under torrefaction, cellulose is slightly converted. TG/MS study showed that the mechanisms of lignin conversion could have a critical role in the observed trend. HR optimisation can enhance EnY up to 10% together with a 3-fold reduction in torrefaction time.

This study highlights the influence of biomass composition on optimisation results. As the optimised HR was found different for torrefaction and slow pyrolysis, a stepwise pyrolysis with two different HR could lead to even better energy yields.

## Characterization of Activated Carbons Obtained from Different Bamboo Residue Carbonizates

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In Thailand, surface and groundwater are the major sources for potable water. However, many of them have been polluted due to an inefficient management of residual waters. Bangkok is an example of this situation: with an estimate population of 20 million people, the daily wastewater production accounts to 4 MCM discharged to 117 canals around the city that are subsequently discharged in the Chao Phraya River and finally into the Gulf of Thailand. However, water flows slowly which results in the accumulation of polluted water that turns black, releasing an unpleasant smell and becoming a major public health issue [1].

Activated carbon is one of the most widespread adsorbents employed for the removal of organic and inorganic pollutants from gaseous or liquid mediums. It is also frequently found in water treatment processes. Bamboo is a plant native from Asia with excellent physical and mechanical characteristics, that can develop an extraordinary porous microstructure with high absorptive capacity [2–4]. Due to its fast growth, high flexibility, low weight and low cost, bamboo is extensively used for the production of several goods that play a crucial role in the daily lives but it is also a large source of agricultural waste (e.g. bamboo dust).

The main scope of this study was to examine the effects of different carbonization techniques on the properties of activated carbon (AC) by using hydrothermal carbonization (HTC) and pyrolysis to prepare the precursors for a subsequent chemical activation with KOH. Additionally, the process water of the HTC was used as impregnation medium for the chemical activation to find an effective application for this sub product. The solid yields of AC from pyrolysis char were the highest, followed by the HTC char, and the lowest yields were obtained from direct biomass activation. The solid yields are significantly different between the carbonization treatments, but not significantly different between dry and wet activation. Iodine number determination was employed to estimate the surface area, which ranged between 1117-1648 mg/g. The iodine adsorption of the ACs from pyrolysis and HTC chars was not significantly different between each other, but significantly higher than that of the ACs obtained from the direct biomass activation. The adsorption capacity of the ACs was studied with methylene blue (MB) adsorption tests and the maximum values ranged between 528-753 mg/g. The results were not significantly different among the treatments, excluding direct biomass wet activation with distilled water, which were significantly lower.

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## Assessment of the Technical Feasibility of Activated Carbon Production from Hydrochar

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In the recent years hydrothermal carbonization (HTC) has become an interesting research subject for biomass conversion into fuels and advanced materials. To date most of this research revolves around the chemical and technical optimization of the HTC process itself, HTC of different biomasses, as well as the hydrochar application. It has been shown that the hydrochar production from different biomass types is economically feasible and has a positive environmental impact when the hydrochar is used to offset the impact of coal-based energy sources. Nevertheless it is still a question if the energetic use of hydrochar is the best alternative, from an economic and also from an environmental point-of-view. Therefore, the question about the most suitable applicability for hydrochar remains open.

The production of sustainable activated carbon (as a high price commodity) from hydrochar might be a suitable alternative in this respect. Chemically activated hydrochar has an outstandingly large surface area and can be used for the removal of contaminants from different water sources. The problem statement of this work was to study the technical feasibility of activated carbon production from hydrochar made from biogas digestate under alternating process conditions (process temperature, retention time, catalyst concentration) together with the applicability of the activated carbon in water treatment process, especially for the adsorption of phenols and phenol-like compounds. The main scope was to trace back the impact of the alternating process conditions for the production of a stable hydrochar suitable for activation. Currently in Germany, biogas digestate has in this respect a large potential since more than 8,000 agricultural biogas plants are currently in operation. The production of activated carbon from biogas digestate via HTC would therefore solve a major disposal problem and lead a step forward to establish new sort of biorefineries for the new and developing bio-economy.



## TGA/DSC STUDY OF ENERGY FLOWS FROM BIOMASS SLOW PYROLYSIS

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Interest in the process of biomass slow pyrolysis has been revived in recent years with the introduction of biochar as a potential carbon sequestration and soil amendment technology. Slow pyrolysis favours char production by encouraging secondary homogenous gas phase reactions and heterogeneous reactions between volatiles and the surface of hot chars. Whereas secondary pyrolysis is generally considered exothermic, for primary pyrolysis a wide range of heats of reaction has been reported. It has been suggested that the process of volatilization is endothermic, while primary char formation is exothermic, so that the overall enthalpy of primary pyrolysis varies with char yield [1].

Biochar production systems are particularly attractive when their net energy yield is positive. The purpose of this study is to investigate energy flows from biomass slow pyrolysis in order to identify energy-efficient production conditions. The thermokinetic behaviour of coarsely ground softwood pellets was characterised by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under a nitrogen atmosphere. Although high heating rates to inhibit secondary reactions are typically preferred in kinetic experiments, both high and low heating rates were employed in this work, since slow pyrolysis is the process of interest. Five thermal programs were adopted: three linear heating programs (2°C/min, 4°C/min and 40°C/min) and two stepwise programs (20°C/min) with four successive 10 min isothermal segments (110°C, 250°C, 325°C, and 400°C; 225°C, 287°C, 363°C, and 425°C).

All mass loss rate curves presented similar features, with a first moisture evaporation peak below 200°C (representing 7.4% of sample mass on average), followed by an asymmetric peak between 250°C and 500°C (with maximum mass loss rates near 350°C) that was deconvoluted into three reaction peaks at around 300°C, 350°C and 425°C attributed to hemicellulose, cellulose and lignin degradation, respectively. Despite the difference in heating rate across experiments, char yields at 600°C agreed within 1.2%. This suggests that secondary reactions are inhibited during TGA.

Although thermogravimetric curves were very similar, heat flows varied greatly across experiments. At low heating rates (2°C/min and 4°C/min) pyrolysis was strongly endothermic. However, at 20°C/min and 40°C/min, the initial endotherm was followed by an exothermic phase beginning near 400°C. The total heat required for pyrolysis (comprising heat required to raise the sample temperature and that required to sustain reactions) was calculated by integrating the area under normalised heat flow curves. 8.4 kJ/g were required to reach a peak pyrolysis temperature of 900°C at a heating rate of 4°C/min. In contrast, at 40°C/min, the exothermic phase of pyrolysis was sufficient to bring the net heat required for pyrolysis to zero once the sample reached 900°C.

Given that no significant differences in mass loss or char yields were observed between experiments, changes in the mechanism of pyrolysis appear responsible for the wide variations in process heat flows. The thermal history of the sample may also be relevant, since different total heat requirements were calculated for the two stepwise experiments, even though both thermal profiles followed the same heating rate with the same number of isothermal segments.

The DSC results showed that heat requirements for pyrolysis of the same feedstock at the same peak temperature can vary with changes in heating rate by as much as 8.4 kJ/g (46% of the higher heating value of the feedstock in this case). If this phenomenon can be extrapolated to large-scale processes, it can be leveraged to maximise net energy yield by selecting production conditions that reduce the process heat requirements. However, differences in properties of both char and fuels should be expected, and these may dictate production conditions. In addition, water evaporation accounted for approximately 60% of the heat required for the endothermic part of pyrolysis at 40°C/min, emphasising the importance of feedstock drying to improve the energy efficiency of the process.

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## Improved Charcoal Yield from Pyrolysis of Biomass for Heating Fuel

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Production of heating fuels from biomass to compete with gas and coal, specifically in smoke controlled areas like those in the UK is a costly business [1]. This cost comes from the wastage due to part conversion of input biomass to gas and liquid side products, at too low a flowrate to justify much treatment other than flaring. This study aims to investigate methods of increasing the total utilisation of the input biomass economically via the use of inert catalysts, in particular bentonite clay. This study presents a system based on pine wood, an abundant and cheap biomass source.

Experimental work has been performed which mixes various concentrations of clay with pine wood and conducted slow pyrolysis at temperatures between 400 – 700°C. The work has found that charcoal yield can be increased by up to 1% per 10% concentration (w/w – wet basis) of clay added, at the expense of oil yield. Gas yield is also increased indicating that bentonite clay is acting as a cracking catalyst. GC-MS results indicate that significant oil cracking is occurring, making the liquid stream more useful for heating and fuel purposes. At the same time, the volatile fraction of the charcoal does not reduce as much as expected, meaning that the charcoal potentially can still be used as a high value fuel with these higher concentrations of clay. Further fire testing is required to confirm that this fuel quality is maintained.

This experimental work has then been used for techno-economic modelling which has shown there can be significant improvements in the production costs and land-footprint of each ton of renewable fuel produced. The significant finding from this work is that a large portion of this benefit comes from the reduction in biomass required. A simple system utilising wet wood (30% MC) saves 15-20% of the initial level of biomass required to produce this heating fuel.

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## Finite element and space-time integral models for biomass torrefaction

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Biomass torrefaction is a mild pyrolysis of biomass where raw biomass is heated in the absence of oxygen at temperatures of 200-300°C for the purpose of upgrading solid biomass fuel. Biomass torrefaction is a complex process involving coupled physical and chemical phenomena including heat and mass transfer and thermochemical reaction kinetics at both the particle scale and the reactor scale. Industrial processes of torrefaction usually use biomass particles or pellets with a size of 1 cm or larger. Temperature gradients are built within this large-sized biomass during torrefaction, which further lead to non-uniform conditions for thermochemical conversion across the biomass particle. In order to have a deep understanding of the intraparticle physical and chemical phenomena during biomass torrefaction, the present work developed two mathematical models based on the finite element method (FEM) and space-time integral method, respectively. The FEM numerical model considers the conductive, convective and radiative heat transfer, convective and diffusive mass transfer, and torrefaction reaction kinetics within the biomass particle. The space-time integral model only considers the main physical and chemical phenomena during the torrefaction of a dry biomass particle, which includes three successive processes: by assumption of an initial pre-heating process, a homogeneous decomposition process followed by a post heating process on the particle scale. Results showed that both the FEM model and the space-time integral model were in good agreement with experimental results from different literature sources. Both the FEM model and the space-time integral model can predict the dynamic temperature profile within the biomass particle and the residual solid mass fraction in the biomass torrefaction. In addition, the effects of process parameters including torrefaction duration and temperature, and the effects of particle size predicted with the space-time integral model were similar to that with the FEM model. Regarding the FEM model on the particle scale being computationally expensive, the space-time integral model is more recommended for implementation into a reactor-scale model.

# Hydrothermal Carbonization of Biomass Constituents

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## 1. Introduction

Carbonaceous materials received a great attention in the last decade because of their wide range of applications such as water purification, electrode materials for super-capacitors, catalyst, catalyst support material and solid fuel. Hydrothermal carbonization is also called hydro-pyrolysis which has been widely used to obtain carbonaceous materials from biomass and its derivatives for a century. Basically, any kind of biomass and its components such as cellulose, hemicellulose (xylose, arabinose, mannose, glucose, galactose etc.), lignin as well as its dehydration products like furfural and 5-hydroxymethylfurfural (HMF) can be used as a carbonaceous material source.

Hydrothermal carbonization is to allow carbonaceous sphere formation in nano and/or micro size. This carbonaceous spheres have a hydrophilic surface due to the presence of the surface functional groups such as -OH, -C=O, -COOH. Hydrothermal carbonization of biomass in aqueous media allows lots of oxygenated functional groups to occur on the surface of the carbonaceous material and these functional groups play a very critical role for some applications such as dye or heavy metal ion adsorption.

## 2. Experimental

The hydrothermal carbonization of cellulose, glucose and lignin as biomass constituents were carried out in 1 L Parr stirred pressure reactor (model 4571) under different reaction conditions changing the temperature, biomass concentration and the reaction time. Obtained carbonaceous materials were also characterized with X-Ray Diffraction (XRD), Raman Spectroscopy, Fourier Transform Infrared Spectroscopy (FT-IR), <sup>13</sup>C CP-MAS NMR, X-ray Photoelectron Spectroscopy (XPS), High Contrast Transmission Electron Microscopy (CTEM), Scanning Electron Microscope (SEM) and Elemental Analysis to understand the effect of operation conditions on the chemical, structural, physicochemical properties and formation process of hydrochar samples.

## 3. Results and Discussion

Reaction temperature is the main parameter for the hydrochar synthesis; however, reaction time and biomass concentration have a slight influence. Synthesized hydrochar samples have higher carbon yield when compared with raw biomass. All hydrochar samples have an aromatic structure and large amounts of O-functionalities on the surface. The resulting hydrochar consists of micron/submicron size spherical and semi-spherical particles, which are formed by the polymerization of furfural species.

According to the H/C and O/C atomic ratios, dehydration is the main reaction at 180 and 220 °C. During the dehydration process; ether, anhydride and lactone bonds are possibly formed. Biomass concentration has no effect on the H/C and O/C atomic ratios in model biomass. Decarboxylation and demethylation reactions took place when temperature and reaction time were raised respectively. Decreasing of H/C and O/C ratios indicate -CH<sub>3</sub> and CO<sub>2</sub> elimination respectively. High O/C ratio is the evidence of low carbonization rates and the existence of polar functional groups on the hydrochars.

## 4. Acknowledge

The authors would like to acknowledge TUBITAK for providing financial support for this work through the Project "113Z635".

## Biochar from medium pyrolysis temperatures for smelting plant applications

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The overall reduction of GHG emission is one of the biggest political challenges of our time. To fulfil the target of a temperature increase of 1.5 to maximum 2 °C compared to the reference year 1990, the European Union suggests a decrease of CO<sub>2</sub> emission of 40 % by 2030 compared to the reference year [1]. Energy efficiency as well as substitution of fossil fuels in the energy sector will provide a large proportion of these reductions. The overall production of ferrous and non-ferrous metals is responsible for approximately 10 % of the anthropogenic GHG emissions [2, 3]. Since reduction of metal-oxides is feasible with carbonaceous reducing agents only, alternative carbon sources are investigated.

Biomass and biochar are renewable resources which can substitute coal, char or coke in smelting plant applications for the production of pure metals. The biochar must provide specific properties which are often not fulfilled for low-temperature carbonization products, while primary biochar yield decreases with increasing pyrolysis temperature. The suitable carbon content from primary and secondary biochar is investigated for spruce, oak and pine wood in a temperature range from 400 to 1000 °C. The fixed carbon content according to the organic residue of ASTM D 3175 is defined as a suitable value for the carbon content as a reducing agent and is compared to elementary composition of the biochar. The reactivity of the primary and secondary biochar is analyzed in O<sub>2</sub>, N<sub>2</sub> and CO<sub>2</sub> atmospheres. The present research will investigate possible process routes to optimize the carbon balance for reducing agents in selected smelting plant applications.

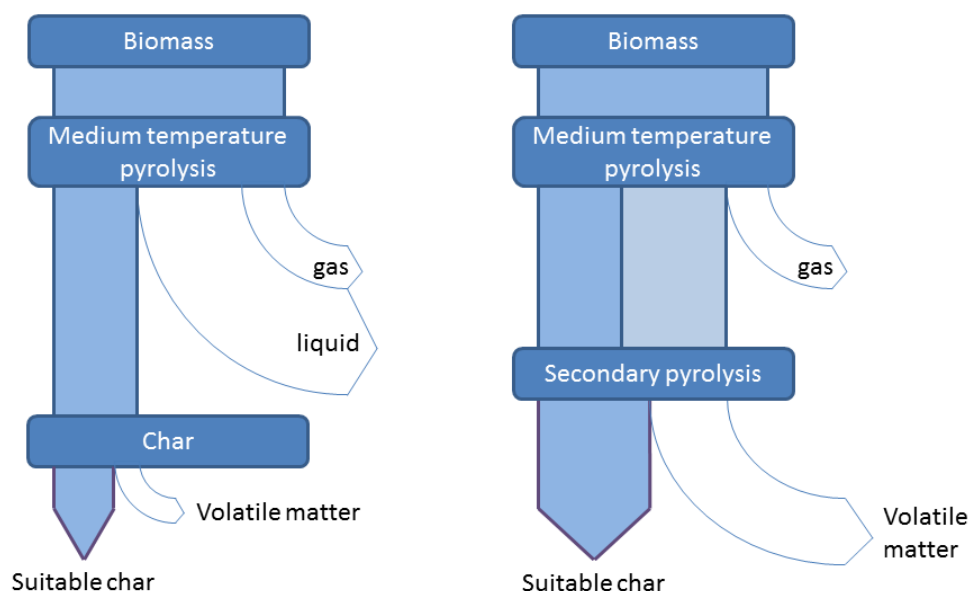


Figure: Example of different process routes for the production of biochar for smelting plant applications

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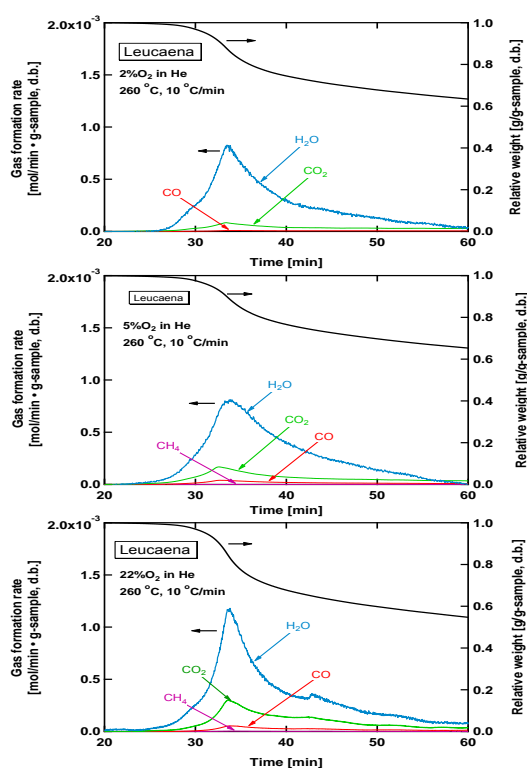
## EFFECT OF OXYGEN CONCENTRATIONS ON THE TORREFACTION OF BIOMASS AT TEMPERATURE BELOW 300 °C

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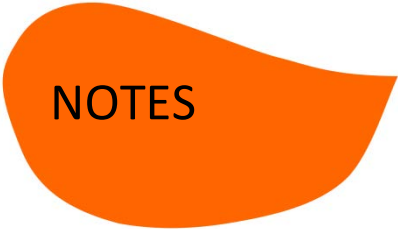
Torrefaction is one of the thermal treatment techniques at relative low temperature range of 200 – 300 °C in an inert atmosphere, which aims to improve the fuel properties attractively for further utilization such as combustion, gasification and/or co-combustion. Many studies have been conducted on the properties of torrefied biomass including woody and non-woody biomass by varying temperature and holding time during torrefaction. It was found that the energy density as well as the higher heating value (HHV) was increased progressively at higher torrefaction temperature and at longer holding time [1]. This is due to the increase in carbon content and decrease in oxygen content in the biomass. The torrefied biomass structure was also found to become more hydrophobic. The improvement of grindability of torrefied biomass which seems to be the feature for this technique was reported. However, few studies have been conducted to examine the effect of oxygen concentrations on the torrefaction at temperature below 300°C. There still remains a need to study the influence of different oxygen concentrations on the thermal reactivity during the torrefaction as well as their effects on the chemical properties of the torrefied biomass. In this study, woody biomass (*Leucaena Leucocephala*) was torrefied at 200, 240, and 260 °C under the oxygen concentration of 2, 5, 10, and 22 %. The gas formation rates during the torrefaction under the different oxygen concentrations were also examined in detail by using TG-MS technique as shown in Fig. 1. It was found that the different oxygen concentrations affected significantly the reactivity of biomass during the torrefaction especially at 260 °C. At 260 °C, the high oxygen concentration affected significantly the chemical properties of the torrefied biomass. The results obtained from the study provide the basic information for the design of torrefaction process.



**Fig. 1** Changes in gas formation rates during the torrefaction of leucaena under different oxygen concentration at 260 °C.

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# NOTES

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ABSTRACTS

# Bio-oil

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## Oral presentations



## STUDY OF THE REACTIVITY OF PLATFORM MOLECULES IN AQUEOUS SOLUTION AND IN THE PYROLYSIS OIL DURING HYDROTREATMENT

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In the last decades, the depletion of crude oil brought up the necessity to develop alternative and renewable methods for the production of fuels and chemicals. Pyrolysis of lignocellulosic biomass produces a bio-oil that can be used for energetic applications as fuels for special boilers and turbines, but its quality is too low to be considered for transportation or for chemicals. A possibility for upgrading pyrolysis oils consists in hydrodeoxygenation (HDO) [1]. This method reduces the oxygen content in the organic molecules producing an upgraded oil, which is more similar to crude oil and therefore can be co-processed in an existing petrol refinery. Despite HDO has been one of the favoured upgrading methods studied in literature, a lot of challenges are still remaining, in particular the stability of catalysts.

Our work was addressed in two main subjects: the study of alternative catalysts for HDO and understanding how the reactivity of some platform molecules (phenol and glucose) changes if they are studied as model compounds in an aqueous solution or in pyrolysis oil. The catalyst subject to this study was NiCu/Al<sub>2</sub>O<sub>3</sub>, which showed in previous works [2,3] a higher hydrogenation/hydrodeoxygenation activity in comparison to other nickel-based catalysts. The experiment with the model compounds in aqueous solution were carried out using a 10% solution of phenol and a solution 10% glucose in a batch autoclave at 340°C (80 bar hydrogen at room temperature). For the experiment in pyrolysis oil, phenol-d<sub>6</sub> and glucose-<sup>13</sup>C<sub>6</sub> were added to the bio-oil in small quantity in order not to alter the matrix, but in a concentration that could still be well detected by GC-MS and <sup>13</sup>C-NMR. The experiments were carried out in the same autoclave and in the same conditions as for the model compounds, and compared to experiments where only pyrolysis oil was used. In order to gain insight into the effective hydrodeoxygenation and compare them to Ru/C as another catalyst often reported in literature, the same experiments were performed also without a catalyst and over Ru/C.

Phenol as model compound was completely converted over NiCu/Al<sub>2</sub>O<sub>3</sub> with high selectivity to cyclohexane, demonstrating its catalytic HDO activity. In the experiments with pyrolysis oil over NiCu/Al<sub>2</sub>O<sub>3</sub> and Ru/C, phenol was still detected in relative high concentration in the upgraded oil despite the global deoxygenation degree of the bio-oil was 67-70%. Mainly cyclohexanone (and only in small concentration methylcyclopentane) was found as product of the conversion of phenol in pyrolysis oil over NiCu/Al<sub>2</sub>O<sub>3</sub>, while methylcyclopentane, cyclohexane and cyclohexanol over Ru/C. The selectivity of NiCu/Al<sub>2</sub>O<sub>3</sub> towards ketonic species in pyrolysis oil was already observed at lower temperatures [3] and it is important to consider that in the pyrolysis oil a lot of factors can influence the reaction favouring other products, like the interaction between different organic compounds, competitive adsorption on the catalytic surface and a probable poisoning of the catalyst during the reaction. The experiments with glucose were more difficult to evaluate because glucose tends to decompose at this temperature, as verified in the blank experiment where coke and gases were mainly produced. Over NiCu/Al<sub>2</sub>O<sub>3</sub>, glucose in aqueous solution was mainly converted in methane (82 mol% carbon), while in the pyrolysis mixture no easily associable products of the glucose-<sup>13</sup>C<sub>6</sub> were detected in the upgraded oil. Probably the reaction produced a large variety of compounds that are under the detection limit of the instrument or it favoured coke formation.

In conclusion a deep HDO study of the platform molecules in the pyrolysis oil helped in understanding their different reactivity in this complex mixture and this can be useful in future to optimize the reaction conditions and the catalyst.

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**Fractionation and analysis of biomass fast pyrolysis oils by liquid chromatography***N. Charon<sup>1</sup>, A. Le Masle<sup>1</sup>, L. Chahen<sup>1</sup>*<sup>1</sup> IFP Energies nouvelles, Rond-point de l'échangeur, BP3, 69 360 Solaize, France

Transformation of lignocellulosic biomass (wood, forest residues, straw,...) into biofuels and chemical intermediates has sparked great interest as one of the main substitutes to fossil fuels in the future energy mix. Fast pyrolysis is one of the thermochemical pathways that enables biomass direct liquefaction, breaking down the lignocellulosic matrix and converting the solid and heterogeneous solid into bio-oils.

Despite a large number of published papers, analytical characterization of fast pyrolysis oils is still a challenge today. Bio-oils are complex chemical mixtures composed of a large diversity of oxygenated compounds (*i.e.* alcohols, sugars, carboxylic acids, carbonyls and phenols) whose characterization is essential to understand conversion reactions and to develop/optimize biomass conversion and bio-oil upgrading processes. Some of these compounds such as sugars are not thermally stable and cannot be fractionated by classical distillation as for fossil oils. Relevant, and sometimes dedicated, analytical methodologies based on sample preparation and complementary chromatographic techniques are required to provide a detailed description of the chemical composition of these oxygenated liquids.

This presentation provides an overview of some recent analytical developments carried out using liquid chromatography techniques that are particularly well adapted for analyzing such bio-oils at low temperature, because of their low thermal stability. In this work, a method based on size exclusion chromatography has been performed at a semi-preparative scale to physically fractionate a biomass fast pyrolysis oil without any thermal degradation of the sample. Three fractions, from complementary molecular weight ranges, have been collected with a satisfactory mass balance. Furthermore, centrifugal partition chromatography is a preparative liquid technique that does not require traditional solid supports and enable to isolate compounds according to their solubility in a mix of solvents. This technique has been successfully used to fractionate a bio-oil in nine fractions ranging from different polarities and can replace physical separation by distillation, only suitable for the light water fraction of bio-oils.

## WOODY BIOMASS PYROLYSIS AND BIO-OIL UPGRADING BY HYDRODEOXYGENATION (HDO)

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Woody biomasses are potentially well suited for the production of renewable fuels and chemicals. Thermal conversion of biomass by pyrolysis is a well understood process to produce three main products; condensable vapours (bio-oil), gases and a solid product known as bio-char. The yield and quality of the produced bio-oil varies significantly with feedstock, reactor, condensation technology and operating conditions. Producing high yields of bio-oil with a low water content is of particular interest for further upgrading by hydrodeoxygenation.

This research is focused on the determination of optimum reactor technology and operating conditions to produce bio-oil suitable for upgrading by hydrodeoxygenation. Two different fluidized reactor technologies for pyrolysis (1 kg/h scale), gas and mechanically fluidized, were investigated to compare bio-oil product yields and quality, with a main focus towards the bio-oil water content. Identical feeding (mechanically agitated with a timed pinch and pulse system) and fractional condensation technologies (five condensers in series maintained at progressively lower temperatures) were used in both cases. Pyrolysis at 500 °C was performed with both reactors. Additional reaction temperatures (450 and 475 °C) were also explored for gas fluidized experiments. Bio-oil fractions that were low in water content, were upgraded using a 100 ml batch reactor using a commercially available ruthenium catalyst.

The mechanically fluidized experiments produced total bio-oil yields similar to gas fluidized experiments. Notable differences were found when examining the distribution of water between the different condensers, which resulted from the higher partial pressure of the condensable vapours from the mechanically fluidized reactor. The temperatures of the first and second condensers were optimized to obtain a high yield of low water content (“dry”) bio-oil (<10 wt.%) from the gas-fluidized experiments (the temperatures were 70 °C for the first condenser and 40 °C for the second condenser and 0-5 °C for condensers 3, 4 and 5). This dry bio-oil was shown to be suitable for upgrading by hydrodeoxygenation. Bio-oil hydrodeoxygenation proved to be an effective upgrading step to reduce the bio-oil oxygen content, reducing the oxygen to carbon ratio, and increasing the higher heating value to over 30 MJ/kg.

## EUROPEAN STANDARDIZATION OF FAST PYROLYSIS BIO-OILS: HEAT AND GREEN ELECTRICITY PRODUCTION

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Fast pyrolysis of biomass, producing Fast Pyrolysis Bio-Oils (FPBO), is reaching industrial maturity, with the first-of-a-kind commercial size installation for fuel production in operation in Finland (Fortum Joensuu/240 tpd), as well as industrial size demo plants, with the 120tpd Empyro plant successfully started in the Netherlands in 2015, or the Ensyn's 65 tpd Renfrew plant in Canada, mainly dedicated to produce FPBO to displace petroleum heating fuel, as well as several Envergent Technologies, a Honeywell Company, plants in design phase in Brazil, Malaysia, Canada, USA.

Properties and behaviour of FPBO are completely different from mineral oils [1-3]. FPBO is a mixture of many components and not uniquely defined. If sulphur content is always at a lower or very low level, some main concerns are related to its unique chemical structure, with only oxygenates and no hydrocarbons, resulting in a much lower net heat of combustion than hydrocarbons, a high acidity, a limited storage stability with time [4] and a significant ash and solid content. FPBO is highly polar and hence immiscible with hydrocarbons, but miscible with alcohols. It contains about 25 wt% water. FPBO cannot be distilled, except for the lighter part including water and are prone to polymerization above 100°C. Analytical methods developed on fossil fuels are not always applicable and shall be adapted /modified.

In order to meet the national legislation requirements, to guarantee a suitable quality for FPBO used in industrial size boilers in existing installations, enable FPBO trading, as well as to make possible the use of FPBO to produce green electricity by using stationary Internal Combustion Engines (ICE) or turbines, FPBO standardization is desired.

A first standardisation of FPBO, to be used in industrial boilers, was performed by the ASTM Committee D02, who establish a method defining two fuel oil grades with 2 different solid and ash contents, ASTM D 7544 [5].

Since the legislation and emission limits differ from Europe to North America, EN standards are also needed. In 2013 CEN received the mandate (M/525) from the European Commission to develop standards for FPBO. A Working Group (WG41) was established under CEN/TC 19 (Gaseous and liquid fuels, lubricants and related products of petroleum, synthetic and biological origin) in early 2014. In the mandate five different qualities of FPBO were foreseen, depending on its application, with two phasing [6]:

Phase 1: 1. An European Standard for FPBO replacing heavy fuel oil,

2. An European Standard for FPBO replacing light fuel oil,

3. A Technical Specification (TS) for the quality for FPBO replacing fuel oils in stationary ICE

Phase 2: 4. A TS or Technical Report (TR) for a quality specification for FPBO suitable for gasification feedstock for production of syngas and synthetic biofuels,

5. A TS or TR for FPBO suitable for mineral oil refinery co-processing

The CEN standardization work has started with the topics corresponding to phase 1, focusing on boiler because of its readiness and current commercial use. Today a draft of an European Standard for FPBO use in boilers (pr EN 16900), gathering the two qualities in one standard, is being nearly completed with an Inter-Laboratory Study (ILS) launched end of 2015, for a scheduled publication in late 2016/early 2017. The TS for ICE and turbine application is in progress.

The pathway to reach such a standard and a technical specification are discussed, with an emphasis on the significant differences between FPBO and fossil fuels and behaviour versus commercial utilisation in burners, ICE and turbines.

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## HOT GAS FILTRATION OF FLASH PYROLYSIS VAPOURS: A FIRST STEP FOR BIO-OIL UPGRADING

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Hot gas filtration (HGF) is an efficient physical method for upgrading bio-oils from fast pyrolysis of biomass oils in terms of solids/ash content, with consequent benefits on their time stability, viscosity. It has been widely accepted that HGF leads to bio-oil yield decreases [1-4]. However, early studies showed that HGF does not directly affect the organic liquid yield, but the molecular weight distribution [5]. Moreover, an extensively analysis of available information reveals a lack of quantitative data about the impact of HGF on the chemical composition of pyrolysis oils.

Experiments were carried out in two scale- fast pyrolysis systems, respectively 100 g/h and 1.5 kg/h. Both of them consisted in a fluidized bed reactor, equipped with i) a HGF unit with ceramic filter candles; and ii) a fractional bio-oil condensation system. Beech wood and sunflower stalks were used as feedstocks with different ash contents. All pyrolysis products were collected and non-condensable gases were on-line analysed by micro-GC. Bio-oil fractions were separately characterized in terms of elemental composition, water content, molecular-weight distribution (size-exclusion chromatography) and quantitative molecular composition (gas chromatography / mass spectrometry).

Results confirmed that overall bio-oil yield drops can be avoided provided careful HGF design and operation control. However, they indicate that chemical composition of bio-oils can be affected by HGF operation. Indeed chemical rearrangements were observed in the liquid organic fractions, more particularly in the isolated aerosol condensed fraction. The extent of these chemical modifications was sequentially investigated with regards to HGF-relative parameters: temperature, regeneration mode (thermal/mechanical), amount and composition of char layer. Ceramic candles were characterized after several pyrolysis and regeneration cycles.

The scientific issues of the paper will be to better understand the homogeneous (gas phase) and heterogeneous (catalytic) reactions occurring in a HGF unit. More generally, this work, conducted at two different scales, will contribute to assess the industrial interest of HGF as a preliminary upgrading method, prior to subsequent ex-situ catalysis.

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Keywords: Biomass, Flash pyrolysis, bio-oil upgrading, Hot Gas Filtration



ABSTRACTS

# Bio-oil

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Poster presentations

## PRODUCTION OF BIO-OILS AND BIO-CHAR THROUGH MICROWAVE ASSISTED PYROLYSIS OF ARUNDO DONAX

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Arundodonax (Arundo) is a perennial cane ubiquitous of the mediterranean area [1], diffuse in all continents. From 19th century it has been introduced in southwest of North America where it was diffused rapidly [2] and without any control. Its uncontrolled diffusion had been expose numerous area to fire and landslide risk and damaged a large number of ecosystems with its high reproductive rate. For this reasons a great attention was focused on methodology to eradicate it from infested area but this is made difficult from tenacity of Arundo rhizomes [3]. Therefore, a large amount of residues of Arundo d. has been formed every year from environmental cleaning. Recently pyrolysis process based on microwave (MW) heating [4] (Microwave Assisted Pyrolysis, MAP) were developed and successfully applied to plastic waste, [5-8] or plastic composites [9-11] and to different biomasses such as lignocellulosic [12] or solid municipal waste [13]. MAP of different organs (leaves, stems, rhizomes) of Arundo was performed using a multimode MW batch reactor with or without a fractionating system using a carbon like MW absorber. The aim of this work was the study of efficient way to dispose waste from different Arundo organs using MAP. A strong attention was devoted to characterization of the three fractions with particular attention to bio-oil characterization. This last fraction was characterized using a quantitative GC-MS method [14], <sup>1</sup>H-NMR, FT-IR ATR. Bio-oil were obtained with good yields (up to 40.9 wt%) and low water content (16.6 wt%). Very interesting compounds were present in high concentrations (levoglucosan up to 47.6 mg/mL, acetic acid up to 107.7 mg/mL).

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## Mild upgrading of fast pyrolysis oil to low corrosive and storage stable bio-oil

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As compared to petroleum-based fuels, crude fast pyrolysis oils are highly acidic, rich in oxygenated compounds, relatively unstable and have tendency to phase-separate. The relatively high content of organic acids (formic acid, acetic acid, etc.) makes pyrolysis oils very corrosive to lower alloy steels and aluminium. The corrosiveness of pyrolysis oils can be handled by selecting high corrosion-resistant grades of stainless steel [1] or by modifying the pyrolysis oils itself to allow usage in existing infrastructure and end applications. The instability of pyrolysis oils are known to cause changes of chemical and physical properties during storage, especially when pyrolysis oils are stored at elevated temperatures. These changes can be observed as increase in pyrolysis oil viscosity, increase in average molecular weight or decrease in the content of carbonyl compounds [2]. In order to widen the area of applications for pyrolysis oils the issues related to corrosiveness and aging need to be addressed. This can be achieved by different upgrading methods e.g. hydro-treatment [1, 3] and catalytic esterification [4]. Furthermore, the water content of pyrolysis oils also plays an important role for the corrosiveness and the risk of phase separation [5, 6].

In this study, mild upgrading of pyrolysis oil by vacuum-assisted dewatering has been studied to investigate the influence of water content on corrosiveness and storage stability. Dewatering of crude fast pyrolysis oil (feedstock: 100% pine wood) was carried out in a rotary evaporator, where water and light organic volatiles were separated from the pyrolysis oil. Four pyrolysis oil samples with different water content were prepared. Characterization included determination of water content, acid number, corrosion tests and accelerated aging tests.

The water contents of the upgraded samples ranged from 0.7% to 10%, while the crude pyrolysis oil water content was 20.7%. The variation of the acid content was less pronounced ranging from 40.1 mg KOH/g for the crude pyrolysis oil to 24.5 mg KOH/g for the most dewatered sample. The results from corrosion testing showed that there is a strong correlation between water content and mild steel corrosion rate. The most dewatered samples had very low corrosion rate, substantially lower than the corrosion tolerance level specified for storage tanks, and surface analysis by scanning electron microscopy showed no significant signs of corrosion attacks. On the contrary, crude pyrolysis oil and dewatered samples with higher water content had clear signs of aggressive corrosion and for some of these samples large solid deposits were found on the metal surface after the corrosion test. Stability testing showed that dewatering improved the storage stability, i.e. reduced viscosity change and reduced the formation of water.

This research has been conducted as part of the ReShip Project which is funded by Norwegian industry partners and the Research Council of Norway (The ENERGIX programme).

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## Comparison of catalytic esterification and vacuum-assisted dewatering of wood-based fast pyrolysis oil and their application in marine multi-component fuels

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Since January 2015, all marine vessels in the Sulphur Emission Controlled Area (SECA) of the Baltic Sea, North Sea, English Channel near-coastal areas of US and Canada, have had to reduce their sulphur emissions to 0.1% [1]. In addition, a number of other sea areas are expected to introduce similar restrictions on emissions before 2020. Fast pyrolysis oils produced from forestry sources constitute a potential low sulphur fuel alternative for the marine sector. However, crude pyrolysis oils are normally not regarded as a suitable fuel for conventional diesel engines since this type of fuels can cause damages and increase the wear on critical engine parts [2]. Additional challenges are related to instability of pyrolysis liquids during storage and immiscibility with fossil hydrocarbon-based marine fuels. The quality of fast pyrolysis oil can be extensively upgraded by e.g. hydrogenation or catalytic cracking, which could help solve the above mentioned challenges but the price of the upgraded fuel would normally be too high to compete with current low-sulphur fossil-based distillate fuel grades. Therefore, the objective of this study has been to produce multi-component fuel blends based on pyrolysis oils stabilized by low-cost upgrading methods. Two different upgrading techniques have been evaluated and compared in this study: catalytic esterification and vacuum-assisted dewatering. Multi-component fuel blends based on crude fast pyrolysis oil has previously been studied, showing that 1-butanol was the preferred co-solvent to form stable blends [3].

The crude pyrolysis oil used as starting material for the upgrading experiments was a laboratory produced fast pyrolysis oil based on 100% Norwegian spruce wood. The upgrading treatments were performed in a rotary evaporator equipped with a temperature-controlled water bath and a vacuum regulator for pressure control. Crude and upgraded pyrolysis oils were blended with 1-butanol and bio-diesel to determine the minimum amount of co-solvent required to produce homogeneous and storage stable multi-component fuel blends.

The mild upgrading treatment with either catalytic esterification or vacuum-assisted dewatering reduced the content of water and acids in the pyrolysis oil. It was also found that the upgraded oils had lower viscosity change than the crude pyrolysis oil in accelerated aging tests (80°C, 24h), which indicates that the upgraded oils had an improved storage stability. The miscibility of the pyrolysis oil with biodiesel was slightly improved by both upgrading methods which implies that less butanol is needed to form homogeneous and storage stable blends. The blends were homogeneous single-phase liquids also after 6 months storage at normal room conditions. The multi-component fuel blends had advantageous properties as compared to crude pyrolysis oil, e.g. higher energy density, lower kinematic viscosity, lower acid number and lower water content. Another advantage obtained by the mild upgrading treatments was reduced corrosiveness. The dewatered pyrolysis oil had 99% lower corrosion rate in immersion tests with mild steel (50°C, 24h) even though this sample still had rather high acid number. Catalytic esterification also reduced the corrosiveness of the pyrolysis oil, but not to the same extent as the pyrolysis oil upgraded by vacuum-assisted dewatering. The reduced corrosiveness of the upgraded oils may, at least partly, prevent wear on engine parts when used in diesel engines.

Multi-component fuel blends based on dewatered pyrolysis oil represent a low-corrosive fuel quality with improved fuel properties as compared to crude pyrolysis oil. Possibilities for implementation of this new fuel in marine engines will be discussed and comparison of fuel quality parameters will be made.

This research has been conducted as part of the ReShip Project which is funded by Norwegian industry partners and the Research Council of Norway (The ENERGIX programme).

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## Deoxygenation of used cooking oil and fatty acids via pyrolysis and catalytic vapours upgrading for aviation biofuel production

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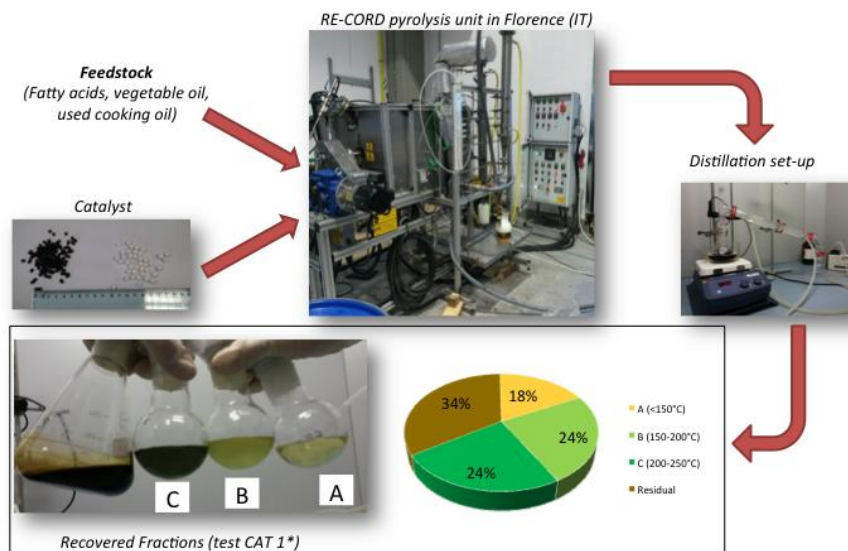
This work presents some preliminary results on a cost-effective application of a pyrolysis process to edible and non-edible oils (vegetable oil, fatty acid, fatty acids mixture, and used cooking oil) for the production of a biofuel-intermediate for transportation, targeting in particular the aviation sector.

Jet fuel from conventional or unconventional fossil resources is a mixture of several hydrocarbons classes, in the carbon number range C8-C16: paraffins (70-80%), aromatics (8-25%), olefins (<5%), without S, N, or O containing compounds. Factors like economic and environmental sustainability, as well as energy supply security are among the reasons behind the introduction of alternative jet fuel into the market. However, to date only two biofuels, i.e. Synthetic Paraffinic Kerosene (SPK) from FT-synthesis and Hydroprocessed Esters and Fatty Acids (HEFA) biofuels, have been certified for up to 50%-50% blends with conventional jet fuel under the ASTM D7566 standard. Beyond current high cost for the feedstock, drawbacks of both production processes are the modest yield and high operating costs, which hinder the large scale deployment of the aforementioned technologies.

This work presents the preliminary results from a novel cost-effective, thermo-catalytic process that leverage the versatility of pyrolysis to produce a biofuel-intermediate in a continuous bench scale reactor from edible and non-edible oils, i.e. vegetable oil, fatty acid, fatty acids mixture, and used cooking oil, without the addition of hydrogen. Each feedstock was subjected to thermal and catalytic conversion in a continuous reactor operated at around 1.5 kg/h; the product was then condensed, collected and analysed by mean of GS-MS, GC-FID, HPLC, elemental analysis. The collected liquid was then subjected to batch atmospheric distillation and micro TGA (sample size approx. 50 mg), in order to identify the boiling range of their constituents and their distillation profile.

A test matrix composed of 4 different feedstock, 4 distinct catalysts, 2 hourly space velocities, 2 catalyst temperatures, 2 sweep gases was completed, and the effects of varying process parameters on overall process yield and hydrocarbon content in the collected liquid product is reported and discussed, along with analytical results from laboratory analyses.

After the treatment, the produced liquid intermediate resulted to be composed of fatty acids, alkanes, olefins and aromatics, plus some oxygenated compounds. Globally, the thermo-catalytic process promoted a significant deoxygenation of the feed, decreased the H/C ratio, and yielded an overall liquid-to-feed in the range 40-80 %wt; in terms of composition, a substantial fraction of the products resulted to be in the range of aliphatic hydrocarbons molecules (C7-C17).



## An investigation into multicomponent fuel blending using pyrolysis oil, marine fuel and alternative blend components

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### Abstract

This study investigates the miscibility and fuel properties of multi-component blends containing fast pyrolysis oil, marine gas oil (MGO) and a number of alternative blend component. Alternative blend components include 1-butanol, glycerol, butyric acid, oleic acid and butyl glycol. Fast pyrolysis oil has had limited success when used directly in engines so by blending with other components it may be possible to extend its application.

In 2012 EU Directive 2012/33/EU was implemented which aims to cut the sulphur content of marine fuels and thereby reduce air pollution. The new limits will be phased in before January 2020. By using sulphur free or low sulphur blend components, marine fuel blends could potentially achieve the limits set by the Directive. Additionally, these blended marine fuels are more sustainable due to the use of bio-based products.

A number of the blend components, excluding MGO, can be readily manufactured from biomass. Glycerol is a by-product of biodiesel manufacture and due to the large increase in biodiesel production there is an excess of glycerol in the marketplace. It is possible to manufacture 1-butanol and butyric acid from biomass fermentation, oleic acid from vegetable oils and the pyrolysis oil is made by the fast pyrolysis of biomass.

The main objective of the work was to improve understanding of fast pyrolysis and marine fuel multi-component blends. The results of the blending activity were used to draw phase diagrams to establish the boundary between single phase and phase separated blends. The properties of the homogenous blends were in order to establish blends of interest for further development. The results were used by the ReShip project in the development of marine fuel blends.

Blends were carefully prepared using a consistent methodology. The sample was left to settle for 48hrs before visual inspection to establish homogeneity. A photograph was taken to document the appearance and quality of the blend. The blend recipes were selected to cover a wide spectrum of compositions in order to build representative phase diagrams. A number of the single phase blends were tested for key fuel parameters such as flash point, viscosity and water content. No research was found in the literature on marine fuel blends containing pyrolysis oil – so this work presents completely novel results. The results may be used to identify new possibilities for pyrolysis oil fuel blends that may widen the application of pyrolysis oil (which is currently limited to boiler applications).

Phase diagrams were plotted successfully for multi-component blends to establish the phase boundary. It was possible to create stable single phase multicomponent blends containing fast pyrolysis oil, marine gas oil (MGO) and other blend components. MGO was the least miscible component when it came to creating single phase blends. A selection of the single phase blends were tested for flash point, viscosity, water content, acid number and pH. A summary of the results will be given in the full paper.

This study represents a step forward in the understanding and development of fast pyrolysis oil marine fuel blends. The work forms part of the ReShip Project which is funded by Norwegian industry partners and the Research Council of Norway (The ENERGIX programme).

## ESTERIFICATION WITH HIGHER ALCOHOLS TO IMPROVE THE QUALITY OF FAST PYROLYSIS CONDENSATES

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The thermal conversion process “pyrolysis” converts biomass in absence of air into two primary products: char and pyrolysis volatiles (vapors and aerosols). By cooling the vapors the condensable fraction can be separated as liquid phase from the permanent gases. Aerosols can be collected sufficiently by using electrostatic precipitators. The ablative flash pyrolysis, where heat transfer to the biomass particles happens in direct contact with a hot surface by mechanical force, aims at maximizing the liquid yield. Total condensates (consisting of vapor condensate and precipitated aerosol) of wooden biomass (e.g. beech wood) are single phase oils and the bio-oils from agricultural biomass (e.g. straw) segregate into two phases (aqueous and organic phase). For most applications, these crude bio-oils have unfavourable characteristics with regard to storage stability, corrosion behavior and energy content. An important point for the economics of pyrolysis processes is the production of bio-oils, which comply with quality standards for the applications. Therefore, the condensate must be treated in order to be available for the market. In literature many upgrading methods are described to improve the oil quality such as fluid catalytic cracking, hydrotreatment or esterification.

Esterification aims at neutralizing the acid groups and removal of water (originally contained and formed by the reactions) during the reaction by distillation to reduce the acid number and water content and increase the calorific value. The method is characterized by esterification of acids and acetalization of aldehydes, ketones and sugars. The reactions take place by addition of alcohols at moderate temperatures (80 - 120 °C) and the presence of acidic catalysts (e.g. Amberlyst 36). Operation with higher alcohols has the advantage that they are only partially soluble in water. Because of this, the reaction water can be better separated compared to ethanol/water mixtures.

The application of higher alcohol mixtures (butanol, hexanol and derivatives) chemically produced from bio-ethanol was investigated regarding acid number, water content, calorific value and viscosity. The quality of the esterification reaction was tested using a single-phase beech wood bio-oil and the organic phase of straw bio-oil. The crude bio-oils were produced in a 10 kg/h ablative flash-pyrolysis reactor at 550 °C with a cyclone for char removal and a condensation chain consisting of an indirect cooler and electrostatic precipitator. Amberlyst 36, a polyvinyl-benzoyl structure containing sulfonic acid groups, was found the most suitable heterogeneous catalyst to improve the bio-oil qualities. A continuous stream of nitrogen as entrainer showed a positive effect on the distillation success. The results by using n-butanol as reference material showed that the water content and the total acid number can be reduced significantly and the higher heating value can be increased (Tab. 1).

Tab. 1 Quality of upgraded bio-oil from beech wood and barley/wheat straw by using n-butanol

|                                | beech wood    |                  | barley/wheat straw (organic phase) |                  |
|--------------------------------|---------------|------------------|------------------------------------|------------------|
|                                | Crude bio-oil | upgraded bio-oil | crude bio-oil                      | upgraded bio-oil |
| water content (wt.-%)          | 25.0          | 1.3              | 20.0                               | 2.6              |
| TAN (mg KOH/g)                 | 113.5         | 50.7             | 70.4                               | 37.7             |
| Viscosity (mm <sup>2</sup> /s) | 19.7          | 39               | -                                  | 11.3             |
| HHV (MJ/kg)                    | 17.0          | 29.3             | 22.8                               | 31.5             |

The results indicate that esterification with higher alcohols represents a good opportunity to improve the quality of bio-oils significantly. With the use of reaction mixtures of higher alcohols generated from bio-ethanol, the economy can be increased compared to the use of expensive n-butanol.

# TOWARDS A BETTER CHARACTERIZATION OF BIOMASS PYROLYSIS BIO-OIL BY ESI-FTICRMS

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The composition of bio-oil produced from biomass pyrolysis is very complex. Therefore the development of high performance analytical techniques is required to characterize them. Particularly, the high resolution mass spectrometry technique (petroleomic approach) has the potential to chemically identify the components at the level of the molecular formula and to ensure the comparison of different bio-oils in respect with biomass type or process conditions (including bio-oils up-grading) [1].

Here, two pyrolysis bio-oils from Miscanthus and oak are characterized by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry coupled to electrospray ionization (ESI-FTICRSMS). The analyses were achieved in positive and negative ion modes for the development of a robust methodology of bio-oil characterization by FTICRMS.

The influence of the sample preparation (use and nature of dopant, solvent) and instrumental parameter (desolvation temperature) on the bio-oil characterization are investigated. Thus, alkaline (Li, Na and K) and ammonium acetate as well as ammonia and formic acid are used in positive ion detection mode to increase the ionization yield. The obtained results are also compared to experiments performed without dopant. When formic acid, ammonium acetate and ammonia are used, almost 90% of the signal is relative to nitrogen species ( $C_xH_yN_{1-5}O_z$ ). The significant detection of these species is due to their capability to easily produce adduct with  $H^+$  and  $NH_4^+$  on the one hand and, for some compounds of the bio-oil, to react with ammonia on the other hand. The addition of alkaline acetate to the bio-oil leads to comparable results whatever the alkaline cation. More than 95 % of the signal is from  $C_xH_yO_{2-15}$  compounds and consequently reflects the real bio-oil composition. In negative ion detection mode, experiments are conducted without dopant and with ammonia. In both cases, the  $C_xH_yO_{2-10}$  compounds lead to an intense signal. Our results were compared with two previous published works in which the bio-oil was primary separated into oily and aqueous phases and analyzed by (-) ESI-FTICRMS. Jarvis *et al.* [2] has presented the relative abundance of the  $C_xH_yO_z$  oily and aqueous phase compounds according to their oxygen amounts. The distribution of the oily phase species is similar to what it is obtained in this study for negative ions and in lesser extend for positive ions (compounds with less than 8 oxygen atoms). The aqueous phase compounds are observed as alkaline adducts  $[M+Alk]^+$  in our experiments. The pyrolytic lignin and the lipids (fatty and resin acids) evidenced by Miettinen *et al.* on the van Krevelen diagrams of both phases as well as the sugarc compounds, which was found to be specific to the aqueous one [3] are simultaneously observed by (+) ESI-FTICRMS with sodium acetate.

Consequently, the modification of ionization conditions ensures to simultaneously detect the oily and aqueous phase components, without any separation step and finally provides a consistent chemical composition of such unresolved mixture. Semi-quantitative information may also be obtained. Moreover, both negative and positive ionization modes yield complementary data for an exhaustive characterization of the bio-oil elemental composition.

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## PREDICTING PYROLYSIS OIL COMPOSITION, HHV AND CATALYTIC ACTIVITY USING CUMULATIVE ATOMIC RATIOS FROM PY-GC/MS DATA

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Superior calorific performance as a result of deoxygenation may be achieved via *in situ* catalytic pyrolysis. Pyrolysis as well as catalyst efficacy may be evaluated using py-GC /MS; however complete characterisation of pyrolysis oil is often unachievable for estimating the HHV and composition. To avoid the necessity to generate sufficient quantities of pyrolysis oil for bomb calorimetry, proximate and/or ultimate analysis, a novel analytical approach for accessing pyrolysis reactions and catalyst efficacy by means of py-GC/MS is presented. This new method makes use of cumulative H/C and O/C data for predicting HHV, atomic ratios and catalyst performance using only py-GC/MS analysis. The accuracy of this method is evaluated against experimental calorific data and pyrolysis oil compositions. The results show that this method can accurately predict both the atomic constituency and HHV of pyrolysis oil. Cumulative H/C, O/C and HHV data used by this method shows interesting trends as the catalytic pyrolysis temperature changes, leading to new insights.

## Prediction of Properties and Elemental Composition of Biomass Pyrolysis Oils by NMR and Partial Least Squares Analysis

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Biomass fast pyrolysis bio-oils are complex chemical mixtures and are extremely challenging to chemically characterize, requiring multiple separation and pre-treatment steps followed by several different analytical techniques. Nuclear Magnetic Resonance (NMR) characterization can provide an analysis of nearly the entire sample that chromatographic techniques cannot (GC, HPLC). NMR analyses have previously been used to determine chemical functional group concentrations via integration of various spectra regions, but much of information contained in the spectra is lost due to their complexity. In this study we have used chemometrics to not only further compare various pyrolysis oils, but to relate the data contained within the spectra to the chemical properties of the bio-oils and even predict said properties. Using partial least squares (PLS) regression we have used <sup>13</sup>C NMR to derive elemental composition information (mass fractions of C, H, N, O), as well as the enthalpy of combustion (higher heating value, HHV), phenol and cresols concentrations, and the total acid number (TAN). Several PLS models were created correlating these various properties with the binned intensities of the <sup>1</sup>H and <sup>13</sup>C NMR spectra of 73 different samples consisting of pyrolysis bio-oils from various biomass sources and using treatment protocols, as well as finished fuels (gasoline, diesel and biodiesel) and small molecule standards. Two models based exclusively on <sup>13</sup>C-NMR data demonstrated the best over-all ability to predict these same properties for unknown samples. The R<sup>2</sup> and RMSE of the predicted values are discussed in detail and are acceptable for many biofuel-related applications. That such properties and compositional measurements may be extracted from <sup>13</sup>C NMR spectra is a direct result of the detailed chemical structural information influencing the chemical shifts and resonance patterns. Since these models were built using a wide range of samples and conditions, they are expected to also be useful for wider applications.

## UTILIZATION OF PROCUTS FROM THERMO-CATALYTIC REFORMING IN INTERNAL COMBUSTION ENGINES

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Producing energy and fuel from residual and waste biomass is essential for a sustainable biomass economy. Fraunhofer UMSICHT has developed a novel intermediate pyrolysis and reforming reactor; introducing the Thermo-Catalytic Reforming (TCR<sup>®</sup>) process which is a key component of the Biobattery concept developed within the framework of the Center for Energy Storage (CES) [1]. The TCR<sup>®</sup> is a process which can convert any type of biomass and organic feedstocks into a variety of energy products like char, bio-oil and permanent gases. The char can be used for combustion or gasification for heat and power production. The permanent gas is rich in hydrogen (up to 50 vol.%) and suitable for gas engines or alternatively for green hydrogen production. The crude TCR<sup>®</sup>-bio-oil has a water content below 2 wt.%, an oxygen content below 12 wt.% and a total acid number under 5 mgKOH/g which makes it suitable for diesel engine application [2]. The TCR<sup>®</sup> technology has been successfully transferred from lab-scale (2 kg/h) to demonstration-scale (30 kg/h) [3].



Fig. 1 : First mobile application of TCR-bio-oil with a Dodge Ram 2500 pickup truck diesel engine

This up-scale now enables dual-fuel engine tests operating on permanent gas and liquid fuel from the TCR<sup>®</sup> process. Quality and purity of the pyrolysis products are an important factor for the successful long term operation of internal combustion engines. Therefore, performance, emission characteristics and other effects on a combined heat and power (CHP) dual-fuel engine were investigated to assess the suitability as sustainable fossil fuel substitute.

Bio-oils from residue biomass, e.g. digestate or sewage sludge, were produced by TCR<sup>®</sup> and blended with biodiesel and fossil diesel. Different fuel blends, containing up to 80 wt.% of bio-oil, were used along with permanent gas on dual-fuel mode. The blends were mixed in a fuel tank and allowed to settle before use. No phase separation was observed. The injection timing of the engine was adjusted to optimize engine performance and to avoid engine knocking from the hydrogen rich gas. Additionally a fuel blend was applied on a Dodge Ram 2500 pickup truck for mobile application tests. For this blend the bio-oil was pre-treated by distillation to produce a defined fuel fraction in the evaporation range of fossil diesel (180-360 °C).

Based on the general bio-oil quality a good engine performance was achieved. Stable engine operation was obtained with different fuel blends containing up to 90 wt.% of TCR<sup>®</sup>-bio-oil and up to 80 % permanent gas by means of combustion energy. The injection timing had to be adjusted to compensate the lower cetan number of the bio-oil compared to diesel fuel. Increased carbon deposits were not observed on the injection nozzles of the CHP engine. Due to the thermal stability of the crude TCR<sup>®</sup>-bio-oil up to 90 wt.% of the TCR<sup>®</sup>-bio-oil was distillable by forming a high viscous residue fraction and a low viscous distillate. The truck performance was overall satisfying. The injection and fuel system of the engine was not negatively influenced by the combustion of the bio-oil blend.

Stationary and mobile engine application of TCR<sup>®</sup> based bio-fuel was successful demonstrated. Successful long term dual-fuel engine tests demonstrate the feasibility of TCR<sup>®</sup>-bio-oil and gas for heat and power production. The suitability of the TCR<sup>®</sup> based bio-fuel for mobile application in a truck engine gives further confidence to the high quality and potential of this kind of bio-fuel to open a new market for bio-oils from residual biomass. Additional research and development for the production of standardized bio-fuel from solid residual and waste biomass has to be carried out.

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## APPLICATION AND VALORISATION OF THERMO-CATALYTIC REFORMING LIQUIDS

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Producing energy and fuel from residual and waste biomass is essential for a sustainable biomass economy. Fraunhofer UMSICHT has developed a novel intermediate pyrolysis and reforming reactor; introducing the Thermo-Catalytic Reforming (TCR<sup>®</sup>) process which is a key component of the Biobattery concept developed within the framework of the Center for Energy Storage (CES) [1]. The TCR<sup>®</sup> is a process which can convert any type of biomass and organic feedstocks into a variety of energy products like char, bio-oil and permanent gases. The char can be used for combustion or gasification for heat and power production. The permanent gas is rich in hydrogen (up to 50 vol.%) and suitable for gas engines or alternatively for green hydrogen production. The crude TCR<sup>®</sup>-bio-oil has a water content below 2 wt.%, an oxygen content below 12 wt.% and a total acid number under 5 mg<sub>KOH</sub>/g [1]. Due to the thermal stability of the crude TCR<sup>®</sup>-bio-oil up to 90 wt% of the TCR<sup>®</sup>-bio-oil is distillable by forming a high viscous residue fraction and a low viscous distillate. The distilled TCR<sup>®</sup>-bio-oil is directly miscible with biodiesel without additives and also miscible with fossil diesel in any ratio by adding up to 5 m% of ethanol. The fuel mixtures have been tested on a stationary Kubota diesel engine and a Dodge Ram 2500 pick-up truck with Cummins turbo-diesel engine [2].

With a focus on biofuels for transportation, the downstream processing of the crude TCR<sup>®</sup>-bio-oil is of special interest to meet high standards of common fuels like gasoline or diesel. To assess the opportunities of TCR<sup>®</sup>-bio-oil upgrading, distillation, hydrodeoxygenation and miscibility tests were carried out in order to produce renewable gasoline and diesel from residual or waste biomass. Furthermore the suitability as co-feed to fossil oil refineries should be assessed.

Various bio-oils from residual and waste biomass, like digestate or sewage sludge, were produced by Thermo-Catalytic Reforming. The TCR<sup>®</sup>-bio-oil was hydrodeoxygenated in order to remove sulphur, nitrogen and oxygen producing TCR<sup>®</sup>-HDO-oil in high yield (90 %). After hydrodeoxygenation the oil was fractionated to separate the biofuel into common fuel fractions, like gasoline and diesel. Additionally crude TCR<sup>®</sup>-bio-oil was mixed with fossil crude oil, distilled and hydrodeoxygenated. The biofuels were then tested at an engine test bench with modern EURO-6 car engines.

The produced renewable gasoline and diesel were analysed after hydrodeoxygenation and rectification and showed the required properties to meet fossil fuel standards (EN 228 and EN 590). The crude TCR<sup>®</sup>-bio-oil and fossil crude oil were miscible, distillable and also successfully hydrodeoxygenated. Therefore, the possibility to co-process bio-oil from the very beginning of a fossil oil refinery is demonstrated. This opens an energy efficient route to renewable gasoline and diesel by downstream processing as it is now known from fossil oil refineries. Especially compared to liquids from other pyrolysis technologies this is a significant advantage, as those are not direct suitable for refining and need significant pre-treatment or instead are used with high effort for synthesis gas production and Fischer-Tropsch synthesis. Furthermore successful car engine tests give confidence to biofuel production based on the Thermo-Catalytic Reforming process.

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Fig. 1 : Hydrodeoxygenated TCR-bio-oil

## **FAST PYROLYSIS BIO-OIL UPGRADING BY CATALYTIC HYDRODEOXYGENATION**

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There is much interest in fast pyrolysis oil upgrading by hydrodeoxygenation of the liquid using hydrotreating technology. An interesting and poorly explored approach is partial upgrading to either improve stability for direct use in heat and power applications so that conventional engines, turbines and boilers can be used with minimal modification; or to upgrade sufficiently so that product can be safely fed to a conventional refinery to produce a completely compatible biofuel or high-value bulk chemicals.

This study provides results from catalytic hydrodeoxygenation of bio-oil by batch autoclave treatment of fast pyrolysis oil using the following catalysts: Ru/C, Pd/C/ and Pt/C. The beech biomass feedstock was characterised by thermogravimetric analysis (TGA) and pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS). Fast pyrolysis oil was obtained from a 1 kg/h bubbling fluidised bed reactor at a reaction temperature of 500°C. The catalytic hydrotreatment reactions were carried out using a 25 ml Parr autoclave at different severity levels - mild hydrogenation at either 175 or 225°C followed by a mild hydrodeoxygenation (HDO) at either 225°C or 325°C, at pressure up to 200 bar. Untreated bio-oil and upgraded liquids were characterised using a wide range of chromatography techniques (GC-MS, GC-FID) and nuclear magnetic resonance (NMR/ 2D NMR).

## UPGRADING OF BIO-OIL QUALITY VIA HYDRODEOXYGENATIVE PROCESS WITH METAL CATALYST IN A CONTINUOUS FLOW REACTOR

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Bio-oil, which is obtained from fast pyrolysis, is considered to be a promising alternative fuel. However, some disadvantages (high water content, acidity, oxygen level, and low heating value) make it hard to direct use of bio-oil. Moreover, reactive oxygenated compounds in bio-oil resulted in polymerization, esterification and etherification, led to aging of bio-oil and reduced the bio-oil stability. To overcome those disadvantages of bio-oil, upgrading process is essential.

Therefore, to investigate the improvement of bio-oil stability to use as biofuel, bio-oil produced by fast pyrolysis. The two-phase hydrodeoxygenation (HDO) reaction of bio-oil with H<sub>2</sub> was investigated over the metal catalyst, using continuous flow reactor with various bio-oil/solvent ratio.

SBA-15 and Al-SBA-15 supports were prepared by sol-gel method. Then, the nickel was doped into the support by wet impregnation. The catalysts were characterized by BET, SEM, XRD, and ICP to estimate whether the supports has well-organized structure, and metals were uniformly dispersed.

During the HDO reaction, bio-oil was converted into gas, liquid (light and heavy oil), and char. The targeted heavy oil was separated and the heavy oil quality (such as water content, acidity, viscosity, and oxygen content) was analyzed.

Targeted heavy oil yielded ca. 30 wt%, while that from batch type reactor yielded 34.9-56.3 wt.%. The yield of char decreased from 5.5-16.1 wt.% (batch type reactor) to ca. 2 wt.% (continuous flow reactor). As well as reduction of char, the bio-oil quality also improved after the HDO reaction with continuous flow reactor. The properties of heavy oil, such as water content, acidity, viscosity and oxygen lever were clearly decreased, and higher heating value (HHV), will be measured. During the HDO reaction, oxygenated compounds in bio-oil, which resulted in instability during the storage, also converted into the stable compounds, via deoxygenation.

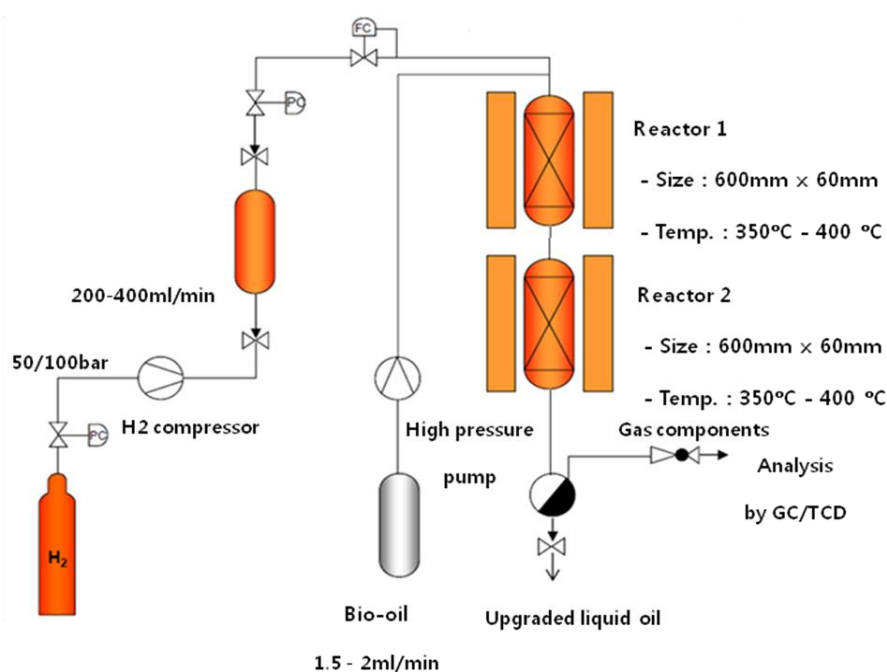


Figure 1. Illustrate of HDO continuous flow reactor

# STABILITY ASSESSMENT OF FAST PYROLYSIS BIO-OILS: EVALUATION OF MICRO-CARBON RESIDUE INCREASE BASED TEST

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Fast pyrolysis is a thermochemical conversion process that enables to produce a liquid product, called bio-oil, from lignocellulosic biomass with high yields (60 – 75 wt.%) [1]. Bio-oil from fast pyrolysis is intended to be used as a renewable source of fuels/chemicals to partially replace petroleum derived products. However, some unfavourable properties of bio-oil (e.g. acidic nature, instability), which are simply a reflection of its chemical composition, may put a limitation to its commercial use.

Bio-oil is typically composed of reactive oxygenated compounds (e.g. aldehydes, ketones, furans, acids), sugars, lignin-derived monomers, oligomers and water. As a result of this complex mixture and high reactivity of compounds present, bio-oil is neither thermally nor chemically a stable product. During storage (especially at elevated temperatures), bio-oil components react with each other through several polymerization mechanisms to form high-molecular weight components and water as a by-product which could possibly end up with phase separation. This observed phenomena is termed as aging and it results in an increase in viscosity, average molecular weight and water-insoluble content of the bio-oil.

The stability of bio-oils is generally assessed by observing viscosity change following an accelerated aging procedure at elevated temperatures (24h at 80 – 90 °C) which correlates with storage over a long-term (6-12 months) at room temperature. This stability test method was the subject of a recent round robin study and it was shown that there were some variations in the viscosity change based results [2]. Thus, it is recognized that there might be a need for supplementary tests to assess the stability of bio-oils.

Micro-carbon residue test is a standardized test method for petroleum products and it is used to measure the coke forming tendency of a fuel [3]. Highly polar, heavy oxygenated feedstocks give high micro-carbon residue values. During aging, bio-oil components also polymerize to give water insoluble, high-molecular weight oxygenated components.

Pine wood bio-oil produced in a continuously operated fast pyrolysis set-up was aged at 80°C for 4, 8, 16, 20 and 24 hours. It was found that as aging time increased, micro-carbon residue values of respective bio-oils increased as well suggesting that change in micro-carbon residue values could be used as an indicator for the stability of bio-oils (Fig.1). It is proposed for the first time in this work that change in micro-carbon residue values of fresh and aged bio-oils could be measured to assess the stability of the bio-oils in the same manner with the viscosity-change based method.

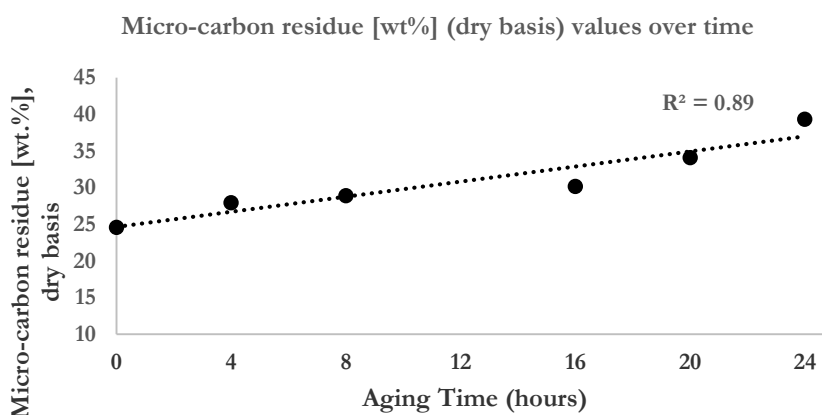


Figure 1. Micro-carbon residue values over time

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## Characterization of the liquid products obtained from the fast pyrolysis in a pilot BFB plant

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The energy insecurity from oil and natural gas and increased CO<sub>2</sub> emission from fossil fuels is driving societies to look for sustainable and renewable energy supply. Although fast pyrolysis has emerged as the most promising technology to convert organic materials to liquid fuels at shorter duration but it still faces some technical challenges in improving product yield, its quality and process energy efficiency. **The objective** of this study is to investigate fuel characteristics of bio-oil to obtain by a BFB reactor on 1b/d pilot scale unit for fast pyrolysis from biomass in Korea. **From the methods**, the conditions of pyrolysis (temperature: 500 °C, feed: 15kg/h) are chosen in order to enhance bio-oils production. The bio-oils are condensed and trapped at different temperatures and quencher types. **In conclusions**, the heating value of the bio-oil is around 13-20 MJ/kg, whilst the water content is between 10 wt.% and 50 wt.%. Liquid fractionation with solvents of the bio-oil has been carried out. Chemical analyses of the fractions have shown that the main components in the bio-oil are alkanes, alkenes and oxygenated. Their physicochemical properties (particles content, viscosity, density, TAN and element content) are also measured.



ABSTRACTS

# Fossil fuels

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## Oral presentations

## Authentication and quality control of coal for coke making in steel production by means of pyrolysis – gas chromatography/mass spectrometry

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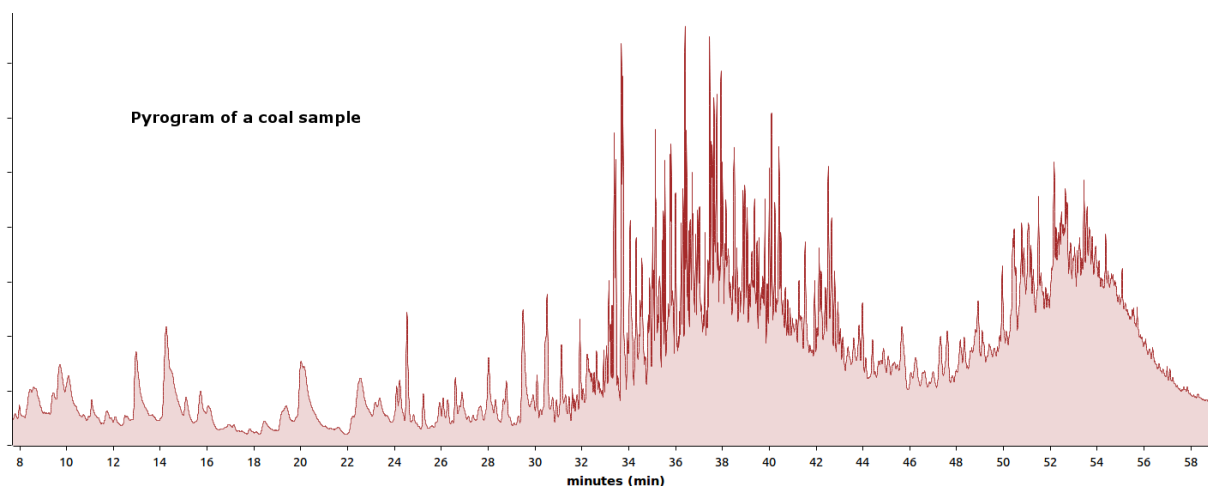
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Next to iron ore and limestone, the steel industry consumes considerable amounts of coal as a fuel for the blast furnace. More precisely, coal is required for the injection with the hot blast on the one hand and for the production of metallurgical coke on the other. Particularly for making quality coke the purchased coal has to possess very specific physical and chemical properties which are only met by a certain class of coals and need to be assessed by an appropriate quality control. The quality measures include chemical parameters like the total amount of sulphur and ash or the volatile matter as well as technological parameters such as fluidity and dilatation. Moreover, the selective use of blends of different coking coal products with defined properties facilitates to steer the steel making process and fine-tune the steel quality. Both, the considerable increase of competition in the steel industry sector and the decline of high quality coal resources led to the necessity to acquire coal from an increasingly larger number of suppliers across the globe. Today, more than in the past, there is a need for a comprehensive quality control and authentication of purchased coal batches in order to ensure consistent steel quality.

In the present study the feasibility of pyrolysis – gas chromatography/mass spectrometry (Py-GC/MS) as a technique for quality control of coking coal products has been investigated. 19 different coal samples from 16 different resources have been analysed and particular care has been put on an unbiased and representative sampling. Although Py-GC/MS yielded highly reproducible fingerprints a major challenge of the study was the appropriate processing of the acquired data. The pyrograms of coal contain far more than 1000 components represented by severely overlapping peaks and peak deconvolution attempts failed to generate reproducible results. With the aid of the software OpenChrom<sup>®</sup> [1] in connection with the plug-in MultiScanIdent<sup>®</sup> it was possible to elaborate a data analysis workflow which allowed a reproducible and flawless authentication of the coal samples. It consists of pre-processing steps such as removal of uninformative *m/z* traces and normalisation, followed by building up a reference database with several replicate measurements of each sample on the basis of summed-up mass spectra over a predefined retention time range. With the aid of appropriate similarity measures all test measurements could be matched correctly. Additionally, MultiScanIdent utilizes statistical approaches to select the most discriminative *m/z* traces for the current set of references in order to aid finding marker components in the dataset and to improve authentication and quality control.



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## **PYROLYSIS-DERIVED GAS STREAMS AS ALTERNATIVE FUELS FOR THE FUTURE ENERGY SECTOR**

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In the forthcoming decades major changes will affect the energy landscape as hydrocarbon scarcity and restrictions of greenhouse gas (GHG) emissions will become major issues.

In particular, the sector of electrical power generation will need to succeed a number of vital mutations, including: the deployment of renewable energies and the abatement of GHG and trans-boundary pollutants. During this transition period, the International Energy Agency (IEA) forecasts that thermal power will nevertheless keep a prominent position in the energy sector namely as it will enable fulfilling the short-term energy needs of emerging countries. In fact, future thermal power plants will have to meet a complex set of requirements, which includes: improving efficiency; reducing CO<sub>2</sub> emissions and coping with surging primary energy prices.

At the same time, the spectrum of fuels used for power generation will evolve, with a move towards alternative fuels and the potential advent of hydrogen as a new energy vector.

In this challenging perspective, products deriving from pyrolysis processes offer interesting alternatives in power generation as this category of fuels, utilized in Combined Heat and Power (CHP) installations, can bring a valuable contribution to centralized and distributed power using gas turbines as prime-movers.

Currently pyrolysis products derived from coal (coking plants) and steel works are used as co-fuels in blast furnace installations. Other pyrolysis products deriving from biorefinery processes can also be envisaged as alternative gas turbine fuels.

The presentation will set out the assets of gas turbine-based power plants for the utilization of pyrolysis-derived fuels in the framework of environment conscious and energy sober power generation policies.







ABSTRACTS

# Fossil fuels

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Poster presentations

## BIOMASS/COAL CONTAINING BRIQUETTES

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Integrated Steel works are known to release a large amount of greenhouse gases because of the use of large amount of fossil fuels [1]. One way to reduce CO<sub>2</sub> emissions, lower costs and widen the raw material selection is to introduce wastes that, at present are incinerated, as substitutes of coal. In fact, waste plastic is nowadays commercially available as a reducing agent in various industrial plants. The introduction of waste plastic in coal blends for use in cokemaking has also been studied in recent years as a way to recycle plastic and to reduce CO<sub>2</sub> emissions. The introduction into coal blends of carbon neutral materials like biomass has received attention in recent years [2]. In fact the use of additives is very common in cokemaking which include a wide range of materials from bituminous wastes to non-coking coals.

The aim of the present work was to optimise the composition of biomass/coal containing briquettes considering the use of various binders and different biomasses with view to the modification of coal plastic properties and briquette density. All the briquettes were prepared using a bituminous coal, a binder and a biomass. The biomasses included lignin, pine sawdust, torrefied pine sawdust and a hydrothermally treated biomass. As binders, tar, molasses and a residue from the bottom of the tar decanter were used. Proximate and ultimate analysis of all the materials was carried using standardized procedures. The fluidity of the blends that compose the briquettes together with the modification of coal plastic properties due the briquettes was measured by means of the Gieseler test following the ASTM D2639-74 standard procedure. The density of the briquettes was measured as the ratio of its weight to its volume. Thermogravimetric analysis of the briquette components and briquettes was carried out in a TA Instruments SDT 2960 thermobalance. Samples between 5-10 mg were heated at a rate of 10 °C/min up to 1000 °C under a N<sub>2</sub> flow of 100 ml/min. In order to investigate the degree of interaction between the components of the blends, the experimental mass loss curve was compared to the calculated profile by applying the additivity law, taking into account the composition of the blend and the mass loss curves of the briquette components.

It was found that the briquettes have fluidity and the values depend not only on the binder but also on the type of biomass. The torrefaction of the pine sawdust also influences the fluidity of the blend, having the torrefied sawdust a more deleterious effect on the fluidity of the coal. The highest density was obtained for briquettes prepared with lignin.

Keywords: biomass, briquetting, thermoplastic properties, thermogravimetric analysis.

Acknowledgement: The research leading to these results has received funding from the European Union's Research Programme of the Research Fund for Coal and Steel (RFCS) research programme under grant agreement No. [RFCS-CT-2014-00006].

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## USE OF ADDITIVES TO AVOID OXIDATION AND TO RECOVER THE COKING PROPERTIES OF BITUMINOUS COALS

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The exposure of coal to mild weathering affects its chemical and physical properties, which is a matter of great importance for the coke making industry. Oxidation causes a decrease in the thermoplastic properties of coking coals, changing their behaviour during the carbonisation process. This is directly reflected in a reduction in carbonisation rate, coke yield, and coke quality. Many authors have studied the effect of aerial oxidation by using artificial oxidation as a model of coal weathering [1]. Moreover, it is known that chemical reagents and different types of additives are able to recover the coking properties of oxidised coals [2].

The aim of the present work was to analyse the role of surface additives in the coal oxidation process, to study the effect of carbonaceous additives in blends with oxidised coals in order to restore their coking properties and establish the effect of both types of additives on coking behaviour and coke quality. Two coals of different rank were used, coal C1 with 20.3 wt. % db and coal C2 with 34.2 wt. % db volatile matter. Four liquid surface additives (diesel, bio oil and two commercial liquids) and two bituminous additives (coal tar and coal tar sludge) were selected. The coals were subjected to oxidation at 50 °C in a dry place for two months with/without surface additives. Raw, oxidised coals and blends were carbonized in a movable wall oven of approximately 17 kg capacity (MWO17) and the cold mechanical strength of the cokes produced was assessed by applying the JIS test (JIS K2151 standard procedure). Coke reactivity and mechanical strength after reaction were evaluated by means of the NSC test (ASTM D5341 standard procedure). The thermoplastic properties of the coals/blend samples were tested by the Gieseler method, following the ASTM D2639-74 standard procedure. A thermogravimetric analysis of the coals and additives was carried out using a TA Instruments SDT 2960 thermoanalyser. In the analysis, 10 mg of each sample was heated to 1000 °C at a rate of 3 °C/min under a nitrogen flow of 100 ml/min.

It was found that in some cases, surface additives are able to reduce coal oxidation. Moreover, the fluid characteristics of oxidised coals can be restored through the use of coal tar and coal tar sludge, which also increase the JIS, CSR and CRI indices.

Keywords: bituminous coal, carbonaceous additives, surface additives, artificial oxidation, thermoplastic properties, thermogravimetric analysis, coke quality.

Acknowledgement: The research leading to these results has received funding from the European Union's Research Programme of the Research Fund for Coal and Steel (RFCS) research programme under grant agreement No. [RFCS-CT-2013-00007].

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## N and S conversion during pressurized pyrolysis under CO<sub>2</sub> atmosphere in fluidized bed

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**Abstract:** Pressurized oxy-fuel combustion (POFC) is a promising technology to realize CO<sub>2</sub> capture from power plant with low penalty. The high partial pressure of CO<sub>2</sub> in a POFC system will certainly have impacts on fuel-N and fuel-S conversion during coal pyrolysis. Thus, coal pyrolysis experiments were conducted in a pressurized fluidized bed at 0.1-0.7MPa under CO<sub>2</sub> atmosphere. The gaseous product and char were analysed to investigate the influence of different pyrolysis parameters like atmosphere, temperature and pressure on the conversion of fuel-N and fuel-S. Results show that high pressure and the enrichment of CO<sub>2</sub> in atmosphere both can enhance the fuel-N conversion to HCN in pyrolysis process, which is a favourable precursor to N<sub>2</sub>O. As the elevated pressure and CO<sub>2</sub> atmosphere promote the volatile yield of coal pyrolysis, meaning more volatile and more HCN produced from thermal cracking of volatile-N.

H<sub>2</sub>S and COS are the major S-containing gas in coal pyrolysis which are not monitored due to the instrument limitation in this study. SO<sub>2</sub> concentration in the gaseous product is relatively low, however as the pressure increases, this concentration has a slight decrease. This may be explained by the conversion reaction from SO<sub>2</sub> to COS with the presence of CO, as R1 and R2 show. S content in the char decreases when the pressure goes from 0.1MPa to 0.7MPa. The high partial pressure of CO<sub>2</sub> enhances the formation of CO, and CO may accelerate the decomposition of pyrite and sulfates, as shown in R3 and R4. Additional test on char like X-ray photoelectron spectroscopy is still in progress to obtain more information on how pressurized CO<sub>2</sub> affect the conversion of fuel-S.

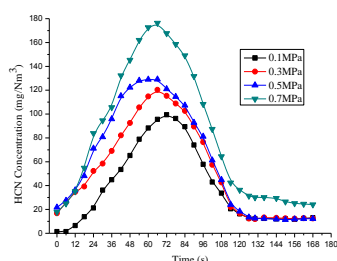


Figure 1. HCN release curves of coal pyrolysis at different pressure (850°C, CO<sub>2</sub> atmosphere)

Table.1 Ultimate and proximate analysis of raw coal w/%

|          | C <sub>ad</sub> | H <sub>ad</sub> | O <sub>ad</sub> | N <sub>ad</sub> | S <sub>ad</sub> | M <sub>ad</sub> | A <sub>ad</sub> | V <sub>ad</sub> | FC <sub>ad</sub> |
|----------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|------------------|
| Raw coal | 67.42           | 4.14            | 8.31            | 1.04            | 2.72            | 6.52            | 9.85            | 35.34           | 48.29            |

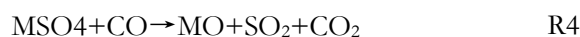
Table.2 Sulfur content in char under various pressures

| Pressure/MPa        | 0.1  | 0.3  | 0.5  | 0.7  |
|---------------------|------|------|------|------|
| w(Sulfur content)/% | 2.37 | 1.93 | 1.75 | 1.64 |

The reactions between CO and SO<sub>2</sub>:



Decomposition of pyrite and sulfates with CO:



## STUDY OF THE FORMATION OF AROMATICS IN THE PYROLYSIS OF CYCLOPENTENE

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The thermal decomposition of cyclopentene was studied in a jet-stirred reactor operated at constant pressure and temperature to provide new experimental information about the formation of the first aromatic rings from cyclic C<sub>5</sub> species.

Experiments were carried out at a residence time of 1 s, a pressure of 106.7 kPa, temperatures ranging from 773 to 1048 K and under diluted conditions (cyclopentene inlet mole fraction of 0.04). Species were quantified using three analytical methods: gas chromatography, synchrotron vacuum ultra-violet photo-ionization mass spectrometry (SVUV-PIMS), and single photon laser ionization mass spectrometry (SPI-MS). Several species could be quantified using the three methods allowing comparison of experimental data obtained with the three apparatuses (Figure 1). Discrepancies observed in mole fraction profiles of some large aromatics suggest that the direct sampling in the gas phase (with a molecular beam or a capillary tube) provide more reliable results than online gas chromatography.

The main reaction products are 1,3-cyclopentadiene and hydrogen. The formation of many unsaturated C<sub>2</sub>-C<sub>6</sub> olefins, di-olefins and alkynes was also observed but in smaller amounts. Benzene, toluene, styrene, indene, and naphthalene were detected from 923 K. SVUV-PIMS data allowed the identification of another C<sub>6</sub>H<sub>6</sub> isomer which is 1,5-hexadien-3-yne rather than fulvene. The quantification of the cyclopentadienyl radical was obtained from SVUV-PIMS and SPI-MS data with some uncertainty induced by the possible contribution to the signal for m/z 65 of a fragment from the decomposition of a larger ion. This is the first time that a radical is quantified in a jet stirred reactor using non-optical techniques. SPI-MS analyses allowed the detection of species likely being combination products of allyl and cyclopentadienyl radicals.

A model was developed for the pyrolysis of cyclopentene. This model includes routes of formation of aromatics from the cyclopentadienyl radical using chemistry schemes proposed in the literature. The comparison of experimental and computed data is overall satisfactory for primary reaction products whereas discrepancies are still observed for large aromatics, especially for indene and combination products (1,5-hexadiene, 5-allyl-1,3-cyclopentadiene and 5-cyclopenta-2,4-diene-cyclopenta-1,3-diene).

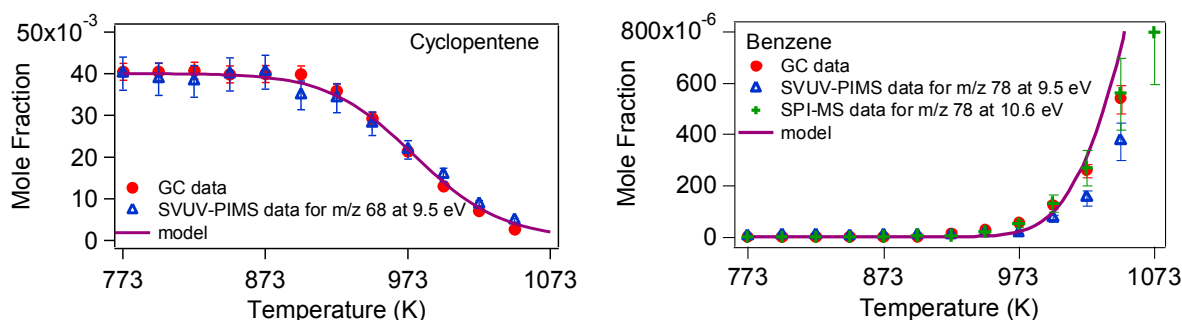


Figure 1: mole fractions of cyclopentene and benzene.

**PYROLYSIS AND GASIFICATION OF HIGH ASH COAL IN STEAM AND CO<sub>2</sub>**K. Jayaraman<sup>a</sup>, V. Belandria<sup>a,b,\*</sup>, S. Bostyn<sup>a,b</sup>, I. Gökalp<sup>a</sup>

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Coal is considered one of the most likely sources of naturally occurring long term energy [1]. Thermal investigations are therefore of crucial importance for more sustainable development of coal thermally assisted technologies (*i.e.* pyrolysis, gasification). Ash content in the coal may have a number of effects on pyrolysis/gasification characteristics [2]. However, available information for coals of high ash content, typically above 25% by weight, is relatively limited. On the basis of ongoing research [3] this work presents the influence of pyrolysis conditions on the gasification efficiency of high ash coal. Char particles of high ash-content Turkish coal are produced in a thermo-gravimetric apparatus. Coal is first pyrolyzed in argon ambience using three heating rates (100, 500 and 800 °C.min<sup>-1</sup>) and the char produced is gasified in single and combined steam and CO<sub>2</sub> ambiances. The effect of pyrolysis heating rate on char production and char gasification is studied. The gasification experiments are carried out in steam and combined (steam+CO<sub>2</sub>) ambiances over the temperature range of 850-950 °C, under ambient pressure conditions. The influence of reaction temperature, char production method, particle diameter, chemical characterisation and physical structure on char gasification is investigated. A discussion is made on char reactivity gasification in steam and combined ambiances with basis on suitable kinetic models.

Pyrolysis and char gasification reaction kinetics, *e.g.* activation energy and Arrhenius constant, are evaluated based on three kinetic models, namely: volumetric model, grain model, and random pore model. The activation energy of the gasification process varies from 156 to 196 kJ.mol<sup>-1</sup> based on the char generation method, particle diameter and reactant concentration. In single and combined steam and CO<sub>2</sub> ambiances, the substitution of CO<sub>2</sub> for argon improves the char gasification efficiency. No inhibitory effects of CO<sub>2</sub> are observed in the char-steam gasification; though some synergetic effects are anticipated. The results indicate that the high heating rate during pyrolysis increased the char gasification rate. This study provides a basis for the rational design of industrial pyrolysis/gasification reactors and, may be useful to optimize the process conditions for high ash coal applications.

Keywords: Thermal degradation, high ash coal, pyrolysis, gasification, steam, CO<sub>2</sub>, kinetic analysis.

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# Applying ionic liquid to inhibit coal spontaneous combustion via green analytical methods and kinetic models by TG/FTIR

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## ABSTRACT

Coal has been widely used as fuel in human history for a long time, but the flammable features of coal can also lead to spontaneous runaway, and so on. These features of coal could prove that coal has some hazardous characteristics when it is in unstable conditions. Over the years, there have been quite numerous coal disasters, resulting in thousands of casualties. Accordingly, we should work to prevent these disasters to guarantee human safety, and decrease financial deprivation, as well as the environmental impact. This research is targeted to establishing thermal parameters and thermal hazard via thermogravimetry (TG). We also could observe the difference of functional groups between coal and coal mixed with ionic liquid by Fournier transform infrared (FTIR) spectrometer. Finally, the calculated parameters were determined by theoretical kinetic models which were used to recognize the degree of the hazard present during thermal accidents.

*Keywords:* Disasters, Environmental impact, Fuel, Thermal hazard, Thermal parameters

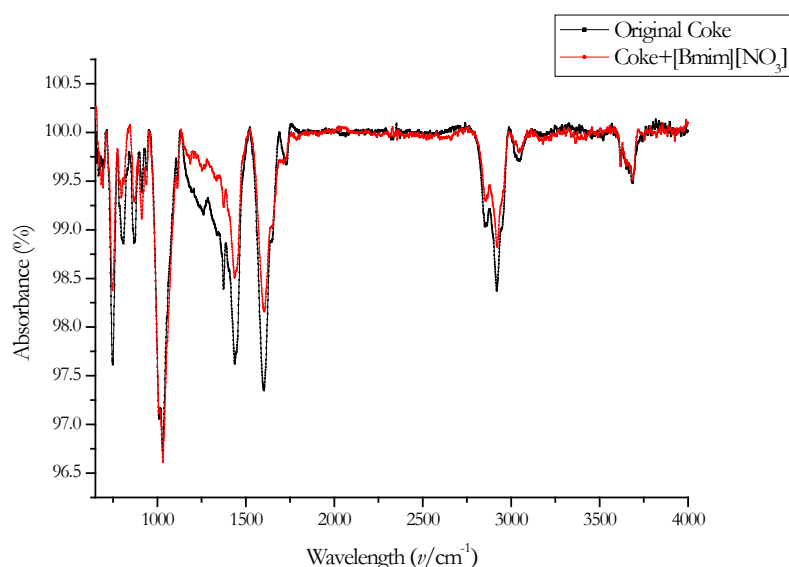


Fig. 1 Absorbance *vs.* wavelength for Coke and Coke mixed with [Bmim][NO<sub>3</sub>] in FTIR tests

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## INFLUENCE OF PRESSURE (1 mbar – 1 000 bar) ON THE PYROLYSIS OF ALKANES: EXPERIMENTS AND KINETIC MODELING

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Hydrocarbon pyrolysis concerns many different fields (petroleum geochemistry, refinery, fuel thermal stability, pyrocarbon deposition, etc.). It is therefore studied in a wide variety of temperature-pressure experimental conditions, which strongly affect the chemistry of hydrocarbons cracking.

n-Octane has been chosen as a model compound of the alkane family and two experimental studies of pyrolysis have been conducted. The first one has been performed in a closed isochoric reactor made of Pyrex at very low reactant concentration (1 mbar Pa diluted in inert gas - total pressure 1 500 mbar) between 350°C and 450°C and reaction time from 1 to 70 hours[1]. The second study was performed by confined pyrolysis in a closed, constant-pressure gold reactor at pressure ranging from 10 bar to 700 bar, temperature between 330°C and 450°C and residence times from 1 hour to 1 month. The reaction products were very different according to the pressure. At low pressure (1 mbar), the major products were 1-alkenes (C<sub>2</sub>H<sub>4</sub> to C<sub>7</sub>H<sub>14</sub>), methane and ethane; other alkanes (C<sub>3</sub>H<sub>8</sub> to C<sub>6</sub>H<sub>14</sub>) were minor products, no alkanes heavier than n-octane were detected. At high pressure (10 bar - 700 bar), the main products were n-alkanes of molecular weight lower than n-octane, and branched alkanes of molecular weight higher than n-octane. Alkenes were minor products. The effect of pressure on conversion depended strongly on reaction temperature: at moderate temperature (330°C – 350°C) the conversion of n-octane increased with pressure up to a maximum and then decreased; for higher temperature (450°C), the conversion increased continuously with increasing pressure.

A detailed kinetic model consisting of 666 free-radical reactions was constructed in a systematic manner and used to model the experimental results. The agreement between the experimental data and simulation results was satisfactory in terms of products distribution and conversion of n-octane in a wide range of temperature and pressure. The kinetic analysis of the model allowed highlighting the causes of the pressure effect: it is directly related to the importance of bimolecular vs monomolecular free-radical reactions. The distribution of the main products is also related to the distribution of the octyl radicals (position of the free-radical centre in the radical), which is determined by the isomerization reactions.

The simulation of the kinetic model on a wide range of pressure (factor greater than 1 million by simulation of the model) and temperature showed that the curve plotting conversion of n-octane as a function of pressure is bell shaped and the maximum of conversion arises at lower pressure when temperature decreases (Fig.1). This conclusion is consistent with observations in oil fields that showed that thermal cracking of oil is retarded by high pressure.

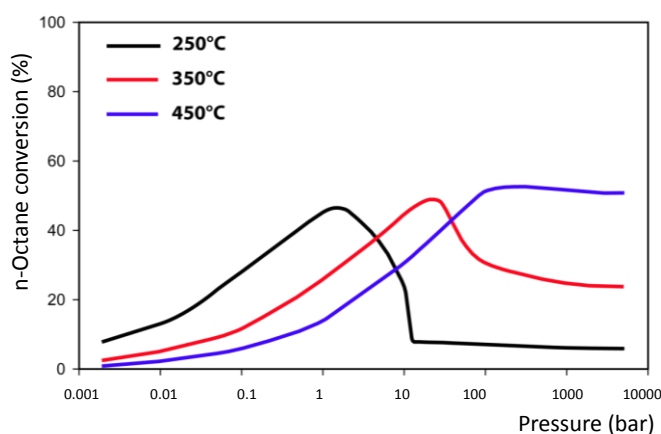


Figure 1: n-Octane conversion as a function of pressure and temperature

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## HIGH PRESSURE PYROLYSIS OF HIGH-DENSITY HYDROCARBON FUEL

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Thermal management is a significant challenge to advanced aircrafts. To fulfil the thermal management requirements, regenerative cooling with endothermic hydrocarbon aviation fuels on board is considered to be one of the most promising technologies. As one of endothermic hydrocarbon fuels with a high density, JP-10 has been gained comprehensive attention for its high-density and low cost. The experiments were carried out by changing feed flows to obtain different conversions at same temperatures. The thermal cracking of JP-10 under high pressure (4MPa) was conducted in a modified high-pressure/supercritical-flow pyrolysis apparatus at temperature range from 550.0 to 620.2°C. Gas chromatograph (GC) and gas chromatograph/mass spectrometry (GC-MS) were used to quantitatively analyze the pyrolysis products. It was found that the conversion of JP-10 and gas yield both had relatively low values (lower than 23% and 5%, respectively) under high pressure. The major gaseous components were hydrogen methane, ethane, propane, ethylene, and propylene, while the major liquid products were 1,3-pentadiene, 1,3-cyclopentadiene, cyclopentene, cis-bicyclo[3.3.0]oct-2-ene. What's more, propylene and 1,3-cyclopentadiene had the highest yields in the gas and liquid products, respectively. Under high pressure, the initial selectivities of major gaseous products were lower than these in literatures under relatively low pressure, indicating that high pressure was unfavorable for unimolecular reactions [1]. Therefore, the generation of gaseous products in thermal cracking was inhibited to some extent at high pressure. Furthermore, the preliminary product, 3-cyclopentylcyclopentene, significantly influenced the cracking reaction, such as product distribution. In addition, Proportional Product Distribution (PPD) model was adopted to predict the product distribution at low conversion which satisfied the experiment results illustrating that the experimental method was reliable and the model was reasonable[2,3].

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## Catalytic Pyrolysis Mechanism of n-Pentane to Produce Light Olefins

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Light olefins, such as ethylene and propylene, are so important for the chemical industry that the concerning researches have never been stopped[1]. Due to the rapidly growing demand for propylene, the final product from alkanes cracking was expected to achieve not only a large number of light olefins (P+E) but also the high propylene yield (P/E)[2]. Recently, light alkanes (C4-C8) have been investigated for light olefin production, not only to elucidate the performance of catalysts and the reaction mechanism, but also to create further improvement in light olefins production.

In this paper, n-pentane cracking experiments were conducted in a fix-bed reactor at 400-600 °C under atmospheric pressure. A typical procedure is as follows: The samples (30-40 mesh) diluted with SiC were supported between quartz wool plugs and fixed in the middle of the reactor where isothermal conditions were maintained. Prior to every reaction, the catalyst was pretreated in situ of N<sub>2</sub> flow at 150 °C for 1 h. The reactant feed was a mixture of n-pentane and N<sub>2</sub>, which was used as carrier gas for online analysis. The n-pentane partial pressure was maintained at 1-2 kPa, and the temperature variation in the bed was less than 2 °C during the reaction. Reaction effluents were analyzed using an online gas chromatograph (Micro 490GC, Agilent) equipped with three separated channels and thermal conductivity detectors: Molecular Sieve column (hydrogen, nitrogen, and methane), Plot U column (ethylene and ethane), and Alumina column (C3-C5 species).

The mechanism pathways of n-pentane conversion have been systematically investigated over solid acid catalysts at low pressure. Considering the stability and concentrations of species involved, the relative importance of monomolecular protolytic cracking routes, hydride transfer routes and  $\beta$ -scission routes have been determined, respectively. The investigations concerning the influences of temperature on mechanism pathways and product distribution of n-pentane conversion have been described. At high temperature, the existence of pathway  $C_3^- + C_3^+ \rightarrow C_6^+ \rightarrow C_2^- + C_4^+$  (S1-B4) significantly transformed propylene into ethylene; while, the route  $C_2^- + C_2^+ \rightarrow C_4^+$  (S4) promoted the formation of C4 species at low temperature. Decreasing the framework SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio, or increasing the pore size of zeolites and reactant partial pressure, can enhance the hydride transfer; at the same time, the generations of ethane, propylene, and butene were restrained, while ethylene and propane were promoted. The coupled process combining reaction temperature and other operating variations was designed to produce light olefins and the highest light olefins yield of n-pentane conversion was achieved larger than 60 wt% with a controllable P/E ratio. The results proved that it was feasible to achieve the desired products through designing reaction condition directed by the mechanism pathways.

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## KINETIC ANALYSIS OF NON-ISOTHERMAL PYROLYSIS OF OIL SAND BITUMEN USING MULTIPLE GAUSSIAN-DISTRIBUTED ACTIVATION ENERGY MODEL

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Pyrolysis processes have been commonly used in industry to produce useful light hydrocarbons from crude oil. However, recoverable reserves of crude oil have been dwindled and its production will be insufficient due to continuously increasing global consumption of crude oil. Consequently, conventional oils are likely to be exhausted in the near future and it is expected that unconventional heavy oils would play an important role because of its copious reserves. As the production of unconventional heavy oil is increasing, upgrading technologies become progressively crucial for its effective utilization and pyrolysis processes can also be applied to convert unconventional heavy oil into more valuable light oils. Adequate understanding of pyrolysis process for unconventional heavy oil is necessary to take full advantage of the process and to design efficient pyrolysis process. Kinetic analysis of pyrolysis process is important because pyrolysis behavior can be understood and described through kinetic parameters. Many approaches have been developed for estimating kinetic parameters from experimental data obtained from non-isothermal thermogravimetric analysis (TGA). Conventional approaches obtain kinetic parameters from linear fitting derived from the TGA results. Unconventional heavy oils contain lots of components and have very complex pyrolysis reaction mechanisms, nevertheless, conventional approaches do not take the complexity into account. On this account, they give inaccurate parameters or only a single set of parameters for complex reactions. Distributed activation energy model (DAEM), a latest analysis approach, shows more descriptive results for the pyrolysis reaction than conventional methods because DAEM consider the complexity of reactions. The purpose of this study is to analyze nonisothermal pyrolysis of oil sand bitumen, one of representative unconventional heavy oils, using multiple Gaussian-DAEM. First, nonisothermal pyrolysis of oil sand bitumen was carried out at different heating rates using a thermogravimetric analyzer to obtain data for DAEM analysis. Then, conversion rate curves of oil sand bitumen pyrolysis were matched with a sum of multiple curves for more precise DAEM prediction. There have been limited applications using DAEM with multiple peaks for unconventional heavy oils, while there are a lot of studies applying to the pyrolysis of coal or biomass. In addition, compensation effect between activation energy and pre-exponential factor was considered. Kinetic parameters of oil sand bitumen pyrolysis, such as activation energy, pre-exponential factor, and standard deviation were determined from DAEM analysis, and the resulting parameters well describe pyrolysis behaviors of oil sand bitumen.

## EFFECT OF ATMOSPHERE REACTION, COAL RANK AND HEATING RATE ON THE DEVOLATILIZATION OF COLOMBIAN COALS

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### Abstract

An experimental protocol was implemented in this work to study the combined effect of the heating rate, rank coal and atmosphere reaction in the devolatilization of Colombian coals, over the final distribution of products in gaseous phase. A model-free method was applied upon a mass loss data, resulting from non-isothermal tests of Thermal-Gravimetric Analysis (TGA) of two coals (Sub-Bituminous Type A (SubbA) and Semi-Anthracite (SA)). Meaningful differences were obtained in devolatilization kinetics depending on the atmosphere (one of them was N<sub>2</sub> environment to simulate the traditional combustion condition and the other was CO<sub>2</sub> to simulate the environmental conditions of a typical oxy-combustion process with gas recirculation). Through TGA it was found that at low heating rate the mass loss rate during primary devolatilization tests is higher in the N<sub>2</sub> enriched environment than with CO<sub>2</sub>. Based on activation energy distribution, CHN analysis on residual char and tracking the evolution of products in gaseous phase during devolatilization in CO<sub>2</sub>, it was demonstrated that at temperatures higher than 660°C, CO<sub>2</sub> reacts with the formed char; thus, this reaction becomes the controlling stage of the thermochemical transformation. The effect of coal rank has a direct impact on the distribution of gaseous products and may favor the occurrence of primary fragmentation during devolatilization. Additionally, experiments were conducted in a Hot Plate Reactor where 2 mm particles pyrolysis was carried out on an cold annealed steel plate, in both environments, using heating rates between 50 °C/s and 1200 °C/s, which allowed showing that at high heating rates similar to those reached in fluidized beds, devolatilization is more intense when the process is given in a CO<sub>2</sub> enriched atmosphere. Differences arising from devolatilization environment are explainable from the effects it has on interaction between thermal and diffusive properties of both environments

## Use of a mechanically fluidized bed pyrolysis for bitumen and asphalts applications

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Forest biomass is an attractive resource to produce transport fuels as an alternative to fossil fuels. It is renewable, and without environmental impact as long as forest harvest residues are considered: *i.e.* if soil production capacity is maintained (note that stumps and root systems are not considered as biomass in Quebec). Presently, most of the technologies and existing applications are energy-oriented; which, for the time being, is not economically advantageous. However, there are other promising opportunities to create a profitable products portfolio both in the short and long terms.

Accordingly, we are evaluating the potential of using fast pyrolysis to convert forest biomass into bio-oils as a renewable component of bitumen instead of binders originating from fossil fuels. The main issue remains the production of suitable pyrolysis oil, *i.e.* consistent and adaptable to bitumen, while ensuring the economic viability of the project.

The JUMBO MFR, a newly designed mechanically fluidized bed pyrolysis reactor with a nominal capacity of 100 kg/h, has the capability to produce high-viscosity bio-oil with basically no water content, quite suitable for bitumen applications. The unit has been conceived by Cedric Briens and Franco Berruti from the Institute on Renewable Fuels and Chemicals (ICFAR) of the University of Western Ontario (UWO). It is a mobile pyrolysis unit integrated in a larger scale project targeted at the valorisation of Haut-Saint-Maurice (northern Quebec) or “Projet La Tuque” forests.

The “Projet La Tuque” main objective is the construction of the first large-scale Canadian biorefinery producing “drop-in” quality biodiesels from harvest residues. It should be noted that the La Tuque forest area is quite large, approximatively the size of Belgium. The biorefinery will have the capacity to treat up to 1.2 million green metric tons of forest biomass. The planned biodiesel production will displace from 2.3 to 4.3% of Quebec transport diesels with a significant impact on Green House Gases emission reduction. Part of the pyrolysis bio-oil, generated from an energy-reduction stand-point, will nevertheless be used as a value-added product for improving the overall economy of the project.

Our goal is to present the pyrolysis unit and the range of products obtained. The grades of bitumen, development interest, and objectives in the field will also be discussed. Preliminary results and findings allow to confirming the high potential for the use of fractional bio-oil as a direct or partial substitute for bitumen production as far as the proper pyrolysis technique is used to produce the primary oil.





ABSTRACTS

# Hydrocarbon / Kinetics

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Oral presentations



## STEAM CRACKING OF BIOMASS-DERIVED C<sub>30</sub>- NORMAL AND BRANCHED ALKANES: AN EXPERIMENTAL AND FUNDAMENTAL KINETIC MODELING STUDY

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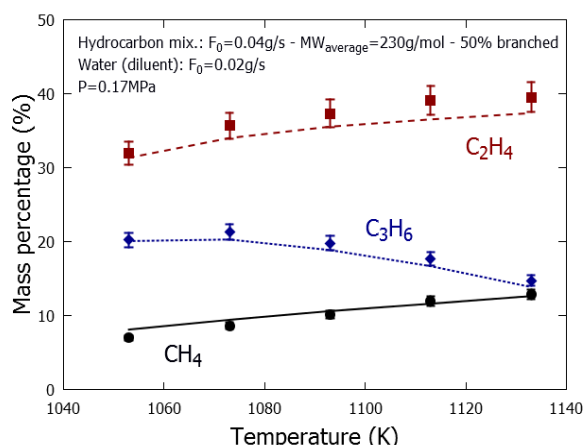
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Vegetable oils, waste fats/greases and algae are promising green feedstocks for the production of renewable ethene, propene and other valuable chemicals[1]. They have a low oxygen content and can be upgraded through catalytic hydrogenation and isomerization processes. The resulting normal and branched alkanes can be processed in conventional steam crackers (which are designed for pure hydrocarbon feedstocks). In this work, the pyrolysis chemistry of several mixtures containing normal and branched alkanes, produced by Neste through the aforementioned process, was investigated. These mixtures consist of alkanes having less than 30 carbon atoms and contain up to 90wt% of branched alkanes (including methyl-, ethyl-, dialkylated-alkanes).

Pyrolysis experiments of the paraffinic mixtures were performed in a dedicated setup, consisting of a feed section, reactor section and analysis section. The feed section ensures evaporation and a stable feed of hydrocarbons and water (diluent) to the reactor. The reactor is a tubular reactor. Heat is provided by an external electrical furnace. The reactor effluent was analysed on-line using several gas chromatographs, including a two dimensional gas chromatograph with a time-of-flight mass spectrometer and flame-ionization detector. The effect of dilution and reactor temperature on the effluent composition was determined. Pyrolysis of the paraffinic mixtures has high ethene, propene and butene yields. The type and degree of branching of the hydrocarbon feedstocks influences the selectivity's to these alkenes. The yields of products that are formed by bimolecular chemistry, such as aromatics, increase with decreasing dilution, given the higher hydrocarbon partial pressure.

A detailed kinetic model was developed for the pyrolysis of normal and branched alkanes up to 30 carbon atoms using an automatic network generation tool called PRIM-O [1]. Reaction rate coefficients and thermodynamic data were estimated using a comprehensive group-additive framework developed by Marin and coworkers [1]. The developed kinetic model was used to simulate literature-reported pyrolysis experiments of pure branched alkanes [2] and the experiments performed in this work. There is a good agreement between model calculated and experimental product profiles. The model is able to capture the effect of dilution and branching on reactor effluent composition. Reaction path analysis reveals that alkanes are mainly consumed by hydrogen abstraction reactions. Subsequent C-C  $\beta$ -scission reactions results in the formation of the observed small alkenes. The presence and type of branching determines the type of alkene that is formed, e.g. isobutene in the case of C-C  $\beta$ -scission of 2-methyl-2-alkyl radicals. Other products in the reactor effluent, such as aromatics, are formed by secondary reactions. Benzene, the aromatic with the highest yield, is formed by addition of vinyl on 1,3-butadiene, recombination of methyl and 1,3-cyclopentadienyl and self-recombination of allyl followed by hydrogen abstraction. Substituted aromatics, such as toluene, xylenes, ethylbenzene and styrene have comparable formation channels, e.g. toluene is formed by addition of propen-1-yl on 1,3-butadiene, recombination of ethyl and cyclopentadienyl and recombination of allyl and butenyl followed by hydrogen abstraction.



**Figure 1:** Experimental (symbols) and model calculated yields (lines) of methane, ethene and propene as a function of reactor temperature

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## AN HOMOGENEOUS AND HETEROGENEOUS DETAILED KINETIC MODEL OF ALCANE PYROLYSIS FOR SIMULATION OF C/C BRAKE DISKS DENSIFICATION BY CVI PROCESS

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Chemical Vapour Infiltration (CVI) is an usual industrial process for the manufacturing of high performance carbon/carbon aircraft brake discs. A continuous fiber porous preform is placed in a low-pressure open reactor supplied with alkane precursors such as propane. The alkane precursors are pyrolysed and the products may diffuse through the porous preform and react with it, leading to the deposit of highly structured pyrocarbon. The deposited material leads to the matrix densification of the carbon/carbon composite. A major drawback of CVI process is the very low processing time and the risk of non-homogeneous deposition rate. The improvement of this process requires a fine tuning of control parameters (pressure, temperature, flow rates, composition...) and a better knowledge of the competing chemical and physical processes (homogeneous reactions, heterogeneous reactions, mass transfer by convection and diffusion, energy transfer by conduction, convection, radiation...). The aim of the work is to develop a specific chemical mechanism for the carbon deposition from alkane in CVI-process conditions (low-pressure/high-temperature) and to apply it at an industrial scale. Propane pyrolysis has been studied in a perfectly stirred lab-scale reactor equipped with two gas-chromatographs for analysis of "light" (C1-C4) and "heavy" (C5+) species [1]. The influence of the temperature (1173-1323 K) and of the residence time (0.5 - 4s) on the concentrations of the effluents has been quantified. A detailed model involving 193 species and 608 elementary steps leading to the formation of polycyclic aromatic hydrocarbons (PAH) has been set-up. The comparisons of the results of the model with experimental data show a very good agreement [2]. The effect of heterogeneous reactions has been studied by introducing a carbon preform in the reactor [3]. A heterogeneous detailed mechanism has been built up. This detailed elementary mechanism involves 66 surface sites and 275 reactions [4]. The deposit model is based on a lateral growth on armchair or zig-zag sites. The rate constants have been estimated by structural analogy with representative homogeneous prototype reactions. The influence of the temperature and of the residence time on the deposition rate and on the composition of the gas phase has been analysed. The model exhibits a good agreement with the experimental data. The major pathways to the pyrocarbon deposition have been identified [5]. A 2D fluid dynamics software has been developed in order to simulate the whole CVI process at a pilots reactor scale. Momentum conservation (Navier-Stokes), mass conservation, energy conservation and species conservation equations are solved with a finite volume approach. A Semi-Implicit Linked Equations scheme (as described by Patankar [6]) on a bloc-structure mesh has been adopted. A subset of the detailed homogeneous and heterogeneous kinetic model has been used for the simulations. The conservation of species is solved in both the reactor gas-phase and in the porous preforms. The local growth rate in the preforms, coupled with a structural evolution model for the porosity, the specific surface and the mean pore diameter of the porous medium let us estimate the densification evolution and quality of the carbon/carbon brakes. The simulations along with the proposed kinetic model are of great interest for studying the impact of process parameters or of the reactor design on the efficiency of the densification. Those computations open up new ideas for the improvement of the process. Some illustrative examples will be provided and analysed.

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## Hydrocarbon Aviation Fuel Pyrolysis under Different Pressures

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Endothermal hydrocarbon fuel (EHF) can not only provide propulsive power but also work as a coolant to remove the heat of the hypersonic vehicle efficiently. The effect of pressure on the heat sink and the pyrolysis productions of the hydrocarbon was investigated experimentally. Thermal cracking of EHF M190-2 was performed in a microchannel tubular reactor from 500 to 750 °C under different pressures of 0.7, 1.5, 3.5 and 6.0 MPa. M190-2 mainly composes of paraffins (46.5 wt%), one-ring naphthenes (34.6 wt%) and two-ring naphthenes (18.0 wt%) with the density of 0.7915 g/cm<sup>3</sup> (at 20°C) and the mean molecular weight of 149.9. The gas products were analyzed by an Agilent 3000A gas chromatography (GC 3000A) online and the liquid products were identified and analyzed by the GC-MS and Bruker 456GC. The conversions, product distributions, coke deposits were studied to get insight into the thermal cracking performance under different pressures.

The conversion and heat sink increased with temperature and pressure. At a given temperature, the increasing pressure could enhance the conversion because of the extending residence time<sup>[1]</sup>, and also, increase the heat sink. The heat sink increased from 2.92 to 3.27 MJ/Kg with the pressure from 0.7 to 6.0 MPa at 750°C. The heat sink at 3.5 MPa was close to the value at 6.0 MPa, which could be explained in the product distributions.

Product distributions showed that methane and ethylene were the most abundant components in the gas product. Selectivity of methane could be attributed to high content of branched paraffins in the fuel<sup>[2]</sup> and increased with pressure. Selectivity of ethylene at 6.0 MPa was lower than that at other pressures probably due to enhancement of bimolecular reaction at high pressure. The yield of alkenes and aromatics versus conversion indicated that the yield of alkenes at 6.0 MPa was even a little lower than that at 3.5 MPa at 750°C, which explained the similar heat sink value for the dominant endothermal contribution of alkenes. The assumption of the alkene under high pressure meant less endothermal reactions, and thus, the weakness of the endothermicity. The yield of aromatics increased rapidly at 6.0 MPa because the higher pressure could promote the bimolecular pyrosynthesis reactions<sup>[3]</sup>. Aromatics were closely associated with coke deposit behaviour, so high pressure may cause the high amount of coke to some degree which would affect the reaction stability.

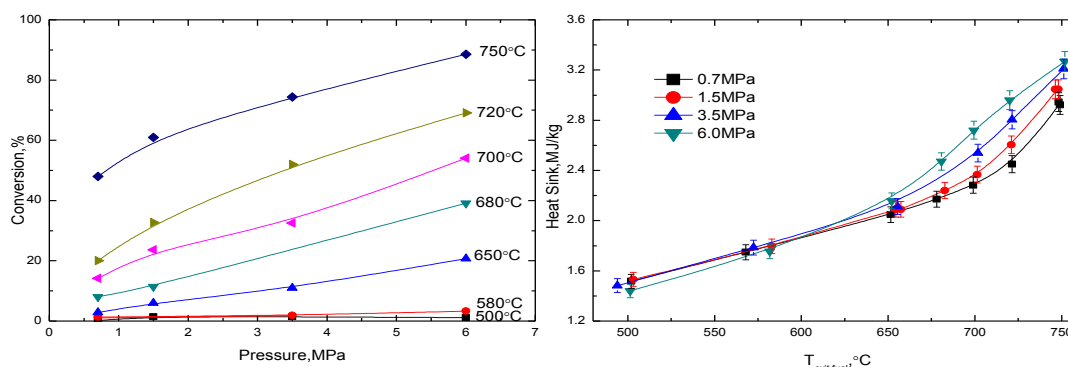


Fig.1 Conversion versus pressure under different conditions and heat sink of the fuel versus the exit fuel temperature.

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# EXPERIMENTAL STUDY OF HYDROCARBON PYROLYSIS IN A REGENERATIVE COOLING SYSTEM OF A COMBUSTOR

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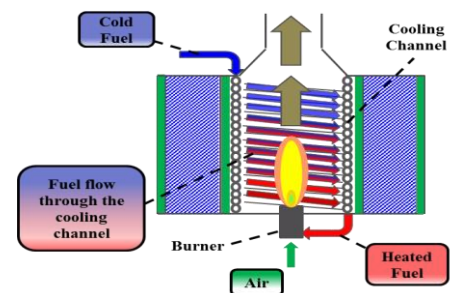
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Regenerative cooling is an efficient way of cooling liquid-fuel engines, such as rocket engines, ramjets and scramjets. The propellant acts as a coolant, flowing through channels located between the inner and the outer wall of the engine, before being injected in the combustion chamber [1]. For hydrocarbon fuels, the coupling between combustion and cooling is stronger in comparison with other propellants such as hydrogen, as the possible decomposition process of the fuel before its injection in the combustion chamber must be taken into account and may change the overall control system. In fact, when a hydrocarbon is used as fuel-coolant, it can under-go pyrolysis. The endothermic behaviour of the chemical reactions enhances its cooling capacity; moreover, pyrolysis generates many species like hydrogen and light hydrocarbons (ethane, ethylene, acetylene, etc.) whose ignition delay time is very low when compared to the initial heavy fuel. This increases the efficiency of combustion [2, 3]. Unfortunately, as fuel pyrolysis in the cooling channels modifies the composition of the propellant injected in the combustion chamber, the dynamic control and the thermal management of the system is a very hard task. The impact of the most important operating parameter, i.e. fuel mass flow rate, on the engine thrust is still not clear and needs to be investigated. In this context, a remotely controlled combustion chamber, suitable for the experimental analyses of pyrolysis-combustion coupling in regenerative cooling has been designed (cf. Figure 1). Similitude rules have been taken into account for the development of this experimental bench, described elsewhere [4]. In the present work, experiments were performed under both stationary and transient conditions by using ethylene as fuel-coolant and air as oxidizer. Ethylene pyrolysis and consequent coking activity have been investigated by varying fuel mass flow rate from  $0.01 \text{ g}\cdot\text{s}^{-1}$  to  $0.04 \text{ g}\cdot\text{s}^{-1}$  and fuel pressure in the range of 1 to 30 bar. Pyrolysis products have been sampled and studied with off-line Gas Chromatograph and Mass Spectrometer analysis and the effect of propellant decomposition flame characteristics (height, temperature profile on the axis, etc.) has been investigated. It was observed that, keeping constant the fuel mass flow rate and the equivalent ratio, ethylene decomposes below  $300 \text{ }^\circ\text{C}$  at a pressure of about 15 bar, instead of  $400 \text{ }^\circ\text{C}$  required at the ambient pressure. Great attention was given to the influence of fuel to oxidizer equivalence ratio on the maximum temperature of ethylene in the cooling channel (consequently on its decomposition rate) demonstrating that an increase of equivalence ratio from 1.0 to 1.5 produces a raise of the maximum temperature of the coolant between 150 and  $200 \text{ }^\circ\text{C}$ , depending on pressure and mass flow rate. Correlations between the main operating parameters (fuel mass flow rate, fuel pressure, equivalence ratio) and ethylene pyrolysis characterised by its decomposition rate have been determined. The combined effect of the intensity of the heat flux absorbed by the fuel and its residence time in the cooling channel (between 1 and 10 seconds) has been studied highlighting a hysteresis effect due to the heat transfer dynamics. Moreover, the catalytic effect of the stainless steel cooling channel on ethylene pyrolysis and coke formation has also been investigated. This work is unique to the authors' knowledge as this topic was studied only numerically. It aims to improve the knowledge of the scientific and engineering community on hydrocarbons pyrolysis in regenerative cooling system of scramjet engines.



**Figure 1.** Schematic overview of the regenerative cooled combustion chamber.

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## PYROLYSIS OF DIMETHYL CARBONATE: PAH FORMATION

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### Introduction

The environmental concern about the use of fossil fuels has increased in the last years, and biofuels and some additives to conventional fuels have generated keen interest. Recently, dimethyl carbonate (DMC) has been considered as diesel additive, because its potential to reduce emissions of particle matter, CO, HC and NO<sub>x</sub> [1, 2], and it can be obtained from biorefinery processes [3]. Other pollutants such as polycyclic aromatic hydrocarbons (PAH) could be also present during a combustion process and could be even emitted to the atmosphere, adsorbed on soot particles or in exhaust gases. The PAH have a carcinogenic and mutagenic potential and, for this reason, USA Environmental Protection Agency (EPA) defined 16 priority PAH, which are regulated by USA government policies [4]. The present work aims to quantify these 16 priority PAH found in the pyrolysis of DMC. The PAH quantified are: naphthalene (NAPH), acenaphthylene (ACNY), acenaphthene (ACN), fluorene (FLUO), phenanthrene (PHEN), anthracene (ANTH), fluoranthene (FANTH), pyrene (PYR), benzo [a] anthracene (B[a]A), chrysene (CHR), benzo [b] fluoranthene (B[b]F), benzo [k] fluoranthene (B[k]F), benzo[a]pyrene (B[a]P), dibenzo [a,h] anthracene (DB[ah]A), indeno [1,2,3-cd] pyrene (I[123-cd]P) and benzo [g,h,i] perylene (B[ghi]P).

### Methodology

The pyrolysis experiments are carried out under well controlled laboratory conditions in a quartz flow reactor, in the 1075-1475 K temperature range, with a fixed DMC inlet concentration (50000 ppm), and at atmospheric pressure. The quantitative PAH method used in the present work was previously developed by our research group [5]. PAH collection is made in the different places where PAH can be present, i.e. adsorbed on the soot surface (or trapped in the soot filter), stuck on the reactor walls, and in the outlet gas and retained by a XAD-2 resin. Soot particles and the resin are subjected to Soxhlet extraction using dichloromethane, and later concentrated by rotary evaporation. The reactor walls are washed with 150 ml of dichloromethane to catch the PAH. Finally, all the samples are analysed by gas chromatography-mass spectrometry (GC/MS). Furthermore, the toxicity of the PAH samples is determined by means of the B[a]P-eq concentration [6].

### Results

The results show a high yield to gases during the experiments at all the temperatures tested, the PAH show a maximum at 1375 K, coinciding with the formation temperature of soot. The soot amount formed is lower compared to that formed from other oxygenated compounds tested in our group [7]. The PAH with the highest concentrations, for all temperatures tested, are: NAPH, ACNY, PHEN, FANTH, PYR and B(ghi)P. From these, the major PAH, at all temperatures, are NAPH and ACNY. The PAH found in minor concentration are: ACN, FLUO, ANTH, B(a)A, CHR, B(b)F, B(k)F, B(a)P, I(123-cd)P and DB(ah)A. Regarding to the toxicity, the highest B[a]P-eq concentration is found in the soot formed at 1375 K.

### Acknowledgements

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ABSTRACTS

# Hydrocarbon / Kinetics

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Poster presentations

## CLOSED-SYSTEM PYROLYSIS OF ALIPHATIC ETHERS AT ELEVATED PRESSURE

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The thermal maturation of natural organic matter in sedimentary rocks involves the preferential cleavage of labile bonds and the gradual liberation of mainly CO<sub>2</sub>, H<sub>2</sub>O, hydrocarbons and polar organic compounds. Due to the complex structure of natural macromolecular organic matter (kerogen), individual thermochemical reactions are difficult to investigate. One avenue to improve the understanding of kerogen maturation is the pyrolysis of organic model compounds representing structural elements of kerogen. The ether bond is a frequent and reactive bond type within different kerogen types [1]. Since ether bonds represent bridging units between different subunits of the macromolecule their cleavage will result in fragmentation of kerogen [2]. This study investigates the stability of ether bonds with respect to temperature and the molecular structure of the model compounds. The preferential decomposition pathways and major reaction products are identified. For one model compound an overall decomposition rate and kinetic parameters are calculated.

Here we present the results of closed-system dry pyrolysis experiments of two ether model compounds (n- and sec-butyl ethyl ether) in sealed gold tubes in high-pressure reactors at a pressure of 20 MPa and temperatures of 473 to 618 K. The decomposition of the model compounds yields mainly C<sub>1</sub>-C<sub>4</sub> alkanes beside CO<sub>2</sub> and minor amounts of butenes. While butanone is a major product of the decomposition of the secondary ether, the corresponding primary ether forms the metastable butanal which decomposes to CO. The formation of the reaction products can be described by a complex radical chain mechanism and – to some extent – by a unimolecular decomposition mechanism. The formation of ketones in the decomposition of the secondary ether offers a new explanation for the formation of these compounds during (artificial) kerogen maturation.

The observed overall activation energy for the decomposition of n-butyl ethyl ether is 143 kJ mol<sup>-1</sup>. This value is significantly lower than those reported in [3] for similar ether compounds like diethyl ether (198 kJ mol<sup>-1</sup>). The latter data are derived from closed-system pyrolysis at pressures below 0.05 MPa and temperatures above 833 K. The discrepancy can be explained by an accelerated decomposition process of ether molecules by multiple chain propagation steps at an elevated pressure [4]. Thus, one thermally induced ether bond rupture results in several successive ether bond cleavages as individual radicals may react with many ether molecules due to the higher concentration of the model compound at a pressure of 20 MPa in the closed system. The multiple reactions caused by the decomposition of one ether molecule result in a lowered overall activation energy for the decomposition process [4]. The observed pressure effect implies that kinetic parameters obtained at elevated pressures seem to be more applicable for the kinetic simulation of processes in the subsurface at elevated in situ pressures.

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## STUDY OF THE FORMATION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) FROM HYDROCARBON PYROLYSIS IN LOW-PRESSURE GAS CARBURIZING CONDITIONS

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Low-pressure gas carburizing is a heat treatment process used to harden surface of steel by enriching the metal with carbon atoms coming from pyrolysis of hydrocarbons. Unfortunately, at the same time, a wide variety of molecules and radicals are also formed in the gas phase. They react together, leading to the formation of Polycyclic Aromatic Hydrocarbons (PAHs), which are soot precursors. Released into the atmosphere or adsorbed on soot, PAHs are toxic to humans and hazardous to the environment. Sixteen were classified as priority pollutants by the United States Environmental Protection Agency (US-EPA): naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene, dibenzo(a,h)anthracene and benzo(g,h,i)perylene. Some of them, such as benzo(a)pyrene (C<sub>20</sub>H<sub>12</sub>), are known carcinogens (see International Agency for Research on Cancer).

A detailed kinetic model was developed in order to describe PAH formation during hydrocarbon pyrolysis in gas carburizing conditions, i.e. at low pressure and at temperature ranging between 900 and 1000°C. It focuses on the prediction of the formation of the sixteen EPA-PAHs. This model attempts to reproduce from elementary reactions the different reaction pathways involved in the pyrolysis of hydrocarbons, in the formation of the first aromatic rings and in the growth of PAHs.

An existing model of ethylbenzene and anisole combustion was used as the starting point. It contained the reactions of formation for PAHs up to four aromatic rings. It was supplemented to take into account the formation of heavier PAHs. Modifications were made for light compounds and existing PAHs either by adding reaction pathways or by updating rate constants to better take into account the pyrolysis and low-pressure conditions.

The model was validated using various experimental data from the literature: results obtained during pyrolysis of different hydrocarbons (acetylene, ethylene, propylene, propane), in different kinds of reactors (plug-flow reactor, perfectly stirred reactor) and with different conditions for pressure, temperature and residence time. The agreement between model predictions and experimental data is uneven depending on the operating parameters but the orders of magnitude obtained for PAHs are broadly correct.

The model was used to compare the amount of the sixteen EPA-PAHs formed during pyrolysis of acetylene, ethylene and propane, the most used in gas carburizing processes hydrocarbons. At low pressure, there are more PAHs formed for acetylene pyrolysis, but acetylene is also considered as the better carbon source for carburizing. Flux analysis was realized in order to highlight the main reaction pathways, which lead to the formation of first rings and of PAHs for each reactant.

Experiments are in progress. Pyrolysis of acetylene at low pressure is realized in two reactors: a perfectly stirred reactor and a plug-flow reactor. Thereafter, experiments will be carried out with an iron part into the reactor to show the influence of its presence on the generation of PAHs. At the outlet of the reactor, light products of pyrolysis are analyzed by on-line gas chromatography, PAHs in solid phase are recovered by filtration and PAHs in gas phase are recovered by adsorption to a resin. All PAHs are then analyzed by gas chromatography (MS and FID detectors) and by HPLC (fluorescence detector). These experiments will allow, on one hand, to improve the model and, on the other, to find operating conditions to make safer the low-pressure gas carburizing process. This work can be applied to other processes which can produce PAHs by pyrolysis, such as atmosphere carburizing and carbonitriding, or by combustion.



## PYROLYSIS OF N-BUTYLCYCLOHEXANE AT HIGH PRESSURE (100 BAR). STABILITY OF NAPHTHENES IN PETROLEUM RESERVOIRS

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The understanding of thermal cracking reactions in oil reservoirs is necessary to better estimate the thermal evolution of oils over geological history and their composition. Thermal processes i.e. cracking reactions occur during geological time (millions of years) at 100-1000 bar and 150-220°C in reservoirs. To simulate these thermal processes at the laboratory scale, pyrolysis experiments on oils, oil fractions or even model compounds are performed at high pressure ( $\geq 100$  bar) but at higher temperatures (between 300°C and 500°C), to obtain acceptable durations of experiments (from a few hours to 1 month). Petroleum is a complex chemical mixture: it is basically composed of three major chemical families in close proportions i.e. alkanes (n- and iso-), cycloalkanes or naphthenes (mostly alkylcyclohexanes and alkylcyclopentanes) and aromatic compounds [1]. Therefore, each chemical class has been studied via model compounds [eg. 2–5] but the knowledge of the thermal cracking at high pressure and low temperature actually lacks for the class of cycloalkanes [6].

The pyrolysis of n-butylcyclohexane at high pressure (100 bar) was studied in gold sealed tube reactor between 300 and 425°C. Conversion obtained was between 3% and 99% [7]. The pyrolysis led to 3 main chemical classes of products: alkanes (methane, ethane, propane and butane), naphthenes (cyclohexane, methylcyclohexane, methylcyclopentane) and alkylbenzenes (benzene, toluene, butylbenzene). This distribution of major products does not suggest any ring opening while thermal cracking but breakings of alkyl side chain along with aromatization. Early production of butylbenzene at low conversion indicates that aromatization occurs beforehand. Reaction pathways mainly based on free-radical reactions were proposed to account for the formation of major pyrolysis products i.e. propane, cyclohexane, methylcyclopentane and butylbenzene. Experimental data enabled to determine apparent global kinetic parameters under the assumption of first-order rate: frequency factor  $A = 6.7 \times 10^{16} \text{ s}^{-1}$  and activation energy  $E_a = 69 \text{ kcal/mol}$ . Several comparisons with n-alkanes, aromatic compounds and naphthenes were made to observe relative thermal stability between classes and the influence of the length of an alkyl side chain.

A detailed kinetic model consisting of 833 reactions has been developed to describe the thermal cracking of n-butylcyclohexane at high pressure. A primary mechanism was written in an exhaustive manner whereas a partial secondary mechanism was considered to describe the formation and the consumption reactions of aromatic compounds. The model was tested against our experimental data for BCH pyrolysis at 100 bar in the temperature range 375-425°C. A global agreement was reached for BCH conversion up to 50% for both conversion and product yields e.g. propane, cyclohexane and toluene. Flow analysis of the proposed mechanism confirmed that ring opening is a minor pathway at 400°C. Alkanes i.e. methane, ethane, propane and n-butane mainly come from the breaking of the side alkyl chain. Cycloalkanes i.e. cyclohexane, methylcyclohexane and ethylcyclohexane mainly come from the breaking of the side alkyl chain. The production of butylbenzene is due to the direct dehydrogenation of BCH whereas other alkylaromatic compounds i.e. benzene, toluene and ethylbenzene seem to come from the breaking of the side alkyl chain of butylbenzene rather than aromatization of cycloalkanes or alkylcyclohexenes.

As a major chemical class in oil reservoirs and due to their particular structure, cycloalkanes are key compounds to better understand interconversions between main chemical classes i.e. alkanes (n- and iso-), cycloalkanes (alkylcyclohexanes) and aromatics (alkylbenzenes) in geological conditions (several hundred bars and 200°C). This model provides some answers of the thermal stability of petroleum fluids.

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## AROMATIC FORMATION DURING THE PYROLYSIS OF TETRAHYDROFURAN IN A JET-STIRRED REACTOR

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Tetrahydrofuran is one of the many oxygenated molecules which can be found amongst promising second generation biofuels. The use of oxygenated fuels in transportation engine is beneficial for the reduction of the dependence on fossil fuels and the reduction of CO<sub>2</sub> emissions as it is produced from renewable resources. But the oxidation and decomposition of oxygenated molecules is a source of new types of pollutants which can be harmful for the environment. It is crucial to better understand the gas phase reactions of these new biofuels to limit emissions as much as possible.

The pyrolysis of tetrahydrofuran was performed in a fused silica jet-stirred reactor operated at steady state over the temperature range 700-1225 K. The residence time was 2 s and the pressure was 106.7 kPa (800 Torr). The fuel was diluted in helium (fuel inlet mole fraction of 0.01) to avoid the formation of temperature gradients due to the reaction heat sink. The outlet gas was analysed using gas chromatography.

23 reaction products were quantified in this work. Species were hydrogen, non-aromatic C<sub>1</sub>-C<sub>5</sub> hydrocarbons (methane, acetylene, ethylene, ethane, allene, propyne, propane, 1,3-butadiene, 1-butene, and 1,3-cyclopentadiene), C<sub>6</sub>-C<sub>10</sub> aromatics (benzene, toluene, styrene, indene, and naphthalene) and C<sub>1</sub>-C<sub>4</sub> oxygenated compounds (carbon monoxide, formaldehyde, acetaldehyde, methyl-oxirane, furan, acrolein, and propanal).

Some reactivity is already observed at 875 K according to the rise which is observed in the mole fraction profile of species like carbon monoxide, methane, ethylene and propene. CO was the main oxygenated intermediate, followed by formaldehyde and acetaldehyde. Larger oxygenated species were present in small amounts. The main hydrocarbons were methane, ethylene and propene. Important amount of hydrogen were observed from 1025 K. Aromatics are formed at temperatures above 1025 K.

The analysis of the selectivity of reaction products revealed that CO (39%) and propene (32%) were the main intermediates at 875 K (the lower temperature at which some reactivity is observed), followed by methane (19%) and ethylene (10%). This suggested that the first steps in the decomposition of the fuel involve the elimination of carbon monoxide.

A model from the literature was used to compute mole fractions under the same conditions as those used in experiments [1]. Some discrepancies were observed between computed and experimental data, showing that the thermal decomposition of tetrahydrofuran is far from being comprehensively understood. The kinetic analysis performed at 1050 K (about 50% of fuel conversion) showed that the most sensitive reactions are the unimolecular initiation to butanal (through the formation of a diradical) and the abstractions by H and CH<sub>3</sub> of the H-atoms from the two carbon ones linked to the oxygen. Kinetic constants of these reactions had to be increased to obtain a better agreement. A factor of 4 was necessary for H-atom abstractions. The activation energy of the unimolecular initiation to butanal was lowered from 103 to 95 kcal.mol<sup>-1</sup>.

This study showed that the chemistry involved in the pyrolysis of cyclic oxygenated fuels is still not well understood and that kinetic parameters of elementary steps involved in this chemistry need to be more investigated.

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## KINETIC MODELING OF TRIS(3-CHLOROETHYL)AMINE PYROLYSIS

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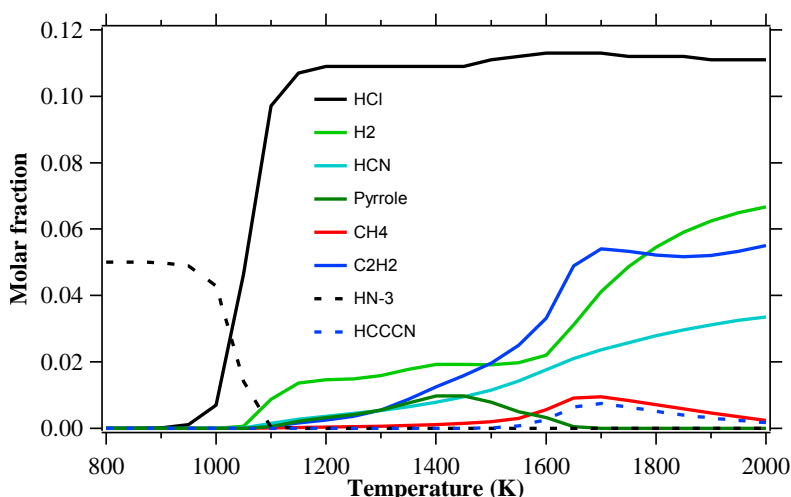
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The destruction of stockpiles or unexploded ammunitions of nitrogen mustard (HN-3) by thermal treatments requires the development of highly safe processes. On the basis of chemical and physical properties such as volatility and susceptibility to hydrolysis, HN-3 is considered environmentally persistent. Thus, this toxic can be found in the ground or in water where it hydrolyzes, particularly under weak alkaline conditions. Previous work available in the literature on the degradation of this molecule essentially involves hydrolytic degradation at low temperature [1-3]. To the best of our knowledge, no study is available concerning the thermal degradation of HN-3. The high-level of toxicity of this compound induces a high level of complexity for any experiments. Consequently, there is a considerable lack of knowledge on the behavior of this chemical under high-temperature conditions.

In this work, a detailed chemical kinetic model for the pyrolysis of nitrogen mustard gas is proposed. A large number of thermo-kinetic parameters were calculated using quantum chemistry and reaction rate theory. The gas-phase pyrolysis of HN-3 has been theoretically investigated assuming a homogeneous close reactor, using the program Senkin of Chemkin II [4] in the following conditions: temperatures ranging from 800 to 2000 K, the reactor volume is 10 cm<sup>3</sup> and an initial pressure of 10 bar, the total concentration of HN-3 is kept constant with a molar fraction of 5% in nitrogen dilution.

The kinetic analyses showed that the degradation of HN-3 is ruled by two different behaviors. For the temperatures below 1400 K, about 95% of the consumption of HN-3 is due to the H-atom abstraction reactions, and the unimolecular initiation reactions implies only 5%, in this case, it can be concluded that the mechanism is in long chains and that the propagation predominate before the other decomposition process. For the temperatures above 1400 K, the degradation pathways of HN-3 show that free radical reactions related to the unimolecular initiations become very important with a flow of about 50%. The molecular elimination represents a flow of 17% while the abstraction reaction represents only 33% of total consumption of HN-3. It can be concluded that the long chain degradation is unavailable at higher temperatures and the mechanism of the degradation of HN-3 becomes more complex.

Generally, the decomposition of HN-3 under pyrolysis conditions lead to high amounts of hydrochloric acid, hydrogen and acetylene. At low temperature (< 1400 K) pyrrole is the main nitrogen-containing intermediate, while at high temperature (> 1400 K), radical decompositions lead more quickly to the formation of hydrogen cyanide (HCN).



**Fig. 1** Simulation of the thermal degradation of HN-3 in a close reactor at different temperatures with a reaction time of 10<sup>-4</sup> s (5%HN-3/N<sub>2</sub>, 10 bar)

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## MECHANISM OF DIBENZOFURAN PYROLYSIS AND OXIDATION

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Municipal waste incineration and other thermal processes lead to the formation of "dioxins" in trace amounts [eg 1]. Dioxins (PolyChloro-DibenzoDioxins/Furans: PCDD/PCDF) are persistent organic micro-pollutant (POP) resulting from incomplete combustions. Most of the studies proposed on dioxins concern their formation, some theoretical studies on their destruction are also available but there is a lack of experimental data. Some recent studies have investigated several oxidation elementary reaction steps by quantum chemistry [2] and Summoogum et al [3] published the first experimental and theoretical study of oxidation of dibenzodioxin.

Our previous work [4] consists in experimentally studying their destruction in a postcombustion area. Dibenzofuran (DBF) is chosen in a first approach as a model molecule of polychloro-dibenzofurans (PCDF). Its abatement is studied at very small amount (i.e. near 2 ppm) both in pyrolysis and oxidation (3 to 16% oxygen) conditions, in a continuous perfectly stirred reactor, at atmospheric pressure. The residence time varies between 3s and 5s, whereas temperature ranges from 500°C to 950°C. The main byproducts are derivatives of benzofuran, polyaromatic hydrocarbons and other volatile organic compounds. All these results will be very useful to understand the early stage of the DBF decomposition and then to improve a detailed kinetic mechanism based on elementary steps and previously validated with experimental data obtained with higher ranges of DBF concentration [5-6].

In oxidation, the major initiation is the bimolecular reaction with oxygen leading to DBF• radicals. In order to take the pyrolysis results into account, new initiation processes are added including the cleavage of C-O bond leading to a biradical, and the bimolecular initiation between two DBF molecules. Several other reactions are added. The ipso-additions of hydrogen or methyl radicals on aromatic cycle of dibenzofuran and secondary products are new important pathways for the decomposition of dibenzofuran and the formation of benzene or toluene. A systematic approach was used to build the reaction mechanism. The final DBF pyrolysis and oxidation mechanism contains 252 species involved in 1369 elementary steps. The kinetics parameters come from database, literature or estimations. The simulations were performed using Chemkin II software.

Our detailed mechanism is used to model the oxidation of dioxins in a postcombustion area of municipal waste incineration; some simplifications were used: PCDD/PCDF families are represented by the dibenzofuran and postcombustion area is 0D modeled (CFSTR reactor). This simplified approach brings a new contribution to understand these complex reactions and to allow the development of an efficient post-combustion (abatement of dioxins by total oxidation). The simulations of dibenzofuran oxidation show that the reactivity strongly decreases when the reactant is very diluted. The key parameter is the concentration of radicals which is controlled by the initiation rate and branching steps. The addition of natural gas in low quantities (eg. 1000 ppm) induces an important increasing of radical concentration and promotes the DBF oxidation very efficiently.

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# FUNCTIONALIZED CARBON-BASED SUPPORT MATERIALS FROM BENCH-SCALE BATCH PYROLYSIS FOR PHOTOCATALYTIC OXIDATION OF VOLATILE ORGANIC COMPOUNDS (VOCS)

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The design of novel and innovative methodologies to maximize current available resources without compromising the future of coming generations is one of the most important challenges of the 21st century. The scarcity of resources and the expected increase in population and energy demands are two of the most important issues to be addressed. In this regard, green chemical and low environmental-impact technologies combined with renewable resources through innovation will be able to offer alternatives to potentially useful processes for a more sustainable carbon-based society. Biomass is one of the most promising and widely available renewable feedstocks that has a significant potential to offer a number of alternatives to be converted to materials, fuels, and chemicals[1]. Photocatalysis is currently considered as one of the most advanced and promising environmentally friendly technologies [2-3]. Biomass pyrolysis is a technology that has the potential to reduce our dependence on fossil resources by providing alternative fuels and specialty chemicals [4], as well as materials.

In this work we prepared a series of new inorganic-organic hybrid materials, based on metal oxide (e.g. TiO<sub>2</sub>) and new carbon-based supports (e.g. Starbon®, biochar), using innovative method of bench-scale batch pyrolysis and/or ultrasound-assisted methods. Thus prepared materials were studied by a spectrum of physico-chemical techniques (e.g. XRD, XPS, HRTEM, FTIR, UV-Vis) to characterise these carbon-mineral composites. The photocatalytic activity and selectivity of these materials were evaluated in our new system for photocatalytic oxidation of VOCs [5]. The proposed methodology and use of renewable raw material (biomass) as a carbon support should provide new readily available functional nanomaterials that enable access to a large variety of functional materials including carbon-based support materials with photocatalytic properties to purify the air with volatile organic compounds (VOCs).

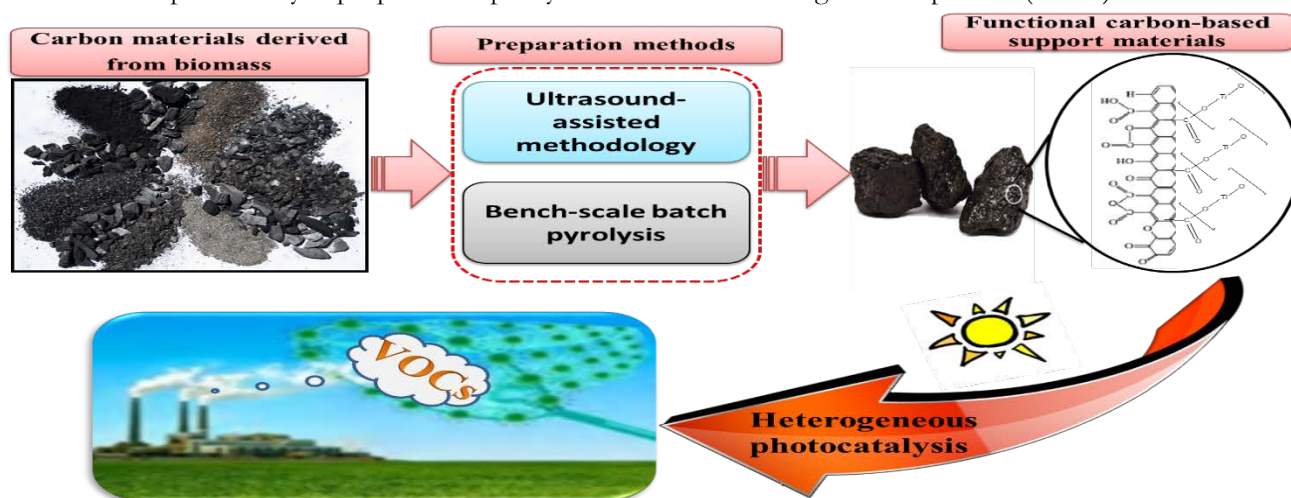


Fig. 1 Synthesis of functionalized carbon-based support materials for photocatalytic oxidation of VOCs

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## KINETIC STUDY OF METHYLCYCLOHEXANE PYROLYSIS

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Hypersonic researches focus on the thermal management of the vehicle and more especially of the engine because of the large heat load due to the high velocity and the combustion of the fuel. One possibility called « active cooling » is circulating the fuel itself through the walls of the engine, with cooling achieved through the strongly endothermic decomposition of the fuel [1, 2]. In order to quantify the heat transfer in the cooled structures and the composition of the cracked fuel entering the combustor, an accurate model of the thermal decomposition of the fuel is required. Jetfuels used in aeronautic are mainly petroleum based kerosenes containing several classes of hydrocarbons. Other Jetfuels are pure hydrocarbons or mixtures containing molecules such as n-dodecane [3,4] or tricyclodecane [5]. In the literature, there is a lack of experimental data on cyclic alkanes pyrolysis. In order to better understand the thermal decomposition of cyclanes (or naphtenes), the methylcyclohexane is chosen in a first approach as a model molecule.

Methylcyclohexane pyrolysis is studied in a continuous perfectly jet stirred reactor at atmospheric pressure, diluted in helium (initial mole fraction of 3%). The chosen residence time is 1second and temperature from 600°C to 725°C ; the methylcyclohexane conversion ranges between 0% and 55%. Several intermediate species are formed during pyrolysis. The main products of the pyrolysis reaction are hydrogen, methane, ethylene, propylene, and in lower quantities, benzene, toluene and cyclohexene. These experimental results have been compared with those obtained in this study for the pyrolysis of n-dodecane. The main products of these reactions are the same for both compounds. The conversion is more important in the case of n-dodecane (2% to 70%) than for methylcyclohexane (0% to 55%) for the same range of temperature.

A previous detailed kinetic model of the thermal decomposition of methylcyclohexane [6] has been improved and completed. The primary mechanism contains all the possible initiation steps, it is built in a systematic manner in order to be very detailed and a partial secondary mechanism is also included. This model is able to represent the experimental results presented here with reasonable accuracy, both for the conversion and for the formation of products.

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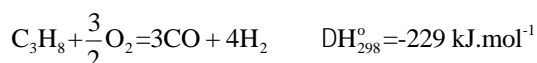
## MICROKINETIC MODELING OF HYDROGEN PRODUCTION BY CATALYTIC PARTIAL OXIDATION OF PROPANE OVER CeO<sub>2</sub>

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Currently, the world depends on the fossil fuels (oil, coal, and natural gas) as energy sources. However, use of fossil fuel led to significant CO<sub>2</sub> emission causing an abnormal increase of the atmosphere temperature. Hydrogen is proposed as an energy vector for the future. Hydrogen is mainly produced by steam reforming of natural gas and light hydrocarbons but steam reforming is costly (highly endothermic reaction). Partial oxidation of hydrocarbons can be a good alternative to equilibrate the thermal balance (autothermal reforming [1]) and the propane use is interesting since it is a constituent of the LPG and so it can be easily stored.



However, the catalytic partial oxidation of hydrocarbons is also attractive for production of syngas or oxidative dehydrogenation of light paraffins. From an academic point of view, propane is the first hydrocarbon with primary and secondary carbon. This could induce a difference in activity and selectivity in oxyreforming due to the difference of energy C-H bond breaking.

Generally, hydrocarbon partial oxidations are performed in the presence of a catalyst. The use of a catalyst can decrease the temperature required for the reaction and/or improve hydrogen selectivity. In previous studies on methane oxyreforming [2] over La<sub>2</sub>O<sub>3</sub>, we saw the interest of the use of a catalyst with basic properties. In this case, the experiments were performed with cerium oxide as a catalyst. CeO<sub>2</sub> has already been used in partial oxidation of methane [3] and it is used in many other applications. One of the interests of CeO<sub>2</sub> is the mobility of the surface oxygen and consequently the creation of lattice.

Therefore, in these catalytic reactions, homogeneous radical mechanism in gas phase is associated with a heterogeneous mechanism at the catalyst surface. These two mechanisms operate in parallel and are highly coupled by the intermediary of radicals with process of Eley-Rideal type. Thus, catalytic hetero-homogeneous reactions involve the use of two disciplines: catalysis and kinetic in gas phase.

In this work, an experimental study of the catalytic partial oxidation of propane in presence of ceria was carried out in a perfectly stirred reactor. To model the reaction with a catalyst, it is primordial to consider both a homogeneous mechanism and a heterogeneous mechanism. Thanks to our previous study of the homogeneous oxidation of propane [4], a homogeneous mechanism has been validated for our experimental conditions. A method based on the Benson theory [5] to estimate kinetic parameters of heterogeneous reactions is proposed. This method allows, without the use of software, to obtain an estimate of the kinetic parameters of elementary reactions. So that these calculations are easy to use by an experimenter wishing to simulate his results.

The experimental results were modelised using Chemkin Surface Software. The development and the validation of a hetero-homogeneous mechanism was proposed based on elementary steps at the catalyst surface and on a homogeneous mechanism in gas phase for a large range of temperature, residence time and amount of catalyst.

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4. Hognon C, Simon Y, Marquaire PM. *Energy and Fuels*. 26(3), pp 1496-1508, 2012.
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## PYROLYSIS OF DIETHYL ETHER IN A JET STIRRED REACTOR

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Soil remediation becomes more and more important for the preservation of the environment and human health and the reuse of polluted areas. Several strategies can be used according to the nature of organic pollutants. Thermal desorption followed by thermal decomposition can be used for the treatment of pollutants such as hydrocarbon fuels, poly-aromatic hydrocarbons, or species containing heteroatoms (e.g. chlorine, sulphur). It is crucial to understand the chemistry of thermal decomposition of these pollutants to predict the influence of operating conditions on the nature and concentration of reaction products.

In this work, a model molecule with an oxygen atom was chosen to highlight the influence of the presence of a heteroatom on the reactivity and the product formation: diethyl ether (DEE). The pyrolysis of DEE was studied at temperatures from 600 to 1100 K using a fused silica jet stirred reactor under dilute atmosphere. The effects of the initial composition of DEE-helium mixture, the residence time and the pressure have been investigated. The outlet gas was analysed using gas chromatography.

A DEE conversion of 99.92 % was observed for an experiment at 800 torr, a residence time of 2 seconds and an inlet mole fraction of DEE of 0.01. The following species were detected: ethylene, acetaldehyde, ethanol, carbon monoxide, methane, ethane, acetylene, benzene, propane, propene, 1-3 butadiene and propyne. The first 5 species in the list were the major products of the pyrolysis of DEE. Experimental data showed almost no influence of the pressure and inlet composition on the reactivity and product selectivity. However, the DEE conversion is influenced by the residence time.

A detailed kinetic model based on the work from Yasunaga et al. [1] has been developed and tested against the experiments. The agreement is overall satisfactory for the fuel conversion and reaction products. This model has been used to highlight consumption paths of DEE, particularly the routes of formation of benzene.

This work has been supported by TERbis, 943 rue Pasteur, 60700 Pont Sainte Maxence, France.

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# EXPERIMENTAL AND AB INITIO STUDIES ON PYROLYSIS MECHANISM OF THREE ISOMERIC DIHYDROXYBENZENES

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## Introduction

The pyrolysis technique is implemented to convert biomass into valuable fuel gases which can be directly utilized or refined as a liquid fuel and chemical products. Phenolic compounds are well-documented byproducts from the thermal degradation of biomass, and in this study *ortho*-, *meta*- and *para*-dihydroxybenzene isomers (Fig. 1) are employed as models of the volatiles. The studies concerning the pyrolysis mechanism are, however, limited. The objective of this research is to analyze the pyrolysis mechanism of the dihydroxybenzenes by combining experimental studies with ab initio methods.

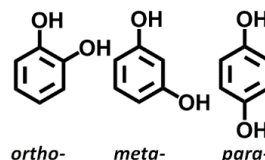


Fig. 1: Dihydroxybenzene isomers.

## Experiment

Pyrolysis mechanism of dihydroxybenzenes was investigated by a two stage tubular reactor (TS-TR)<sup>[1]</sup> connected with gas chromatography (GC). Fig. 2 illustrates the yields of CO and CO<sub>2</sub> at 650 – 950 °C with residence time of 0.3 s. Although CO was mainly produced from the three isomers, much more CO<sub>2</sub> was detected from *m*- than from *o*- and *p*-dihydroxybenzenes.

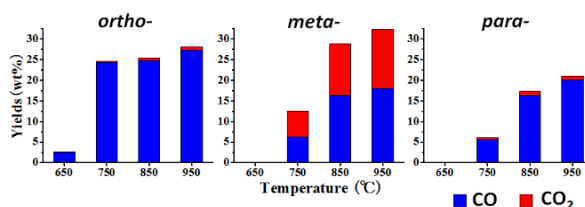


Fig. 2: Yields of CO and CO<sub>2</sub>.

## Ab Initio Calculation

Fig. 3 shows the possible pyrolysis pathways for *m*-dihydroxybenzene, **R**, losing CO and CO<sub>2</sub>. Equilibrium geometries and transition structures were optimized by use of a series of high accuracy methods including a complete basis set extrapolation, the CBS-QB3 composite method. The activation energies at each reaction step were obtained from the difference between the energies of the transition state and the reactant.

The pyrolysis pathways of **R** commenced with the O-H bond fission (step 1), and then generating *m*-semiquinone radical, **M1**. There are two decomposition pathways for **M1**. In the first channel, the aromatic ring contracted to form **M2**, followed by breaking a C-C bond of the three-membered ring and subsequently decomposing to **M5** and CO molecular. The second channel affords the formation of *m*-benzoquinone biradical, **M6**, generated by the O-H bond dissociation (step 2). Ring-closing and opening in **M6** occur to form **M7** and **M8** respectively, and cyclizing to a five-membered ring intermediate state **M11**. Then, the ketone radical group combines with carbon site on the carbonyl radical group to form **M12**. **M13** is generated by opening the four-membered ring in **M12**, and subsequently losing CO<sub>2</sub>. The rate-determining steps will be step 1 and step 2 with a high barrier of 86.2 kJ/mol.

Fig. 4 shows the rates ( $k$ ) for two main channels, step1 and step 2, calculated at the B3LYP/6-311G(d,p) by using variational transition state theory (VTST). This figure indicates that the two rate constants showed little difference over the entire temperature range. All reaction pathways toward CO and CO<sub>2</sub> elimination inevitably go through step 1 associated with a rate-determining step. Consequently, our theoretical calculation supported the experimentally-detected CO<sub>2</sub> expulsion from *m*-dihydroxybenzene pyrolysis.

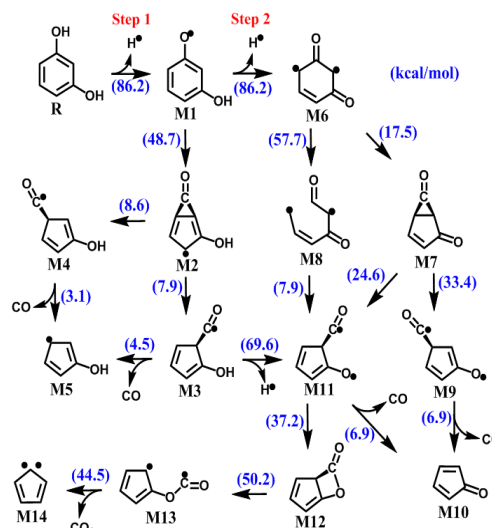


Fig. 3: Pyrolysis pathways of **R**. All values are activation energies (kcal/mol) at each reaction step.

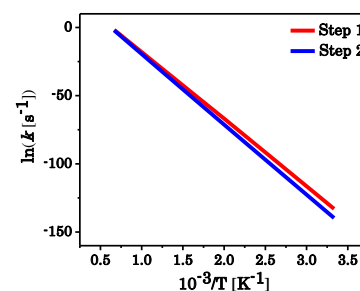


Fig. 4: Rate constants  $k$ .

[1] K. Norinaga, H. Yang, R. Tanaka, S. Appari, K. Iwanaga, Y. Takashima, S. Kudo, T. Shoji, J. Hayashi, Biomass Bioenergy 69, pp. 144-154, 2014.



ABSTRACTS

# Instrumentation

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## Oral presentations

## MODELING PHYSICAL PHENOMENA DURING FAST PYROLYSIS OF BIOMASS IN A HEATED FOIL REACTOR

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### Abstract

Heated foil reactors have been widely used for the characterization of solid fuels mainly because of their ability to reach high heating rates and for the minimization of secondary reactions of primary devolatilization. However, because of the small size of these types of reactors and the speed of the phenomena involved, precise control of experimental conditions is difficult. In order to overcome this difficulty a numerical model, in COMSOL Multiphysics™, was developed to provide a better insight into the conditions and the phenomena occurring. More specifically the heat distribution inside the reactor, on the foil and inside the pyrolysing sample was investigated. The model showed an area at high temperature and low velocity around the foil suggesting that secondary reactions could still occur around this area. This occurrence was verified by the projection of the volatiles trajectory. Design of shorter supports for the foil could aid towards further minimization of secondary reactions. The main mechanism of heat transfer was found to be radiation while negligible heat was found to be dissipated through the thermocouple connected at the bottom of the foil. Finally, a significant temperature gradient was found between the foil and the pyrolysing sample, especially at high temperatures. A relationship between these two temperatures was deduced and its effect during extrapolation of kinetic data from fast devolatilization experiments is shown.

## KINETIC OF POLYSTYRENE PYROLYSIS IN MICROWAVE TGA

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Rapid population growth combined with a spread of the modern lifestyle gives rise to an increase in overall consumption. This leads to a more globalized use of plastics resins and therefore a more important generation of plastic waste. According to the EPA [1], about less than 10% of the plastic produced in the USA is recycled. The principal reason for this is the incapacity to reprocess the plastic waste in such way that the output can be re-used into virgin plastic applications, such as production of food and beverage containers or other consumer goods. Although technologies exist for PET where it can reintroduce PET into some FDA compliant applications [2], it is not the case for most of other post-consumer plastics, such as polystyrene, especially when they are contaminated, e.g., organic materials and paints. The present paper wants to show how microwave pyrolysis (MP) can be applied at commercial scale for recycling post-consumer contaminated plastics and allow them to be re-used in FDA compliant applications. The mechanism of action is simple: the use of MP breaks down the post-consumer plastics into monomers and waxes that are then re-introduced in the existing ecosystem of refining and polymerization industries. What differentiates microwave pyrolysis from other conventional pyrolysis processes is the heating rate which is fast because energy is transferred on a volumetric basis, whereas other conventional approaches are slower because the heating occurs on a conduction/convection basis. The pyrolysis step allows handling of a broader amount of contaminants compared to mechanical/physical technologies such as organics, fibres and minerals.

From a more fundamental perspective, this change in the heating mechanism affects the heating profile and it is known to induce changes in the reaction kinetic. Differences in the activation energy and the Arrhenius pre-exponential constant have been found by Farag & Chaouki [3] and Dong & Xiong [4] when comparing kinetics from microwave and conventional pyrolysis. In order to properly understand the reactions involved during pyrolysis using microwave heating, kinetics analysis is crucial. Due to the technical difficulties, mostly related to controlling the heating rate accurately and maintaining safety conditions acceptable, very few researchers have developed kinetics models in a microwave radiation environment. Works in similar conditions have been attempted in the past but the parameters obtained had rather large uncertainties and their methodology enlightened difficulty of maintaining and measuring temperature across the sample.

This present paper aims at providing more accurate data on the pyrolysis kinetics using microwave heating. In order to attain this level of precision, a novel setup microwave thermogravimetric analyser (MW-TGA) was developed. The reactor is a custom-made quartz test tube 5/8 inches in diameter and 12 inches in length. The MW-TGA is equipped with a bed of novel silica-based microwave receptor small enough (4g) so that the temperature of the reaction is constant throughout the bed. The amount of reactant is small enough (<1g) so that the heat and mass diffusion across the sample is negligible. The reaction temperature is measured by an ungrounded type K thermocouple that is hooked to the cavity of the microwave to eliminate its reactivity with the microwave. The mass loss of the sample is recorded by a load cell and a continuous flow of nitrogen (500 mL/min) is used to purge the pyrolysis gases. The reaction chamber is powered by four adjustable 800W magnetrons for a total of 3600W of adjustable power. The fast heating rate of the microwave combined with a PID controller allows for both isothermal and non-isothermal kinetics studies.

The conference will present the MW-TGA apparatus along with its features. A case study using polystyrene as a post-consumer plastic will also be presented and compared with results from kinetics developed by conventional heating.

[1] United States Environmental Protection Agency (EPA), 2015.

[2] United States Food and Drug Administration (FDA), 2015.

[3] S. Farag and J. Chaouki, *Applied Thermal Engineering*, 75, (2015) 65.

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## Investigation of Epoxy Resins with Different Analytical Pyrolysis Systems

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Epoxy resins are used as binders in many high tech applications due to their excellent material properties and easy application. In most cases they are comprised of a resin, typically the glycidyl ether of bisphenol A, bisphenol F, or a phenol formaldehyde resin, and a hardener. The latter one can be organic anhydrides (hot binder), various polyamines or mercaptanes (cold binder).

We have analyzed a series of different binders and hardeners before curing and combinations of these after exposing them to different curing conditions and compared the results obtained on different analysis systems. One is a CDS Pyroprobe another is a Gerstel pyro and the third one is a Pyrola system. Whereas the CDS system mostly produces breakdown products such as phenol, isopropenylphenol, or bisphenol A (in case of a bisphenol A based epoxyresin), the Gerstel and Pyrola systems produce high amounts of bisphenol A diglycidyl ether and only low amounts of the breakdown products.

Fig. 1. Degradation pathway of bisphenol A diglycidyl ether.

A systematic optimization of parameters has been performed on model compounds not only for conventional pyrolysis but also for thermally assisted hydrolysis and methylation using tetramethylammonium hydroxide.

## Development of tandem micro-reactor GC/MS system with pressure control module suitable for medium pressure catalytic reactions

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Rapid screening of a wide range of chemical process conditions is often desired prior to performing larger-scale practical operations. A dedicated reactor combined with an on-line analyzer has been eagerly desired for this purpose. The authors developed a tandem reactor consisting of individually temperature-controlled two vertical micro-furnaces, which was directly connected to a GC/MS system [1, 2]. In this system, however, the reaction pressure was controlled by GC's built-in back pressure regulator, thus the reaction pressure was equal to the column inlet pressure. Therefore, when a higher pressure around 0.1~1.0 MPa, termed "medium" pressure, was applied as the reaction pressure, the separation on the chromatogram was significantly deteriorated and the mass spectrometer cannot achieve high vacuum due to too high column flow rate. In this work, a new medium pressure flow control module (MP controller) was developed to solve the problems at the raised reaction pressures and to control individually the reaction pressure and the column inlet pressure.

Fig. 1 shows the flow diagram of the tandem reactor-GC/MS coupled with a newly developed MP controller. A tandem reactor consisting of individually temperature-controlled two vertical micro-furnaces; 1<sup>st</sup> and 2<sup>nd</sup> reactors, are directly connected to the split/splitless injector of a GC/MS. Sample can be introduced into the heated 1<sup>st</sup> reactor using a micro-syringe and a micro-feeder pump for a gas and liquid, or a sample cup for a solid and the introduced sample is flash pyrolyzed at high temperature to generate gaseous products. The catalyst is packed into a quickly-replaceable quartz tube (3 mm i.d., 4 mm o.d., 80 mm length) and placed in the 2<sup>nd</sup> reactor prior to testing of the catalytic activity. Volatiles released from the heated or thermally decomposed sample are swept by a carrier gas flow into a quartz tube in the lower 2<sup>nd</sup> reactor where they react with the catalyst. The chemical species generated by vapor phase contact reaction with catalyst can be on-line analysed by GC/MS.

The carrier gas flow in the reactors is controlled by the GC's built-in flow controller. The reaction pressure is regulated by the built-in back pressure regulator (BP1) upto 0.98 MPa. The flow is splitted at the GC injector into the restrictor and the split vent through BP1. The carrier gas (ten to several dozen mL/min) flows into the open split interface via the restrictor. Then, it splits into the back pressure regulator (BP2) of the MP controller and interface (ITF) tube or separation column. Thus, the pressure in the open split interface (equals to column head pressure) can be controlled to any desired pressure by BP2 independently of the reaction pressure which is controlled by BP1.

By using the MP controller, the column flow rate could be adequately controlled and proper separation was obtained under the reaction pressure range of 0.1~0.98 MPa.

In the presentation, the influence of reaction pressure against the rate of glycerine conversion using a palladium catalyst is also demonstrated.

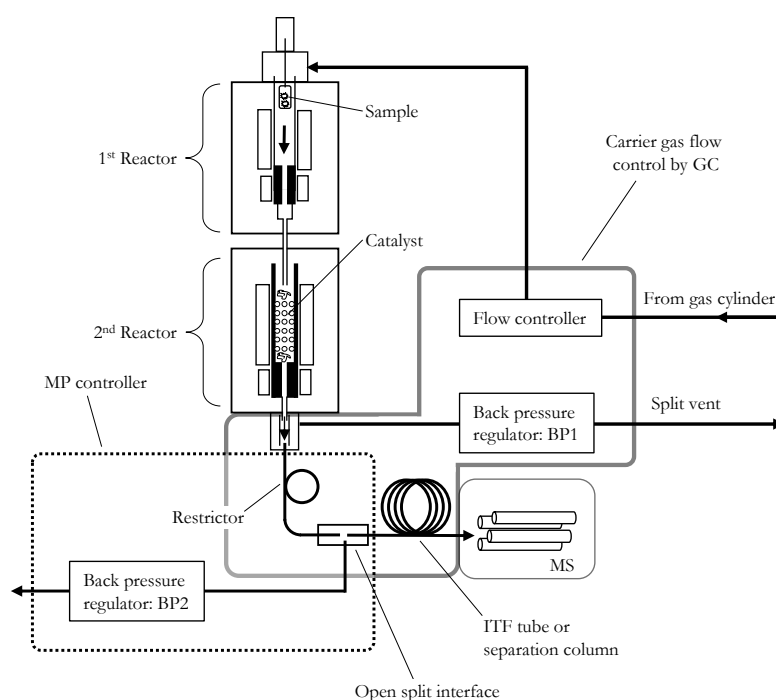


Fig.1 Diagram of tandem reactor-GC/MS with MP controller

- [1] C. Watanabe, T. Ramus, R. Meijboom, R. Freeman, *Environ. Prog. Sustainable Energy*, 33 (3), pp. 688-692, 2014.  
 [2] R. Freeman, A. Watanabe, C. Watanabe, N. Teramae, K. Wang, *J. Anal. Appl. Pyrol.*, 111, pp. 41-46, 2015.

## Characterization of crude oils and asphaltenes by pyrolysis GC/MS and thermal analysis coupled to photo ionization mass spectrometry

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Crude oil is one of the most complex chemical mixtures consisting of mainly hydrocarbons and consisting of several thousands of compounds. Unravelling its composition on a molecular level remains a challenge for analytical chemistry. However, a preferably detailed knowledge of the composition is requested with respect to oil production, refinery and storage, especially when considering the steadily sagging quality of remaining crude oil resources. In this regard, information on aromaticity and sulphuric compounds is crucial as well as more detailed knowledge on the composition of heavy low volatile fractions such as asphaltenes. Two analytical systems for the characterization of complex samples have been developed and modified, respectively, that enable the sampling introduction via thermal desorption and pyrolysis.

In the first device, pyrolysis is followed by gas chromatographic separation with subsequent mass spectrometric detection applying two simultaneous ionization methods. On the one hand, electron ionization quadrupole mass spectrometry is used for the structural identification of compounds. Resonance enhanced multi-photon ionization (REMPI) in combination with a time-of-flight mass spectrometer provides a selective and sensitive detection of aromatic species. With the REMPI technique, detection of less abundant polycyclic aromatic hydrocarbons as well as their sulfur containing derivatives is enhanced, since they are separated from the paraffinic matrix [1]. Since REMPI is a soft ionization method generation only molecular ions, an additional separation dimension is gained.

The second device is a thermo balance coupled to photo-ionization mass spectrometry. In addition to REMPI, single photon ionization using Vacuum-UV light with 118 nm was applied to characterize the thermal decomposition products. Besides crude oils two different asphaltene fractions (using either pentane or heptane as solvent) and oil sand have been analyzed. The asphaltenes were revealed to have a composition yielding mostly aromatic decomposition compounds and only a few aliphatic species. Depending on the solvent used, the aromatic pattern of the asphaltene fraction show distinct differences. Such results could prove valuable for better understanding asphaltene precipitation during oil production and refinery.

[1] Otto, S, Streibel, T, Erdmann, S, Sklorz, M, Schulz-Bull, D, Zimmermann,R, Anal. Chim. Acta, 855, 60-69 (2015)

# PYROLYSIS STUDY OF PINE WOOD USING THERMOGRAVIMETRY /SYNCHROTRON VUV PHOTOIONIZATION MASS SPECTROMETRY

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## Introduction

As pyrolysis is the initial step involved in thermochemical processes of biomass, understanding of the pyrolytic behavior of biomass is crucial to biomass thermochemical conversions. Thermogravimetry is an important method for studying pyrolysis kinetics of biomass, while molecular-beam mass spectrometry is a high sensitive technique which is capable of detecting reactive species [1-3]. This work presents a new facility for studying the pyrolysis behavior of solid fuels. The experimental setup features the combination of a thermogravimetry and a time-of-flight mass spectrometer via a single-stage molecular beam sampling interface with synchrotron VUV photoionization.

## Experimental

Fig. 1 shows the sketch of the experimental setup for the study of biomass pyrolysis. The experimental setup consists of a thermal gravimetric analyzer (TGA), a photoionization chamber with a single-stage sampling nozzle and a home-made reflectron time-of-flight mass spectrometer (TOF MS). The sampling nozzle is made of quartz with included angel of 25°, thickness of ~ 1 mm and total length of 60 mm. The diameter of the orifice is about 70 μm, and the small orifice ensures the vacuum in the ionization chamber is in the order of 10<sup>-1</sup> Pa while the reactor is kept at ambient pressure. The distance between the orifice of the nozzle and the crucible is about 2 mm. The sampled species are ionized by the synchrotron VUV light and detected by TOF MS.

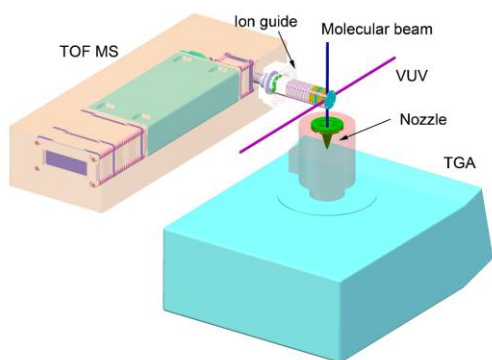


Fig. 1 Schematic diagram of the biomass pyrolysis apparatus showing the combination of the TGA and TOF MS via molecular beam sampling technique.

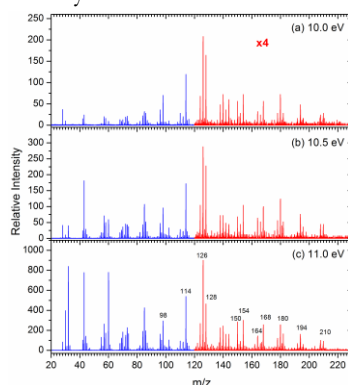


Fig. 2 Photoionization mass spectra of the pyrolysis products of pine wood collected at the temperature of XXX and various photon energies: (a) 10.0 eV, (b) 10.5 eV and (c) 11.0 eV

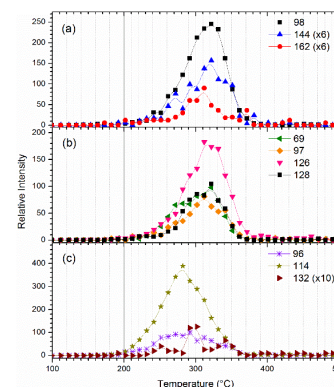


Fig. 3 Evolution profiles of some typical cellulose and xylan markers during pyrolysis of pine wood as a function of temperature.

## Results and Discussion

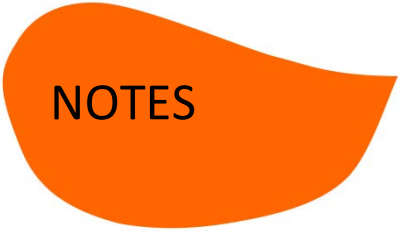
The experiments were conducted at the heating rate of 20 °C/min. Fig. 2 shows three VUV photoionization mass spectra of the pyrolysis products of white pine wood at the photon energy of 10.0, 10.5 and 11.0 eV, respectively. The main components include carbohydrate-derived compounds such as levoglucosane and lignin-derived compounds such as guaiacol, syringol, etc. Small carbonyl species including acetic acid, acetaldehyde, acetone, hydroxyaldehydes, hydroxyketones, and carboxylic acids are also observed. Fig. 3 presents the evolution profiles of some typical cellulose and xylan markers during pyrolysis of pine wood as a function of temperature.

[1] F. Qi, Proc. Combust. Inst., 34 (2013) 33-63.

[2] E. Kaisersberger, E. Post, Thermochim. Acta, 295 (1997) 73-93.

[3] E. Kaisersberger, E. Post, Thermochim. Acta, 324 (1998) 197-201.





NOTES

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ABSTRACTS

# Instrumentation

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Poster presentations

# BIOMASS PYROLYSIS REACTIONS AND PRODUCTS AS STUDIED BY THERMAL ANALYSIS TECHNIQUES

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The range of compositions of lignocellulosic biomasses (agricultural, forestry or wood transformation residues, domestic or industrial organic wastes, short rotation coppice...) is a major problem when it comes to controlling a thermochemical process [1]. Moreover, the instability of green matter makes it a tricky input material for industrial energy production processes.

From heterogenous biomass, pyrolysis allows producing more homogeneous tar (oils) or char (carbonaceous solids) that are then easily stored and transported. The process conditions are known to affect the tar / char ratio and compositions [2,3]. A key step is the release of volatiles during the biopolymers early decomposition.

Thermogravimetry consists in monitoring the mass of a reacting sample against time and temperature when it is placed in an atmosphere controlled furnace. It allows acquiring data on pyrolysis steps involving mass losses, such as the above mentioned gas releases [4]. Simultaneous differential scanning calorimetry detects all the heat effects of the sample, even when no mass change occurs during a transformation. Moreover, volatiles can be transferred to gas analyzers for identification during the whole pyrolysis test and thus provides complementary information on the chemistry of the reactions. The technique is called Evolved Gas Analysis (EGA) and typically involves the coupling of a Mass Spectrometer, FT-IR Spectrometer or combined Gas Chromatography-Mass Spectrometer.

Influences of heating rate, sample mass, grain size, and gas flow rate on the slow pyrolysis of cellulose, lignin, hemicellulose and resinous wood samples were studied by differential scanning calorimetry, thermogravimetry, and the release of volatiles was monitored by on-line Fourier transform infrared (FTIR) spectrometry. Using a new concept of high pressure thermogravimetric instrument able to operate up to 150 bar and 1200°C, the influence of pressure on the slow pyrolysis of biomass has also been studied.

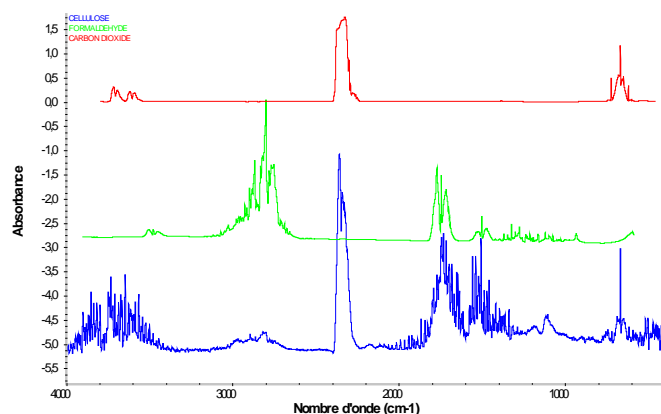


Figure 1– Experimental FTIR spectrum obtained at 356°C (bottom), compared to library spectra of CO<sub>2</sub> (top) and formaldehyde (middle)

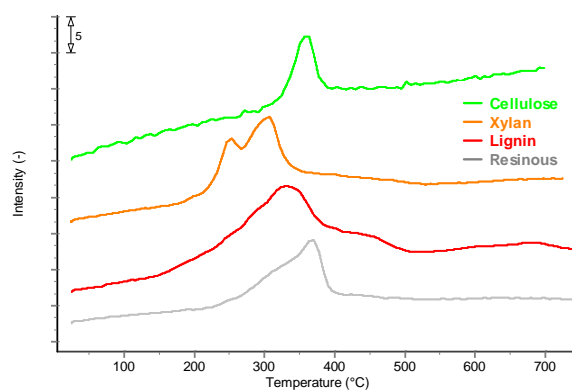


Figure 2 – Intensity variations of the stretching vibration band of CO<sub>2</sub> as a function of temperature for the 4 tested samples

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- [2] B. B. Uzun, A. E. Pütün, E. Pütün, J. Anal. Applied Pyrolysis, 79 (2007) 147.
- [3] H. Luik, L. Luik, L. Tiikma, N. Vink, J. Anal. Applied Pyrolysis, 79 (2007) 205.
- [4] M.V. Gil et al., Bioresource Technology 101 (2010) 8859–8867.

## DEVELOPMENT OF A NOVEL SILICA-BASED MICROWAVE RECEPTOR FOR MICROWAVE PYROLYSIS APPLICATIONS

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The commercial application of microwave heating is expanding to several industrial sectors particularly in chemical processing, polymer synthesis and environmental engineering applications. Microwave heating presents several advantages over conventional heating methods namely, selective and volumetric heating, instantaneous temperature control, high power density, reduced energy consumption, decreased heat transfer limitations, high reaction and product selectivity and process flexibility[1]. The intensity of microwave heating is mainly associated with the dielectric properties of materials. However, due to physical and chemical characteristics, most common materials are transparent or exhibit insignificant intractability with microwave. Subsequently, microwave receptors, materials that possess high microwave intractability and dielectric properties, are used to mitigate for the lack of heat generation. These receptors are namely carbonaceous and metallic compounds[2,3]. However, the introduction of microwave receptors in particulate forms to the system leads to disruption of the magnetic field pattern, which enhances the formation of local hotspots. Consequently, the presence of local hotspots interferes with the uniform distribution of temperature and generates large temperature gradients. Also, in fluidized bed applications and in the case of a significant density gradient between the bed material and the microwave receptors, the heating process is strongly influenced by the segregation phenomenon. Segregation deteriorates the uniform temperature distribution by transferring the low-density materials to the top of the bed, hence dividing the reactor into high and low temperature zones[4].

Consequently, an innovative silica-based microwave receptor was developed with exceptional heating properties using a fluidized bed chemical vapor deposition (FBCVD) carbon coating on sand particles via an induction heating system, thereby coupling the bed and receptor materials together. In this study, methane as precursor provided the depositing carbon through thermal degradation process (TDM), for the coating of silica sand particles. Synthesis of this novel receptor was carried out at temperatures of 800, 900 and 1000 Celsius and for FBCVD duration of 60, 120 and 240 minutes, to investigate the effect of operating conditions on carbon layer uniformity and composition. The amount of deposited carbon was identified by thermogravimetric analysis (TGA) and combustion infrared carbon detection (LECO) method for each coated sample. Moreover, the morphological analysis of the novel receptors were implemented by scan electron microscopy (SEM), focused ionized beam milling (FIB), X-ray photoelectron spectroscopy (XPAS) and energy dispersive X-ray spectroscopy (EDX), to study the effect of FBCVD operating conditions on carbon layer thickness, uniformity, structure and composition. Ultimately, the effect of FBCVD temperature and duration, microwave input current and surficial erosion on microwave heating performance of the developed receptors were investigated using a single mode microwave apparatus. Furthermore, the microwave heating performance of the coated sand particles were compared with sand and graphite particle mixtures at different mass ratios. Major features of the developed microwave receptors have been highlighted as: 1) low carbon content, 2) extreme microwave heating rate, 3) high durability, and 4) applications in gas solid fixed and fluidized bed reactors, microwave pyrolysis specifically.

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- [2] Z. Hussain, K.M. Khan and K. Hussain, *Journal of Analytical and Applied Pyrolysis*, 89, (2010) 39.
- [3] A. Undri, M. Frediani, L. Rosi and P. Frediani, *Journal of Analytical and Applied Pyrolysis*, 105, (2014) 35.
- [4] A. Gómez-Barea and B. Leckner, *Fuel*, 107, (2013) 419.

## DEVELOPMENT OF A NEW SAMPLING METHOD BY CARBON NANOTUBE BASED GECKO TAPE FOR PY-GC/MS

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Py-GC/MS is widely used in polymer analysis field and it is applicable to a variety of polymeric materials. However, if the sample is a very small amount powder, it is difficult to put in a sample cup and transfer to the pyrolyzer. One of methods which solve the problem is using ideal sample collecting and holding materials, which can collect powder sample easily like adhesive tape and are not decomposed at the thermal decomposition temperature of sample.

Therefore, in this study Gecko Tape [1], which is a new adhesive and made of only carbon nanotubes (CNT), was used as a sample collecting and holding material, and various polymer materials were analyzed by Py-GCMS. As a result, each of pyrograms was different from the usual Py-GC/MS pyrogram, and there was regularity in the change of the pyrograms.

[Acknowledgment]

This work was supported by JSPS KAKENHI Grant Numbers 25282076, 26282070.

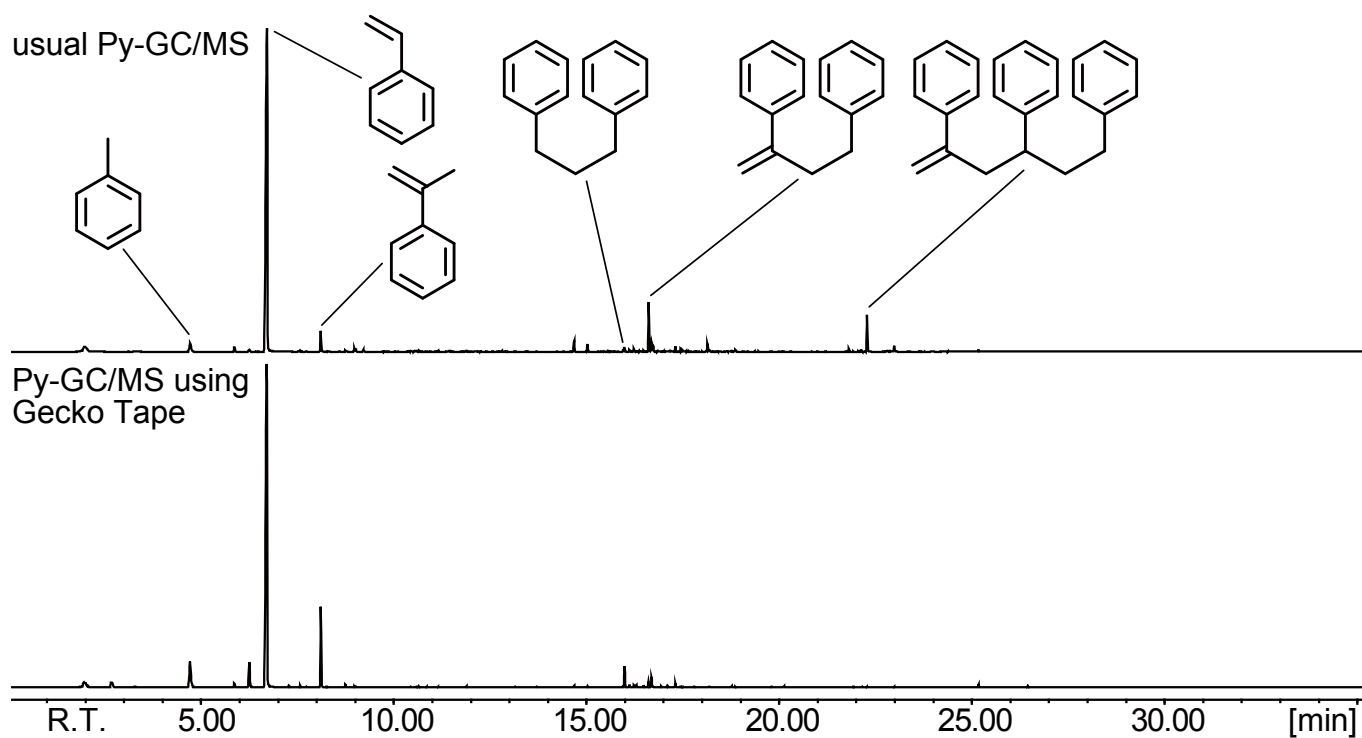


Figure Pyrograms of polystyrene by Py-GC/MS and using Gecko Tape

## EXPANSION OF THERMAL ANALYSIS TECHNIQUE BY USING A PYROLYZER

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There is a problem that an insoluble sample was not able to measure by many analytical techniques because analysis of highly polymerized compounds is generally performed in a state dissolved in a solvent. In this study, the collecting method was devised by using a pyrolyzer to solve this problem (Figure 1) [1]. This collecting method was simply performed to use an existing Py-GC/MS. In addition, it is possible to collect an insoluble sample due to transform a highly polymerized compound into a low molecular weight compound. Therefore, it is possible to analyze detailed structure and composition by analysis equipment. The purpose of this study was extension of analytical techniques due to mutually analyze.

A sample was polystyrene. The collected sample was analyzed by GC/MS and <sup>1</sup>H-NMR (Figure 2). As a result of GC/MS, pyrolysis components of polystyrene were confirmed styrene, styrene dimer and styrene trimer. As a result of <sup>1</sup>H-NMR, peak derived vinyl group of styrene and derived polymer were confirmed. Therefore, the sample collected by using a pyrolyzer was revealed to include pyrolysis components. The results mean to be connected with expansion of analysis method by analysis of other equipment. In addition, we are set to show the results of measurement of the collected samples separated by HPLC. (213 words)

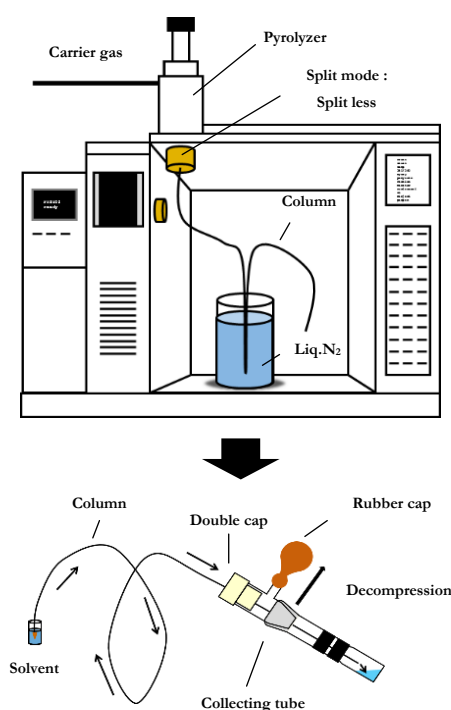


Figure 1 Sample collecting method

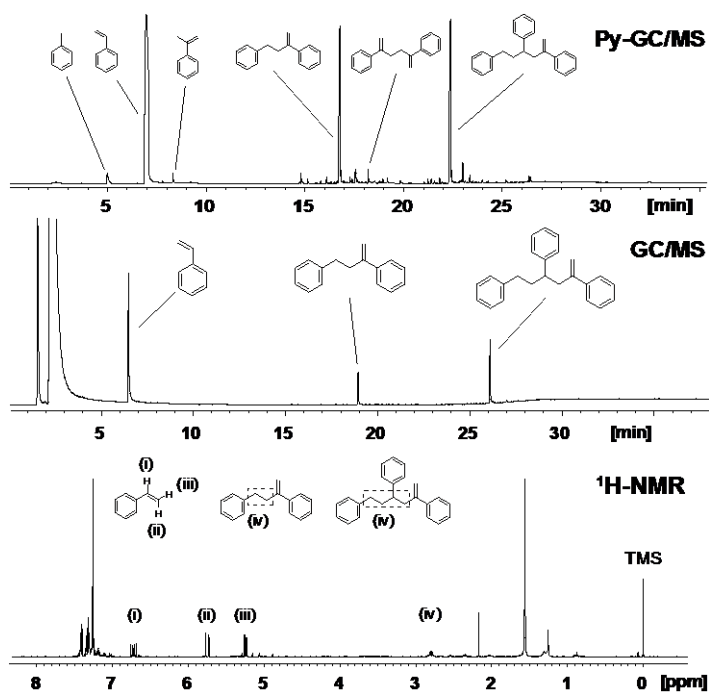


Figure 2 Results of Py-GC/MS, GC/MS and <sup>1</sup>H-NMR

[1] T. Maki, T. Honda, 19<sup>th</sup> National Symposium on Polymer Analysis and Characterization, pp. 179-180, 2014.

# MODIFIED PYROPROBE FOR STUDYING THERMOCHEMICAL REACTIONS: DESIGN, CHARACTERIZATION, AND EXPERIMENTATION

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**Abstract:** There are many types of reactors to study fast pyrolysis; most are very complicated to design and implement. By adding a pressure sealed housing to a Pyroprobe 5000 (CDS Analytical), the authors converted a common analytical tool into a system capable of performing robust studies in various thermochemical processes at different heating rates, temperatures, and pressures. The main contributions of this work are: (1) A new experimental set up was designed and built. (2) The temperature profile inside the reactor showed the real heating rates on the sample surface was characterized. (3) Studies were performed to use the reactor for a variety of novel experimentation, as described below.

In the first study, a very thin film of cellulose (thickness  $\sim 80 \mu\text{m}$ ) was pyrolyzed under vacuum ( $200 \text{ Pa}_{\text{abs}}$ ) to examine thermochemical reactions without significant heat or mass transfer limitations [1] and with limited liquid phase secondary reactions. Pressure excursions, solid-gas temperatures, and fast speed photography were performed to track reaction progress. The authors see the potential for kinetic studies with this system in the future.

In a second study the authors report the effect of vacuum pressure ( $200 \text{ Pa}_{\text{abs}}$  to  $950 \text{ kPa}_{\text{abs}}$ ) on the pyrolysis of cellulose at temperatures from 400 to 600 °C. The authors collected gas samples and washed the reactor walls to perform a full characterization of the products by established methods: char mass, GC for gases, GC/MS for organic compounds, HPLC for sugars, and Karl Fischer for water yield.

A third study details the use of this system to study microexplosions. Taking advantage of fast speed photography, the authors report novel studies on the bubbling of the liquid intermediate (see Fig 1). Bubbling characteristics were described for cellulose, hemicellulose, lignin, and wood. The authors also modified the pyroprobe reactor to collect and analyse aerosol ejections by confocal microscopy.

In the fourth study, the authors further demonstrate the capabilities of this system for looking at gasification reactions with live gas temperature and pressure monitoring to examine the thermal behaviour of lignin chars. Parametric studies were performed and gas product yields were characterized by gas chromatography.

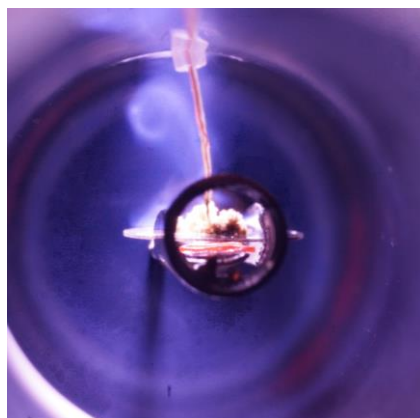


Figure 1: End view of pyroprobe reactor modified to visualize bubbling of the liquid intermediate in pyrolysis of hemicellulose on a quartz disc while simultaneously recording surface temperature with a fine thermocouple.

[1] A. Paulsen, M. Mettler, P. Dauenhauer, *Energy & Fuels* 27, pp. 2126-2134, 2013.

## New furnace-type pyrolyzer feasible for high-performance analytical pyrolysis measurements with easy installation, operation, and maintenance

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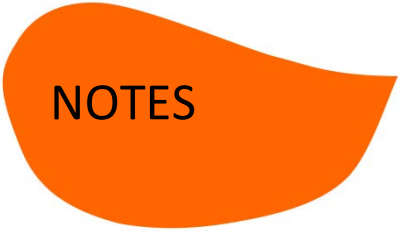
We have developed a vertical micro-furnace pyrolyzer utilizing a free-fall sample introduction mechanism along with various functions such as temperature programmable heating<sup>1</sup>). The vertical micro-furnace pyrolyzer combined with gas chromatography/mass spectrometry (GC/MS) system has become one of the powerful analytical instruments in various fields such as characterization of synthetic polymers, art materials, soil organic matters, biological samples, and pyrolysis processes of biomass and plastic wastes. The installation of the pyrolyzer generally requires attaching a fixing bracket around the GC injection port and partial replacement of the carrier gas line of GC, which might cause cumbersome procedures for switching pyrolysis method to a regular syringe injection method as well as doing maintenance of the system. Accordingly, it has been eagerly demanded to simplify the installation procedures without sacrificing basic performance in analytical pyrolysis measurements. This paper describes a new pyrolyzer which adopts the basic features of the conventional furnace-type pyrolyzer, but allowing the simpler installation to GC without replacing the GC carrier gas line while keeping the high performance comparable to the conventional pyrolyzer.

In comparison with the current pyrolyzer (EGA/PY-3030D, Frontier Laboratories), the new pyrolyzer became nearly half in volume and weight. The carrier gas flow in the pyrolyzer is controlled by an external mass flow controller, while the original carrier gas supplied by GC is also set at smaller flow rate, for example 5 mL/min, in order to minimize dead space inside its line, which requires no modification of the GC carrier gas line in the pyrolysis experiments. The connection to GC was simplified and could be done in one-step by integrating the pyrolyzer body with a fixing bracket. A stainless steel pyrolysis tube was developed and its inner surface was deactivated by forming a quartz thin film. In the new pyrolysis tube, a quartz insert tube is incorporated and an interface (ITF) needle is directly attached to the pyrolysis tube. The assembled unit of the pyrolysis tube and ITF needle allows quick removal and replacement of the unit from the pyrolyzer body. Since the quartz insert tube can be removed from the top of the pyrolyzer without removing the pyrolyzer from the GC injection port, clean-up of the insert tube for maintenance can be readily performed. The free-fall sample introduction procedure to pyrolyzer furnace was changed to that by retracting a magnetic bar located at the bottom of the sample cup, by which the use of a sample stick to hold a sample cup before the introduction in the current pyrolyzer was avoided.

The basic performance of the new pyrolyzer was examined on the basis of the formation ratio of styrene monomer and trimer obtained by pyrolysis-GC/MS measurements of polystyrene at various temperatures, and the reproducibility (relative standard deviation; RSD) of the measurements ( $n=3$ ) was 2.0% at 600°C, which is greatly improved from 3.1% obtained for the current pyrolyzer. The improved RSD may be ascribed to the use of deactivated stainless steel pyrolysis tube which leads to higher thermal uniformity of the pyrolysis position than that of the quartz tube used in conventional pyrolyzers. The effect of active sites on stainless steel surface, i.e. deactivation efficiency, on the pyrolysis performance was examined by thermal desorption (TD)-GC/MS analysis of decabromodiphenyl ether (DeBDE), a typical brominated flame retardant, which is prone to be decomposed by metal catalysts. RSD of the peak area of DeBDE observed in the TIC chromatograms were 1.9% for the 3 independent repeated measurements, indicating the stable desorption of DeBDE. In addition, peaks assigned as octabromodiphenyl ether and nanobromodiphenyl ether were not observed in the chromatograms. This fact suggests the less chemical activity of the stainless steel pyrolysis tube, since both compounds are typical products formed by catalytic debromination of DeBDE. Further, a mixture of hydrocarbons with a wide range of carbon numbers ( $C_{18}$ - $C_{44}$ , 2.5  $\mu\text{g}$  each) was measured at a furnace temperature of 400°C, and the RSD values ( $n=3$ ) of the peak area of  $C_{18}$ ,  $C_{40}$ , and  $C_{44}$  were 0.14, 0.22, and 0.15%, respectively. In addition, the recovery of high boiling compounds,  $C_{40}$ , and  $C_{44}$ , was around 100%. The observed high reproducibility and recovery indicate that there are no cold sites in the flow path for thermally desorped species or pyrolyzates. The newly developed pyrolyzer can serve as a user-friendly analytical tool with high performance ability in a compact body.

[1] C. Watanabe, K. Sato, A. Hosaka, H. Ohtani, S. Tsuge, *Am. Lab.*, 14-15, Oct. (2001)





# NOTES

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ABSTRACTS

# Organic geochemistry

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Oral presentations

## EXPLORING THE MOLECULAR COMPOSITION OF TERRESTRIAL ORGANIC CARBON USING TETRAMETHYLAMMONIUM HYDROXIDE (TMAH) THERMOCHEMOLYSIS

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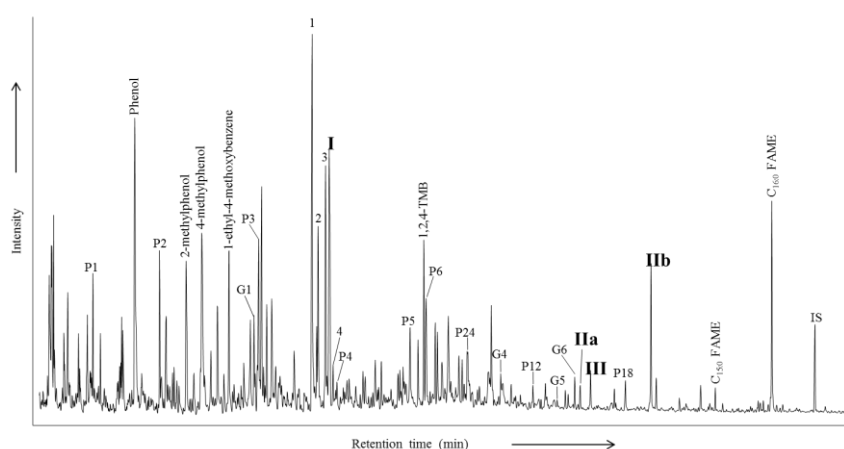
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Increasing temperatures, altered precipitation regimes and elevated atmospheric carbon dioxide concentrations are likely to have complex and non-linear effects on terrestrial organic carbon ( $C_{org}$ ) cycling. Thermally assisted hydrolysis and methylation (THM) in the presence of tetramethylammonium hydroxide (TMAH) (also known as TMAH thermochemolysis) offers one of the best prospects for the molecular characterisation of terrestrial  $C_{org}$ . This study explores the TMAH thermochemolysis phenolic products from bryophytes (i.e. mosses), vascular (i.e. higher) plants, peat and the other forms of fossilised  $C_{org}$  that these plants eventually form. Litter produced by the peat-forming moss, *Sphagnum*, is the dominant input of  $C_{org}$  into peat bogs and some fens and yields thermochemolysis products which are characteristic of phenolics that act both as structural support components and as inhibitors of microbial decomposition. Vascular plants associated with peatlands contribute lignin and other polyphenols including tannins which can all be unequivocally identified using thermochemolysis with  $^{13}C$ -labelled TMAH. Bryophytes do not synthesize lignin and instead the bryophyte genus *Sphagnum* biosynthesizes other phenylpropanoids including *trans*-sphagnum acid. Two new quantitative indices are proposed namely i)  $\sigma$  which is defined as the total amount of the *Sphagnum* phenolic products normalised to 100 mg of TOC; and ii) SR% which gives a measure of the relative amounts of *Sphagnum* to vascular plant phenols released during the TMAH thermochemolysis of peat moss and the surficial peat layers. The sphagnum acid products are respectively 1-methoxy-4-(prop-1-en-2-yl)benzene (**I**), (E/Z)-methyl 3-(4-methoxyphenyl)but-2-enoate (**IIa/b**) and methyl 3-(4-methoxyphenyl)but-3-enoate (**III**) [1,2]. The changing distribution of these products as a function of distance from the water table (WT) were observed during the THM in TMAH of peat cores from a Swedish (Ryggmossen, central Sweden) and a British peatland (Butterburn Flow, northeast England). The increase of **I** relative to **IIa/b** and **III** indicates that the mode of binding of sphagnum acid into the peat changes as a function of burial depth and hence position relative to the WT in both the hummocks and hollows of the Swedish bog plateau. Down-core profiles for the British bog will be compared with those from the Swedish bog plateau with some attention given to the importance of seasonal fluctuations of the WT. This will highlight the sensitivity of *Sphagnum* surficial peats to climate-induced changes in water levels.

### GC/MS trace of the TMAH products from *Sphagnum fallax*

Note peaks labelled **I**, **IIa**, **IIb**, **III**



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## A FAST AND NEW METHOD TO QUANTIFY PAHS IN CONTAMINATED SOILS BASED ON FLASH-PYROLYSIS COUPLED WITH MOLECULAR ANALYSIS

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The diagnosis of soil contamination requires the screening of the soil for regulatory substances. Among them, PAHs represent the most encountered family of organic contaminant, impacting 200 000 sites in Europe [1]. The screening and quantification of PAHs in soils is usually done using chromatography technics (GC, LC) in combination with various detections (MS, FID, FLD...). These methods require sample preparation involving solvent extraction [2] (Soxhlet, sonication, pressurized liquid extraction: PLE) and often purification steps in order to get satisfactory analysis quality. These steps are rather time-consuming and not environment-friendly, even though several extractions methods based on supercritical CO<sub>2</sub> [3] or pressurized hot water [4] extractions, reducing the use of organic solvent, have been developed in the past decades. Moreover, the sample amounts usually required using these extraction methods are on the order of the gram to several hundred grams which can be problematic when working with limited amount of samples.

The objective of this study was to propose a new method for PAH quantification in contaminated soils that does not require extraction and purification steps, which consequently reduces the preparation time, and allowing to work on low sample amounts. This method consists in flash-pyrolysis (Py) coupled with GC-MS/FID. The pyrolyzer was equipped with a cryogenic trap allowing the concentration of the released compounds at the column head prior the GC analysis. The GC was equipped with a fast-GC column which reduced substantially the analysis time. The GC flow was split with an electronic pressure controller between the MS which allowed compound identification and the FID which was calibrated in order to quantify the PAHs.

This method was tested on five PAH contaminated soils, including one certified reference material (CRM) BCR-524. The amount of samples necessary for the analyses varied between 0.5 and 2 mg. The quantification results were compared to those obtained by the "classical" quantification method used in the lab (PLE followed by GC-MS analysis).

The first results showed satisfactory similarities between the two quantification methods. The best results were obtained for the CRM sample whereas the variability was higher for the other samples. These differences can be explained by different heterogeneity level of the samples. The concentrations of low molecular weight compounds (especially naphthalene and acenaphthylene) were always higher when obtained with the Py method. These higher concentrations can either be explained by a slight cracking phenomenon occurring during the pyrolysis or by a loss by evaporation of these volatile compounds during the concentration step of the "classical" quantification method.

These different hypotheses are currently under investigation to explain the slight differences observed between the quantification methods. In addition, supplementary samples are analyzed in order to fully validate the method but the first results are encouraging and underline the great potential of such technique for a fast and clean diagnosis of PAH soil contamination.

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**PALAEOCLIMATIC CONDITIONS IN CENTRAL IBERIAN PENINSULA IN  
THE SENONIAN EPOCH (c. 72 Mya) AS INFERRED BY PYROLYSIS  
COMPOUND SPECIFIC ISOTOPIC ANALYSIS (Py-CSIA)  
OF THE FOSSIL CONIFER *Frenelopsis oligostomata***

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*Frenelopsis oligostomata* (FR) is an extinct Cretaceous conifer adapted to severe water stress. Well preserved fossil remains found in marls from the Upper Cretaceous (Senonian c. 72 Mya) in Guadalix de la Sierra (Madrid, Spain) (Almendros et al. 1982) are studied using isotope ratio mass spectrometry in bulk (C, H, O, N IRMS) and in specific compounds released by pyrolysis (C, H, Py-CSIA). Stable isotopic analysis of bulk samples was done in a Thermo-Scientific Flash 2000 HT coupled to a Delta V Advantage IRMS. Py-CSIA was done with a Frontier Labs. Pyrolyzer (3030D) attached to a Trace GC Ultra chromatograph with a GC-Isolink System and via a ConFlo IV to a Delta V IRMS. Chemical structure of compounds was inferred by comparing classical electron impact mass spectra from Py-GC/MS with Py-GC/FID and Py-GC/IRMS chromatograms under the same GC conditions.

Heavy bulk  $\delta^{13}\text{C}$  values were found ( $-20.5 \pm 0.02$  ‰) pointing to a depleted stomatal conductance and FR paleoenvironmental growth conditions of water and salt stress. Values obtained for  $\delta\text{D}$  ( $-101.9 \pm 2.2$  ‰),  $\delta^{15}\text{N}$  ( $10.7 \pm 0.2$  ‰) and  $\delta^{18}\text{O}$  ( $20.9 \pm 0.39$  ‰) lay within those previously reported for fossil floras growing in warm environment and probably with very high evaporation rates.

We were able to obtain  $\delta^{13}\text{C}$  signatures for a number of biogenic compounds released by pyrolysis from FR (Py-CSIA) including polysaccharides, lipid series (Fig. 1 left), lignin methoxyphenols and altered lignin (alkylbenzenes and alkylphenols). Plant-air C fractionation in compounds derived from altered lignin for a C3 photosystem plant is c.  $\Delta^{13}\text{C} \approx 20.0$  ‰ and considering a fractionation (c.  $\Delta^{13}\text{C} \approx -3.0$  ‰) due to the plant depleted stomatal conductance conditions, we estimate that the atmospheric  $\delta^{13}\text{C}$  value in the area during the Senonian epoch in c.  $\delta^{13}\text{C} = -5.3 \pm 0.2$  ‰. This indicates that FR grew on a  $^{13}\text{C}$  enriched atmosphere that could be caused by emissions of  $^{13}\text{C}$  to the atmosphere from warm and acidified oceans by volcanic depositions and/or net terrestrial C uptake with selective removal of light  $^{12}\text{C}$  isotope by plants. Also we were able to measure  $\delta\text{D}$  for alkyl series in the range  $\text{C}_{24}\text{--}\text{C}_{29}$  ( $\delta\text{D} = -124.44 \pm 5.2$  ‰) (Fig. 1 right). This value was taken as a proxy to infer the H isotopic signal of water in the area in the Upper Cretaceous, giving a value for palaeowater  $\delta\text{D} = -24.44 \pm 5.2$  ‰. This indicates that 75 Mya our plant probably uptaked deuterium enriched rain water that again points to warm growing environmental conditions.

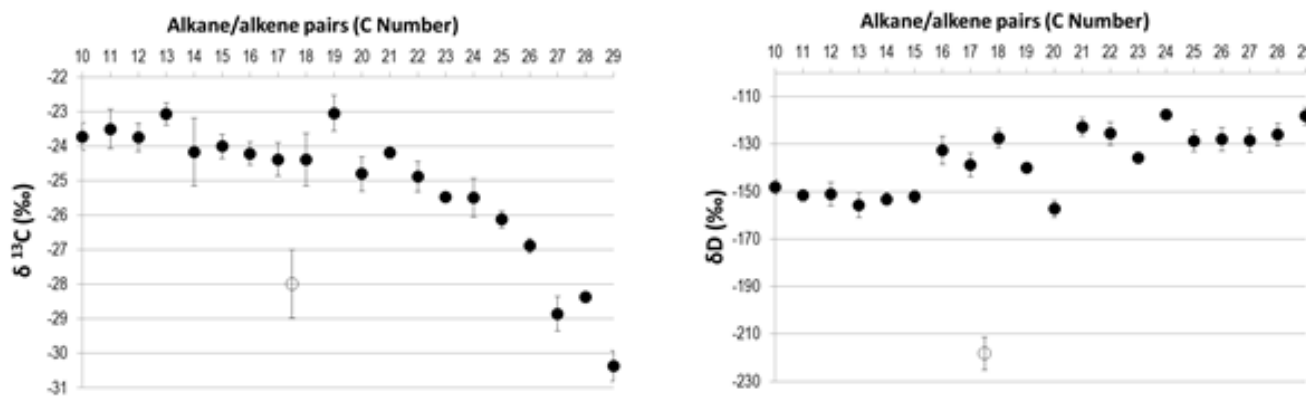


Figure 1 *Frenelopsis oligostomata* Py-CSIA of alkanes. The void circle is an isoprenoid.

# **THERMOCHEMOLYSIS FOR THE SIMULTANEOUS ANALYSIS OF THE MAIN BIOMOLECULAR FAMILIES IN SOIL. APPLICATION TO THE MEASUREMENT OF THE IMPACT OF INOVATIVE RENEWABLE PRACTICES FOR REFORESTATION IN A CLIMATE CHANGE CONTEXT.**

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Every year millions of Euros are invested on the maintenance (especially weeding and watering) of newly planted trees in landscaping, afforestation, reforestation, gardening, fruit production... This maintenance frequently implies a massive use of herbicides, petrol-based fuels and labour. These trees are often dependent on these tending operations, which are not always foreseeable or implementable by public or private managers, which lead to the partial or total failure of many trees planting projects. The aim of the European SUSTAFFOR project is to conceive, produce, develop and on-field validate novel techniques aiming at improving afforestation/reforestation projects from an environmental, technical and economic point of view. These novel techniques include a new generation of soil conditioners and new mulching products: either 100% biodegradable or reusable. These novel techniques aim at mitigating the negative effect of temporary water scarcity and competitive vegetation, which are the two main factors that can result in the failure of a young tree in the current context of irregular water availability and climate change.

For studying the potential of the novel techniques in tree planting projects a network of field trials was installed across a range of strongly contrasted climatic areas in NE Spain, representative of the main climates in Europe and the Mediterranean such as semiarid, Mediterranean humid or subalpine conditions. Each field trial includes 17 treatments, with 30 trees per treatment organized in a split-plot design: 6 blocks of 5 trees. The treatments are combinations of soil conditioners and weeding techniques.

In order to achieve project aims a thorough monitoring is applied at the field trials. Collected data refers to weather (through weather stations), tree survival, growth and biomass allocation; tree physiology (leaf water status, nutrition status) soil moisture and temperature; fertility-related soil variables (texture, organic matter content, total N, carbonates, pH, etc) and variables related to biogeochemical changes in soils.

Because of the huge quantity of samples (more than 200 after one year of experiment), tetramethylammonium hydroxide-assisted thermochemolysis performed in an off-line mode were employed for the rapid and simultaneous analysis of the main biomolecular families [1,2] and followed possible qualitative and quantitative changes in soil organic matter. Analytes in these molecular-level based studies included diagnostic fatty acid biomarkers, as well as lignin-based phenols and carbohydrates derivatives. These results were also compared to the other collected data.

Results show the relative increases of microbial (included bacterial) fatty acids and carbohydrates when compared with values obtained for classical practices (e.g. with herbicides). In addition the quality of lignin-based phenols seems to present no significant differences. These results contribute to understand how and why these new biodegradable or reusable soil conditioners and mulching reach the survival of young trees to 100 % against 70% when herbicides were used.

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## ASSESSMENT OF THE SPATIO-TIME VARIABILITY OF ORGANIC MATTER IN THE UPSTREAM SECTION OF THE SEINE ESTUARY

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Organic matter (OM) of natural waters plays a major role in the global cycles of carbon and nitrogen at several levels. In particular, its role is of main importance on the geochemistry of metallic and organic micro-pollutants since it potentially influences their speciation and bioavailability. Additionally, from an operational point of view, it is a key parameter in drinking water treatment.

Within the frame of the *Piren-Seine* French project, it was thus decided to trace sources of OM (allochthonous vs autochthonous, natural or anthropic) in several rivers of the Paris Basin (namely, the Seine, the Marne and the Oise) and to investigate their spatio-time variability.

Twenty-two samples of particulate OM (POM) were collected through filtration of riverine waters from various places of the Seine, the Marne and the Oise watersheds, during two sampling campaigns corresponding to low and flood water periods (summer of 2012 and winter of 2013, respectively). These samples were analyzed using solid state cross-polarization magic-angle-spinning Carbon-13 nuclear magnetic resonance (CPMAS <sup>13</sup>C NMR) to determine their chemical functionalities, and through Curie point thermally assisted hydrolysis and methylation with tetramethylammonium hydroxide (TMAH) in combination with gas chromatography and mass spectrometry (CuTHM-GC/MS) to investigate their chemical composition at the molecular level.

Comparison of the solid state <sup>13</sup>C NMR spectra obtained for a given sampling site at low water vs flood water led to distinguish three main groups of samples, based on the relative abundance of aliphatic carbons with respect to polysaccharidic carbons: (i) samples exhibiting a strong relative decrease in the polysaccharides reflecting an input of more humified OM during the flood, (ii) samples showing a strong increase in the polysaccharides reflecting an input of fresher OM during the flood and, (iii) samples characterized by carbohydrates and aliphatic signals of similar abundances whatever the sampling period.

The CuTHM-GC/MS traces of thermolysates revealed the presence of methoxy and dimethoxy aromatic compounds attributed to lignin and/or tannins (the methoxy group being preexisting or resulting from *in situ* methylation thanks to TMAH), and various aliphatic linear compounds consisting mainly in the methylated derivatives of C<sub>16:0</sub> and C<sub>18:0</sub> mid-chain hydroxyalkanoic acids, even C<sub>16:0</sub> to C<sub>24:0</sub> ω-hydroxyalkanoic acids, even and odd C<sub>12:0</sub> to C<sub>28:0</sub> alkanedioic acids, C<sub>9:0</sub> and C<sub>16:0</sub> alkanedioic acids, and even C<sub>16:0</sub> to C<sub>26:0</sub> alkan-1-ols which reflect a higher plant contribution (wax esters, cutin/suberin biopolymers). Nevertheless, contrary to <sup>13</sup>C NMR spectra, products directly related to polysaccharides could not be detected in the CuTHMpyrolysates. Moreover, based on the relative abundance of the pyrolysis products, CuTHM-GC/MS and <sup>13</sup>C NMR data could not be fully correlated for all samples. It therefore appeared necessary to investigate in more detail the hydrophilic constituents of these samples.

To this end, the samples were reanalyzed using a recently developed alternative sequential microwave-assisted HCl hydrolysis and TMAH hydrolysis [1, 2]. Indeed, it has been reported that microwave energy interacts efficiently with the polar moieties of the macromolecular structure and is able to disrupt such polar bonds. At each step, the residues were investigated using CPMAS <sup>13</sup>C NMR, CuPy-GC/MS and CuTHM-GC/MS and both organic and aqueous extracts were analyzed by GC/MS with a focus on monosaccharides, 2-amino sugars and amino acids.

This analytical approach emphasizes the potential of microwave-assisted hydrolysis coupled with GC/MS for the characterization of polar moieties in complex macromolecular OM. It reveals itself an attractive and promising technique, complementary to pyrolysis, and should be considered as an additional technique to be used in natural OM investigation, especially when dealing with hydrophilic fractions.

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## Release of Molecular Hydrogen (H<sub>2</sub>) from Carbonaceous Rocks during Laboratory Pyrolysis Experiments

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**Abstract:** It is widely acknowledged that laboratory pyrolysis experiments fail to reproduce the gas composition observed in conventional and unconventional reservoirs. This finding has been attributed to the formation of molecular hydrogen (H<sub>2</sub>) due to increased cleavage of C-H bonds as compared to C-C bonds at temperatures > 500°C (Behar et al., 1995, 1997). Although H<sub>2</sub> occurs only in trace amounts in natural gas (e.g. Kotarba et al. 2014) atomic or molecular hydrogen potentially plays an important role in the gas generation upon thermal maturation of organic matter. The formation of alkanes by thermal cracking with H<sub>2</sub> (Lewan, 1997) and the reaction of CO<sub>2</sub> and H<sub>2</sub> (Tang and Xia, 2011) have been discussed in this context.

In our study we investigated the liberation of H<sub>2</sub> during open and closed system pyrolysis of carbonaceous shales and coals. Li et al. (2015) showed that under open system pyrolysis conditions considerable amounts of H<sub>2</sub> are liberated from organic matter and its yields are much higher than the corresponding CH<sub>4</sub> yields.

In closed system Micro-Scale Sealed Vessel (MSSV) pyrolysis experiments, H<sub>2</sub> yields are much lower than in open system pyrolysis, and the mass-normalized H<sub>2</sub> yields decrease with increasing sample quantity. This suggests that at high H<sub>2</sub> partial pressures the intensity of hydrogenation of organic matter to form hydrocarbons like CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> increases. Recombination of higher molecular hydrocarbons with free hydrogen and molecular hydrogen plays the main role in CH<sub>4</sub> generation during MSSV pyrolysis at temperatures > 450°C.

TOC-normalized pyrolytic CH<sub>4</sub> and H<sub>2</sub> yields for different shales show reverse evolution trends with temperature. From this it is concluded that low methane generation capacity can be mainly attributed to the release of molecular hydrogen. The results obtained provide implications for hydrogen balance considerations and clues on the relationship between H-isotopic composition of H<sub>2</sub> and hydrocarbon gases, especially CH<sub>4</sub>.

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## THE STUDY OF PETROLEUM GENERATION AND REACTIVITY BY ARTIFICIAL MATURATION: FROM EXPERIMENTATION TO GEOLOGICAL CONDITIONS

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The understanding of the origins and reactivity of petroleum in geological systems relies on the collection of natural samples: source-rocks and kerogens, petroleum, natural gas, rock extracts, bitumen. Yet, organic geological samples rarely allow determination of accurate mass balance at given temperature-pressure-composition conditions. Indeed, co-genetic products (solids, liquids and gases) will separate during the evolution of the geological setting: cracking, expulsion, migration, mixing, phase separation are combined as temperature and pressure change. The synthesis of geological as well as geochemical data lead to establish the fundamentals of petroleum organic geochemistry (e.g. Tissot and Welte, 1978; Hunt, 1979) but nowadays computer modelling of petroleum systems requires quantitation of the physico-chemical dynamics implied during thermal diagenesis. This implies to investigate the fundamental physico-chemical controls of kerogen, hydrocarbon liquids and gases reactivity in the presence of minerals and water. Thus, artificial maturation aims to study the thermal transformation of fossil organic matter in the laboratory as to bridge the gap between geochemical studies of geological samples and chemical reactivity. Indeed, the collection of solids, liquids and gases as co-genetic phases, the study of their evolution during ongoing reaction, the control of physico-chemical key parameters is only permitted by laboratory experimentation.

However, artificial maturation of fossil organic matters is confronted to many challenges. The most difficult is certainly the consideration of time-temperature compensation. Indeed, oil generation and cracking in sedimentary basins occurs at lower temperatures and considerably longer times ( $T < 200^{\circ}\text{C}$ , duration of millions of years) than in the laboratory ( $T > 250^{\circ}\text{C}$ , duration of hours to month). This implies that reaction parameters will differ between the experiments and the natural systems, in intensity if not in dominant reaction mechanism. It is then necessary to understand the physico-chemical factors implied in the control of the reactions at high temperature as to allow the modelling of their quantitative effect in geological conditions.

For the past two decades we have studied many different experimental variables influencing the outcome of artificial maturation : time-temperature pairs, pressure, addition or removal of organic constituents, addition of water, hydrogen sulphide, minerals. Objectives were to understand the respective roles and disentangle possible coupling of chemical and physical variables.

In regards to the complexity of the reactive systems studied combined to the lack of knowledge concerning the structure and chemistry of natural reactants (e.g. kerogen, resins, asphaltenes) as well as organic vs mineral geochemistry, we developed in parallel a systematic study of the reactivity of the hydrocarbons. Indeed, the reactivity of single hydrocarbons or mixtures during thermal cracking can be described using the formalism of radical chemistry and its associated kinetic modelling. The advantage of using simplified systems (pure compounds and their mixtures) lies in the possibility to follow conversion of the reactants, formation of reaction products, systematically write the linking elementary reactions, take into account co-reactions and construct reaction mechanisms. This methodology is fundamentally different from the determination of empirical rate laws which is the method most commonly used in the organic geochemistry literature.

We will illustrate major aspects of organic matter reactivity as studied by our experimental research. Thus, even though artificial maturation is conducted at temperatures higher than sedimentary basins conditions, its results allows to make progress in our understanding of the chemical reactivity of kerogen and petroleum. In particular, chemical modelling of reactions is a powerful methodology to simulate the behavior of hydrocarbon mixtures in geological time-temperature conditions.

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## SHORT-CHAIN KETONES IN REACTION NETWORKS OF HYDROUS PYROLYSIS EXPERIMENTS: METASTABLE PRECURSORS OF HYDROCARBON GASES AND NEW BUILDING BLOCKS FOR MATURING KEROGEN

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The interest in a more detailed understanding of processes during gas and oil formation has been spurred by the growing importance of gas and light oil from unconventional reservoirs, e.g. shale gas and shale oil as well as deep basin-centered gas. In addition to the classical view of the formation of hydrocarbon gases by thermal cracking of bitumen or kerogen mainly by first-order reactions, several researchers have published hypotheses to explain some not accounted for observations in hydrocarbon occurrences and their molecular or isotopic compositions. These hypotheses always include a component not investigated in most dry, open-system pyrolysis studies of isolated kerogen/bitumen: The presence and role of water [1], the possible catalytic activity of mineral surfaces and metals [2], metastable equilibria of hydrocarbons and more oxidized organic compounds in pore-fluids in the subsurface – and the role of minerals as part of pore-fluid redox- or pH-buffers [3,4].

This contribution is investigating the importance of short-chained ketones for reaction pathways during hydrocarbon gas formation – and reports an unexpected finding of re-entrance of the C<sub>3</sub> moiety of acetone into kerogen during artificial maturation. A consistent observation in a series of hydrous pyrolysis experiments in gold capsules was that the amount of acetone being formed equalled that of propane at short experiment times and low temperatures (e.g. after 24 h at 300°C, 500 mg of Posidonia shale formed 679 nmol propane and 641 nmol acetone). Therefore several experimental avenues have been followed to elucidate on the formation and transformation processes of acetone. On the one hand a time series of isothermal hydrous pyrolysis experiments in gold capsules of 6 to 336 h duration at temperatures of 300, 315, 330, and 345°C and at a pressure of 30 MPa has been investigated. The experiments archived an increase in maturation of the kerogen from an initial maturity of 0.53% R<sub>0</sub> up to calculated maturities of 1.8 % EASY-R<sub>0</sub>. On the other hand several hydrous pyrolysis experiments have been carried out in flexible Dickson-type gold/titanium cells at a pressure of 12 MPa bar. In these experiments sampling is possible throughout the run time – and the addition of model compounds, here a <sup>13</sup>C-labeled acetone, is possible during the course of the experiment. The identification of significant <sup>13</sup>C-label in specific molecules (e.g. propane) facilitated the description of important reactions in addition to thermal cracking reactions – and an interesting route for “maturing” the kerogen by reincorporation of small C<sub>3</sub> units. This has important implications for kinetic models of hydrocarbon formation.

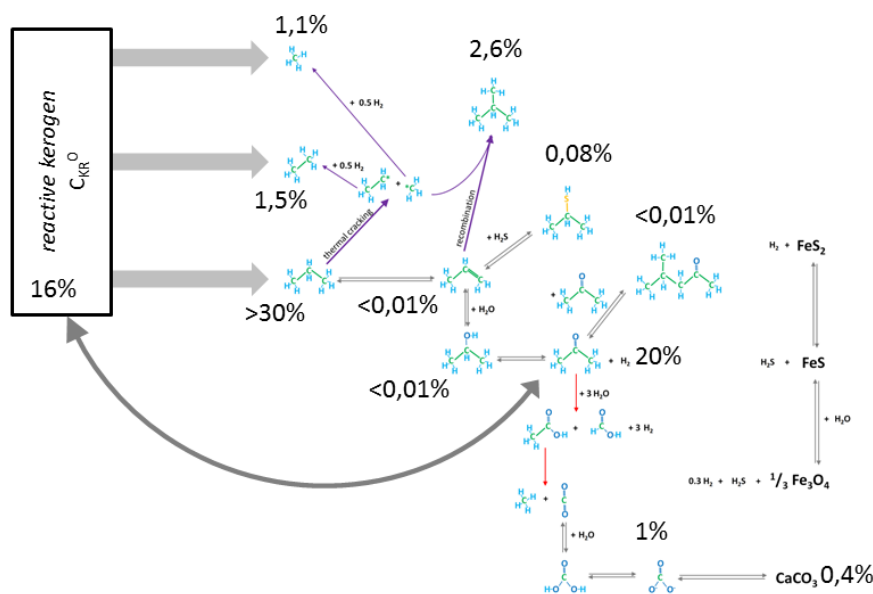


Fig. 1.

Percentage of <sup>13</sup>C-label from added <sup>13</sup>C-acetone ending in C<sub>1</sub>- to C<sub>4</sub>- compounds produced during hydrous pyrolysis and in the kerogen after the 336 h pyrolysis experiment of Posidonia shale. Reaction scheme modified after [5].

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## ROLE OF WATER DURING PYROLYSIS OF CRUDE OIL: EVIDENCES FROM SYNTHETIC FLUID INCLUSIONS

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Pyrolysis of source-rocks or non-mature oils is a common procedure to reproduce in lab the natural processes of oil and gas genesis. It is realized using high pressure and high temperature vessels taking into account the kinetics of organic chemical reactions. Adding of water and sometimes minerals mimics fluid-rock interactions in nature. The objective of this study is to reproduce hydrous pyrolysis in autoclave in presence of quartz crystals in order to trap the fluid during experiment. Trapping occurs in microcavities in newly formed quartz as fluid inclusions. Fluid inclusions are tiny windows giving opportunities to detect the presence of different fluid phases at PT conditions of experiment and to determine the composition of each phase at a various range of PT conditions using microanalytical means. Evidences of oil cracking will be checked.

Our experiments were carried out by the hydrothermal method of the temperature gradient using a heat resistant autoclave with a volume from 50 to 280 ml. Autoclaves were heated in shaft electric furnaces equipped with two independent heaters with an accuracy of temperature measurement of  $\pm 2^\circ\text{C}$ . The pressure in the autoclaves was controlled by the coefficients of filling determined by the P–V–T diagrams for pure water and solutions of the relevant compositions. Charge quartz rods of the ZY-orientation were placed in the autoclave. A seed quartz rod was hung along the whole length. After the experiments, synthesized crystals and residual solutions were removed from autoclaves. Two quartz samples (A and B) have been synthesized in the autoclave in presence of oil and aqueous solution with 5 mass % of  $\text{Na}_2\text{CO}_3$ . Sample A has been created with a temperature gradient of 290/310 °C, a pressure of 12 MPa, with a water proportion of 20 vol%, the rest being crude oil (figure 1). Sample B produced inclusions in presence of 10 vol. % of crude oil in water at a temperature gradient of 490/500 °C and a pressure of about 120 MPa.

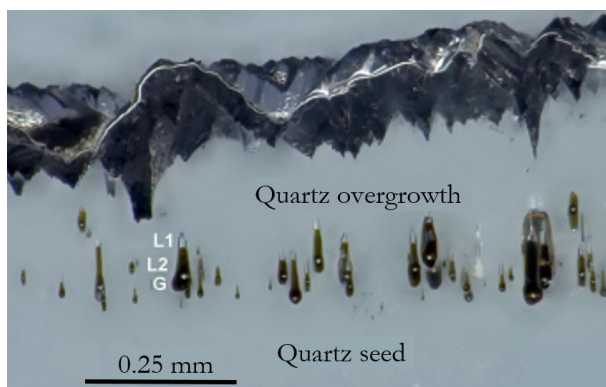


Figure 1: Synthetic fluid inclusions in quartz from sample A. L1: liquid water, L2: liquid oil, G: gas

After synthesis, fluid inclusions have been reheated by an autoclave treatment at 380 °C, 100 MPa during 15 days for sample A and at 510 °C, 120 MPa during 30 days for sample B. This treatment led to i) the precipitation of bitumen, ii) the production of methane and iii) the disappearance of liquid oil in sample A, whereas liquid oil remains unchanged in sample B.

Heating treatment has been also conducted using a microthermometric Linkam stage equipped with  $\text{BaF}_2$  windows in order to be transparent in mid-infrared range, coupled to a

micro-FTIR spectrometer (Bruker Equinox 55). It allows IR spectra recording at various temperatures in the different fluid phases of the inclusions (liquid water, liquid oil, and vapour). In parallel, fluorescence of oil is controlled during similar heating processes using an optical microscope equipped with UV light and coupled to a Linkam conventional heating stage.

The analytical results obtained during heating of a three-phase inclusions with an oil phase dominant (sample A) show the increase of water solubility in oil with temperature. Bulk homogenization has been achieved at around 350 °C. For sample B the behaviour is different. Oil dissolves in the vapour phase till 290 °C and then into the liquid water phase up to the bulk homogenization at around 375 °C. No evidence of cracking has been observed along the 4 hours of duration for each experiment. The phase behaviour is reversible.

The comparison of the two experimental sets demonstrates that water/oil volumetric ratio governs the oil cracking phenomena. When oil is the main phase, it acts as a solvent and when it is the minor phase it becomes a solute, preserving oil from thermochemical reaction of cracking.

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## VARIATION IN THE STABLE CARBONACEOUS FRACTION (BC<sub>HYPY</sub>) WITHIN BIOCHARS PRODUCED AT DIFFERENT TEMPERATURES

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Biochar is the solid material obtained from the carbonisation of waste biomass for use as a soil amendment and to reduce emissions from biomass that would otherwise naturally degrade to greenhouse gases. To assess its efficacy as a means of carbon sequestration it is necessary to develop a measure of biochar stability and persistence in the environment. Catalytic hydropyrolysis (hydrogen pyrolysis or HyPy) has been proposed as a method for quantifying pyrogenic (black) carbon in soils and sediments, with the refractory fraction isolated, termed BC<sub>HYPY</sub> thought to be composed of highly aromatic carbonaceous material of >7 rings [1]. The technique has recently been used to isolate what was termed stable polycyclic aromatic carbon (SPAC) from thermosequences of biochar, with this fraction representing the carbonaceous component that is likely to be stable in the environment on centennial timescales [2].

In this study 21 biochar samples produced from 14 different feedstocks at temperatures between 400 and 700°C were subjected to HyPy to quantify their BC<sub>HYPY</sub> contents. The samples were loaded with 10% ammonium dioxodithiomolybdate [(NH<sub>4</sub>)<sub>2</sub>MoO<sub>2</sub>S<sub>2</sub>] catalyst and pyrolysed with resistive heating from 50°C to 250°C at 300°C min<sup>-1</sup>, and then from 250°C to 550°C at 8°C min<sup>-1</sup> and held for 2 minutes. The BC<sub>HYPY</sub> content (%) of each sample was derived by comparing the organic carbon (OC) content of the catalyst-loaded samples prior to HyPy, with those of their HyPy residues. A hydrogen pressure of 150 bar and sweep gas flow of 5 L min<sup>-1</sup>, ensured that the thermally labile fraction cleaved from the macromolecular structure of the biochar was quickly removed from the reactor and then trapped on dry ice cooled silica for later characterisation by GC-MS.

It was found that the proportion of BC<sub>HYPY</sub> within each biochar sample is largely controlled by its temperature of formation, with the 400°C chars showing the lowest values and the 700°C the highest. Those feedstocks for which two biochar formation temperatures were available all show higher BC<sub>HYPY</sub> values in the higher of the two temperatures. There is however considerable variation between the proportions of BC<sub>HYPY</sub> isolated from biochars produced from different feedstocks at the same temperature.

HyPy also allows for the thermally labile “non- BC<sub>HYPY</sub>” fraction to be recovered and characterised by GC-MS. Previous analysis of the non- BC<sub>HYPY</sub> fraction released by HyPy from charcoals show the GC amenable fraction to be comprised of polycyclic aromatic hydrocarbons (PAHs), ranging from 1 to 7 rings together with alkyl-substituted homologs [3]. These compounds are cleaved during HyPy from the macromolecular structure of the biochar and represent a portion of the carbonaceous aromatic material that might be environmentally labile [2]. When comparing chars produced at 400 and 700°C there was no evidence of an increased average ring size of the labile PAH fraction with increasing temperature, as measured by the 3+4/5+6 ring PAH ratio. Indeed for some of the 700°C chars a small amount of 2, 3 and 4 ring PAHs were found, but no 5/6/7 ring structures were present in the very small amount of labile carbonaceous material generated. Therefore, while it is well known that increased charring temperature results in an increase in the average size of PAH clusters within a char [2], it is apparent that even at high charring temperatures e.g. 700°C very limited amounts of small aromatic clusters of 2-4 rings remain part of the char structure.

The phenanthrene/methylphenanthrene ratio illustrates the relationship between the temperature of biochar formation and the relative abundance of parent and alkyl-substituted PAH. It showed a clear trend of the decreasing occurrence of the 4 isomers of methylphenanthrene relative to phenanthrene itself with increasing temperature in the products from 400°C, 550 and then 700°C chars. While it is thought that the BC<sub>HYPY</sub> is likely to be stable in the environment on a centennial timescale, further research of the fate of the non- BC<sub>HYPY</sub> fraction including the PAHs characterised here, which is likely to be semi-labile is required to understand the longevity of biochar in the environment.

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## EVALUATION OF SHALE GAS RESOURCES USING A HIGH PRESSURE WATER PYROLYSIS MATURATION METHOD: APPLICATION TO THE UK BOWLAND SHALE

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The study by Andrews [1] estimated that the shale gas resource of the UK Carboniferous Bowland Shale is significant, containing 822-2281 trillion cubic feet of gas. However, this resource estimation was based on screening geochemistry and source rock potential. Shale gas is often relatively dry (composed mainly of methane), implying that it is largely generated at high maturities, yet the study by Andrews [1] and others carried out so far based on Rock-Eval pyrolysis on UK shale gas systems did not directly address the fundamental scientific questions of what the composition of a typical UK shale gas will be, how much methane is in the gas, and what was the source rock thermal maturity range at which gas enriched in methane is generated, and how the amount of generated gas varies with source rock maturity. To properly estimate the UK shale gas resources in the absence of producing well data, we have used a novel high water pressure sequential pyrolysis method that simulates conditions in geological basins to investigate gas generation in shale gas reservoirs, as a function of both temperature and pressure to address these issues. We have demonstrated previously how this approach can be used at pressure retardation effects both on hydrocarbon generation from source rocks and subsequent oil cracking. water pyrolysis [2-4]. In this method, a relatively immature source rock (TOC of 6.69%, HI of 410 mg/g, VR of 0.58% Ro) from the upper Bowland Shale unit within the Rempstone-1 well was successively heated (using a 25 ml autoclave Hastalloy vessel at 180-800 bar pressure range, at 350-420 °C for periods of 24-120 hr) to archive source rock thermal maturity stage equivalent to the oil window, wet gas window and dry gas window. After each maturity stage, the experiment was stopped and the oil and gas generated recovered and the gas analysed.

When pyrolysed at 800 bar, the peak gas yield was in the late oil window (1.26% Ro), with wet (C<sub>2</sub>-C<sub>5</sub>) gas predominating. With increasing maturity, the overall gas yield reduces markedly, but the proportion of methane starts to increase such that the gas generated (C<sub>1</sub>-C<sub>5</sub>) was 7 mg/g TOC of pyrolysed rock and contains 80% methane above VR of 2.0%. This increased further to 90% methane, with the methane yield being 4.2 mg after a VR of 2.25%. This study concludes that shale gas (> 80% methane as found in US shale plays) will only be generated at high maturity (VR > 2.0% Ro), and the gas yield will be less due to very little generative potential remaining at this maturity. Although more gas will be generated at lower maturity (VR > 1.2% Ro), the gas will certainly be wet (< 50% methane) and not dry. The implications of this study to the Bowland Shale are that the thermal maturity range (1.1-1.9% Ro) suggested by Andrews (2013) for extensive gas generation, is actually insufficient for extensive dry gas generation. Therefore Bowland Shale source rocks with higher maturity need to be targeted for shale gas exploration. The decreasing gas yield with increasing thermal maturity observed here suggests that the study by Andrews (2013) may have overestimated the UK Bowland Shale gas resource (based on the assumption that a typical shale gas generation starts at VR of 1.1% Ro), and a re-evaluation is required that will need to include a more reliable laboratory data set.

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ABSTRACTS

# Organic geochemistry

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Poster presentations

## MEASUREMENT FOR FIRE DAMAGE LEVEL IN FOLIAR BIOMASS USING PYROLYSIS COMPOUND SPECIFIC HYDROGEN ISOTOPIC ANALYSIS ( $\delta D$ Py-CSIA)

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Fire is one of the most important drivers of soil organic matter (SOM) sequestration. In fact, accurate knowledge of wildfires' effects on the SOM may provide information on its resilience and physico-chemical properties, as well as on the subsequent soil recovery without human intervention. While the quantitative assessment of fire damage levels on SOM is an issue of great interest to researchers, there is not general consensus on the reliability of the physical and chemical methods frequently used to provide surrogates on the real impact of the passage of fire on the soil. In fact, fire effect on soils depends on a complex interaction of factors (temperature, time, moisture, soil depth...) and in general, characterization of SOM samples from fire-affected ecosystems implies the use of several instrumental techniques. This work aims to provide reliable quantitative proxies for pyrogenic SOM in whole environmental samples, taking advantage from changes in hydrogen isotope ratios ( $\delta D$ ) of specific compounds released by analytical pyrolysis (Py-CSIA). With this aim in mind, we carried out a series of controlled burnings of progressive intensity, under laboratory conditions, applied to dry samples of foliar biomass from a typical Mediterranean forest species (*Juniperus thurifera*) heated at 367 °C for different time periods (5', 5'30", 6' and 7').

The results showed that isotopic analysis of up to 9 compounds (eicosanol, eugenol, stigmastan-3,5-diene, phenol, phenol, 2-methoxy-4-methyl, pimaric acid, limonene, hexadecenoic acid and methylabietate), common in all samples, allowed a valid assessment of the changes in the  $\delta D$  with the different times of burning. Pimaric acid was the only major compound that had a linear correlation  $y = 3.7x + 153.6$  with a  $R^2 = 0.9209$ , where  $y$  corresponds to  $\delta D$  and  $x$  is the burning time. The rest of compounds showed different behaviour with the progressive heating, with no defined trends: after the first heating stage, some compounds suffered depletion of the heavy isotope, others were not isotopically altered and others had slight deuterium enrichment (Fig. 1). Nevertheless, all compounds detected in

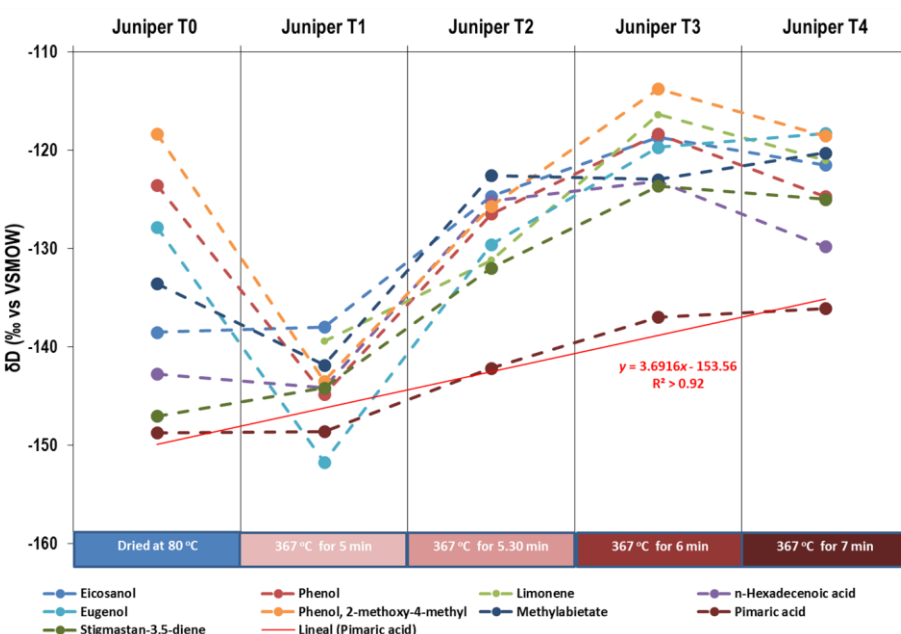


Fig. 1: *Juniperus thurifera*  $\delta D$  variations of 9 specific pyrolysis compounds through different heating periods at a constant temperature of 367 °C.

samples subjected to the most intense heating suffered conspicuous deuterium enrichment. The change of isotope signature between control and sample that was burned for 5 min was high in several pyrolysis compounds; therefore, we need to continue the experiment within a broader range of burning times. Our results illustrate that the combination of analytical pyrolysis and isotopic analysis of specific compounds (Py-CSIA) opens a new application for the quantification of fire damage levels, and also in the understanding of fire-induced structural changes in SOM, avoiding sample fractionation or wet chemical extractions.

## A NEW, QUICK, CLEAN AND EASY WAY TO MEASURE PAH AVAILABILITY IN CONTAMINATED SOILS USING THERMODESORPTION COUPLED WITH MOLECULAR ANALYSES

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The determination of the available fraction of a contamination is a major concern in risk assessment and management of contaminated sites as the impact of the contamination on the biota and the efficiency and/or the necessity to apply remediation treatments are ruled by this parameter. Availability measurement of organic contaminants, including PAHs, can be achieved through several methods (mild-solvent extraction, Tenax extraction, cyclodextrin extraction, passive sampling, biosensors...). However, several studies aiming to compare some of these methods point out inconsistencies in the results [1-4], underlining the need of a standardized method. Another challenge is to determine the available fraction in relation to a specific treatment/process (e.g. bioremediation, oxidation with specific oxidants...).

Therefore, the aim of this study is to develop a new method using thermodesorption (Td) for the determination of the fraction of the contamination available for different remediation treatments. This method is based on linking the desorption temperature to the binding strength between the contaminant and the soil constituents, i.e. the higher the desorption temperature of a compound, the higher its binding strength with the soil and the lower its availability.

This method was tested on PAH contaminated soils presenting different properties, exhibiting a varied range of PAH concentrations and different levels of PAH availability. The soils were desorbed during six 50 °C-temperature ranges (from 100 to 400 °C), followed by a 400-500 °C desorption and finally from 500 to 800 °C. The desorbed compounds were analyzed by GC-MS/FID coupling allowing the separation, the identification and the quantification of the PAHs, respectively.

The desorption steps allowed to determine a temperature profile for each PAH in each soil which was then compared to the efficiency of several chemical and biological remediation treatments performed in the lab. It was then possible to determine for each compound and for each treatment (microbial incubation, H<sub>2</sub>O<sub>2</sub> oxidation, Fenton-like oxidation and KMnO<sub>4</sub> oxidation), the desorption temperature range corresponding to the available fraction of the contamination.

These first results are encouraging and underline the potential of the Td-GC-MS/FID for a quick determination of the available fraction of the contamination and could prove to be a powerful tool to assess the risks associated with the presence of contamination and/or to select the appropriate remediation treatment for sites contaminated with organic compounds.

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## THERMOCHEMOLYSIS FOR AN ALL IN ONE ANALYSIS OF THE MAIN BIOMOLECULAR FAMILIES IN SOILS AND SEDIMENTS. COMPARISON WITH CLASSICAL CHEMICAL DEGRADATIONS FOR THE ANALYSIS OF LIPIDS, LIGNIN AND CARBOHYDRATES IN A PEAT BOG.

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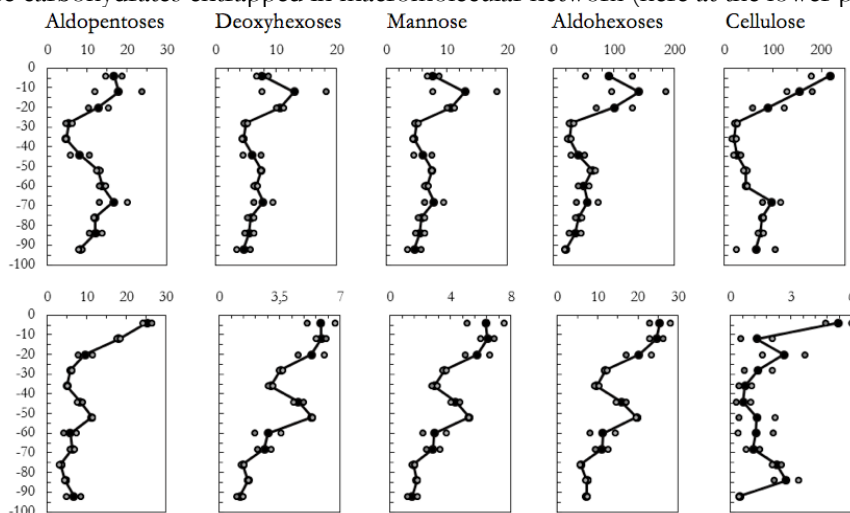
Tetramethylammonium hydroxide-assisted thermochemolysis performed in an off-line mode were employed for the rapid and simultaneous analysis of the main biomolecular families (lipids, lignin, carbohydrates) [1,2] on three replicates of a 100 cm depth (divided into 2.5 cm-thick slices) peat core from the Sagnes peat bog (Limousin, France).

Results were compared with classical chemical degradations and extraction methods for lipids (Bligh and Dyer method [3]), lignin (CuO-NaOH oxidation [4]) and carbohydrates (acid hydrolysis with HCl [5]) bio(geo)markers.

Tetramethylammonium hydroxide-assisted thermochemolysis performed in an off-line mode allows following qualitative and also quantitative changes (addition of internal standards) within the peat core.

TMAH thermochemolysis shows roughly similar distributions than with chemical methods. Nevertheless, notable differences can be observed. They are mostly due to differences in the degradation mechanisms involved with TMAH and with each chemical method.

As an example, TMAH allowed the analysis of cellulose hidden to acid hydrolysis and the specific analysis of free and terminal monomers [6]. Acid Hydrolysis analyzes the free and hemi-cellulosic fraction. TMAH thermochemolysis shows the decrease of cellulose all along the acrotelm and its relative increase in the upper part of the catotelm (sedges and/or reeds input). Even if TMAH thermochemolysis does not analyse hemicellulosic carbohydrates and discriminate each individual carbohydrate *sensu stricto*, it allows the analysis of a cellulose pool hidden to acid hydrolysis and the specific analysis of free carbohydrates entrapped in macromolecular network (here at the lower part of the peat core).



Depth distributions of carbohydrate concentrations within the peat core released after TMAH thermochemolysis (up) and HCl hydrolysis (down) (in mg g<sup>-1</sup> of dry peat)

As a consequence, simple and direct comparisons of thermochemolysis data with those generated by acid hydrolysis cannot be done because of the different mechanisms involved in each process.

TMAH thermochemolysis must be viewed and used as an important complementary method for the analysis of soil and sedimentary organic matter.

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## LABORATORY MATURATION OF SEVERAL CONIFER RESINS IN AN ATTEMPT TO TRANSFORM PLANT RESIN INTO AMBER

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Terpenoids are the major components of plant resins and many of them have a chemotaxonomic specificity. This explains why each resinous plant synthesizes a resin characterized by its own molecular signature. Resinous material can be fossilized in sedimentary rocks as amber particles. During the transformation of plant resin into amber, some terpenoids polymerize to produce a hard polymer that embodies unpolymerized terpenoids and other compounds (like succinic acid). Unfortunately, the chemical changes that transform plant resin into amber affect the initial molecular signature, making difficult the identification of the source plants of ambers.

Actually, amber is mainly studied because it can contain exceptionally well preserved biological inclusions (animals, plants, but also bacteria, spider web and feathers) and even fluid inclusions like droplets of rainwater or air. Obviously, the chemical composition of all these inclusions can carry many palaeontological and palaeoenvironmental information. Unfortunately, an exceptionally good physical preservation does not necessarily reflect a good chemical preservation and nobody really knows if the initial chemical signatures of these inclusions have been preserved/modified. In the last case, it would be interesting to get back to their initial chemical signature in knowing how their chemical features have been altered during the formation of amber.

A way to monitor the chemical evolution of the resinous material and its occluded inclusions during fossilization lies in the fast laboratory synthesis of an amber-like material using fresh plant resin as the starting material.

So, this work is an attempt to synthesize in the laboratory, and much more quickly than during a natural fossilization, an amber-like material from several conifer resins. Resin samples produced by *Pinus lambertiana*, *Pinus radiata*, *Cedrus atlantica*, *Larix occidentalis*, *Larix laricina*, *Pseudotsuga menziesii* and *Araucaria araucana* have been submitted to laboratory maturation. Two maturation protocols were tested : a thermal maturation within an oven at 90-100°C under ambient atmosphere and a maturation by UV light irradiation. Regularly during several months, plant resin aliquots have been collected then dissolved in a dichloromethane/methanol mixture. When an insoluble product was formed during the laboratory maturation, it was collected by filtration before being analyzed by flash pyrolysis-GC-MS. Soluble unpolymerized terpenoids have been analyzed by GC-MS after fractionation.

After a maturation of only several days to a dozen of weeks, all conifer resins remain fully soluble within a dichloromethane/methanol mixture, whatever the maturation protocol. This indicates that no polymerization reactions occur within the resin. Furthermore, the molecular signatures of these matured resins are quite similar to those of the fresh resins, indicating a low advanced state of the maturation process.

After a longer maturation of several months, and with the exception of *Larix occidentalis* and *Araucaria araucana*, all conifer resins still remain fully soluble within a dichloromethane/methanol mixture. Concerning *Larix occidentalis* and *Araucaria araucana*, an insoluble material is finally recovered, at least after a thermal maturation. GC-MS analyzes of all soluble fraction indicate a more advanced stage of maturation. Py-GC-MS analyzes using TMAH of the insoluble fractions clearly show the presence of many unsaturated naphthalene derivatives that are diagnostic for polylabdanoid polymer that constitute the polymer network of most of the ambers found around the world. So, maturation experiments succeed to produce an amber-like material after several months of maturation by heating in an oven. The absence of formation of a polymer from the 5 other conifer resins is probably due to the absence/low content of free labdanes in their fresh resins. This suggests that all conifers resins are not suitable to form amber during their fossilization, depending on whether they synthesize or not labdanoid compounds like biformene and communol (or any other resin compounds known for their ability to polymerise during diagenesis, like cadinenes and styrenes).

## ASSESSING THE DIAGENETIC PATHWAYS OF RESIN ACIDS OF THE ABIETANE & PIMARANE CLASSES BY CONFINED PYROLYSIS

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Diterpenic resin acids are major terpenic constituents of plant resins, more particularly those of conifers. They mainly belong to three structural classes : labdane (eg. agathic acid), pimarane (eg. pimaric acid) and abietane (eg. abietic acid). They are diversified compounds that can carry a chemotaxonomic specificity, meaning that each resin acid is synthesized by a restricted number of plant taxa. Besides their biochemical importance, diterpenic resin acids also have a geochemical significance. Indeed, their carbon structure is particularly resistant and they can be preserved within sedimentary deposits for several hundreds of millions years with only minor diagenetic transformations. Some can polymerize to form resinite/amber. Others are degraded into geoditerpenoids that may kept their initial chemotaxonomic specificity and thus can be used as palaeobotanical tracers in organic geochemical studies.

This is why it is important to investigate the diagenetic pathways of the main diterpenic resin acids. In this study, we carried artificial maturation by confined pyrolysis of 4 major diterpenic resin acids. They were carried out by confined pyrolysis of each resin acid, pure & mixed with LiAlH<sub>4</sub>, in sealed gold tubes during 24 hours at 700 bars [1]. This technique has the ability to lead to reaction products which are similar to those observed in the sedimentary record. Pyrolyzed materials were then analyzed by GC-MS. These four resin acids are represented by 1 abietane (abietic acid) of which the diagenetic pathway is rather well known and 3 pimaranes (pimaric, isopimaric & sandaracopimaric acids) of which the diagenetic pathways are much more poorly understood.

Abietic acid has been pyrolyzed at three different temperatures (280, 350, 400°C-24h). After a maturation at 280°C, abietic acid is mainly transformed into dehydroabietic acid, a compound quite similar to abietic acid. In contrast, the pyrolysis at 400°C was amply degraded into retene, its final diagenetic compounds. More interesting is the pyrolysis at 350°C, it generates a broad distribution of degradation products. Most of these compounds are abietane plant biomarkers classically recovered in the geosphere and known to be diagenetic products of abietic acid. Interestingly, other compounds generated during the maturation, while still unknown and unassigned, were also identified in sedimentary deposits containing many abietane biomarkers. They may be interesting plant biomarkers for future palaeobotanical investigations. This set of pyrolysis also indicates that a higher temperature (350°C) is required for the maturation of pure compounds than for raw plant material (280°C, [1]) to generate the broadest distribution of plant biomarkers. Furthermore, this set of pyrolyses helped to determine and list all the chemical mechanisms that occur during the diagenetic degradation of abietic acid (and meanwhile probably all the other abietanoic acids) into retene.

Laboratory maturations by confined pyrolysis of pimaric, isopimaric and sandaracopimaric acids also generate a broad distribution of diterpenoids. Many aromatic compounds were produced by the maturation of pure acids. Many of these compounds belong to the abietane class and are similar to those produced by the maturation of abietic acid. This indicates that a pimarane skeleton is likely to be transformed into an abietane skeleton during diagenesis. This is consistent with the fact that aromatic pimaranes have never been recovered in sedimentary materials in which aliphatic pimaranes are nevertheless present. This is probably due to the fact that the ring C (the first that should be aromatized during an aromatization process) cannot be aromatized without any transformation of the carbon skeleton because of the methyl-ethyl branching at the C(13) position. This set of pyrolysis also allows us to distinguish unambiguously saturate pimaranes and isopimaranes. These 2 kinds of compounds are difficult to discriminate and are thus often undistinguished in many studies although they can have different botanical sources.

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## SIGNATURE OF PYROLYTIC ALKANES FOR THE ASSESSMENT OF SOIL CARBON SEQUESTRATION

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Surrogate descriptors of the performance of soil C sequestration, which is reflected in the highly variable content of organic matter in the different ecosystems, are not yet well established. Therefore, their identification is relevant in understanding Earth's biogeochemical cycle and global change. This research consists of an exploratory multivariate statistical approach on the qualitative and quantitative assessment of biogeochemical factors involved in organic C sequestration in the soil, using an 'omic' approach not requiring a detailed knowledge of the structure of the material under study. With this purpose, we have carried out a series of chemometric approaches on a collection of differing soils. The work is focused on the information provided solely by the *n*-alkane homologues released by analytical pyrolysis from samples of 32 representative Mediterranean soils under a large variety of vegetation, use and geological substrate.

The identification and quantification of *n*-alkanes by pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS) of whole soil samples was carried out using a double shot pyrolyzer PY2020iD (Frontier Labs Ltd., Fukushima, Japan). The *m/z* 85 ion trace was selected to identify the homologous series, which were integrated and tabulated from nonane (C<sub>9</sub>H<sub>20</sub>) to hentriacontane (C<sub>31</sub>H<sub>64</sub>) in all soil samples.

In order to quantify the complexity of the alkane series the Shannon-Weaver biodiversity index was calculated. Partial least squares (PLS) regression was applied to forecast soil C concentration in terms of the composition of the alkane assemblages. A series of previous multivariate data treatments mainly cluster analysis of variables (alkanes) by multidimensional scaling and principal component analysis to classify observations (soil samples) lead to the suggestion that significant correlation exists between soil C storage and the molecular composition of the pyrolytic alkanes. In particular the biodiversity index calculated exclusively from the *n*-alkanes was significantly correlated with the soil C content ( $P < 0.05$ ). Furthermore, the statistical significance of the correlations found increased when the diversity was calculated from the odd-C numbered alkanes (presumably consisting of biogenic compounds rather than pyrolytic fragments). Further logarithmic transformations of the data to reduce the influence of the outliers lead to highly significant ( $P < 0.01$ ) correlation models.

In fact, automatic classification of the *n*-alkanes by i.e., principal component analysis, revealed three sharp clusters, reflecting the possible different origin depending of the chain length: a first group of alkanes between 9 and 18 carbons (presumably pyrolytic fragments or microbial products), a second group from 19 to 24 carbons, and a well-defined group of alkanes with 25 to 31 carbons, presumably including alkanes released by rapid thermoevaporation such could be those derived from epicuticular waxes of vascular plants.

In conclusion, our results show that the sole analysis of the pyrolytic signature of *n*-alkanes from whole soil samples provide information useful to explain the potential C sequestration of the soil. In particular it is hypothesized that the high complexity of the *n*-alkane assemblages is reflecting overlapped activity of widely differing groups of organisms present in the plant-soil trophic system. This would be connected with a high functional redundancy of the soil, which is considered an index for soil health and resilience, at least in terms of the potential of soil endogenous resources to response to external perturbation.

## SOIL ORGANIC MATTER ALTERATIONS RESULTING FROM POST-FIRE RESTORATION ACTIONS

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Burned soils restoration/rehabilitation techniques include tillage, tree logging, reforestation with native or non-native species, and other management. In some cases, restoration may cause additional impacts on soils, producing more severe damages than those caused directly by fire. Triggered soil erosion processes, loss of soil fertility and alterations in the hydrological cycle are among these negative impacts. Analytical pyrolysis (Py-GC/MS) together with graphic interpretation tools like van Krevelen's diagram [1] may be used to shed light on alterations caused by burning and restoration plans to soil organic matter (SOM). The objective of this research is to study fire impacts on SOM in a sandy soil under pine (*Pinus pinea*) forest affected by a severe fire in August 2012 in Doñana National Park (SW Spain).

The impact of fire on SOM was studied in bulk samples and sieved soil fractions (coarse, 1–2 mm, and fine, <0.05 mm) collected from burned adjacent areas before (B) and after restoration practices (BR) (logging and extraction of burned trees). An adjacent unburned (UB) area was used as a control. Bulk soil samples and its fractions were studied by Py-GC/MS and the results were interpreted taking advantage of a van Krevelen diagram using the H/C and O/C atomic ratios calculated from the chemical formulas of compounds as inferred from their mass spectra.

The percentage of main compound families obtained by analytical pyrolysis, including alkane/alkene pairs, unspecific aromatic compounds (UAC), peptides, methoxyphenols, fatty acids, carbohydrate-derived, N-compounds and polycyclic aromatic hydrocarbons (PAH), showed conspicuous differences among bulk samples from the B, BR and UB control areas. Compared to the UB site, the samples from the B site showed lower proportions of lignin methoxyphenols and increased ones of UAC and PAH. It could be hypothesized that fire produced defunctionalization of methoxyphenols, increasing the proportion of soil recalcitrant compounds. In all cases, the coarse fraction showed a high content of carbohydrate-derived compounds and methoxyphenols followed by fatty acids that could be explained by litter inputs after the fire [2]. While the coarse fraction from BR soil showed the highest proportion of methoxyphenols, the UB coarse fraction showed the major proportions of alkyl compounds. On the other hand, although the SOM composition from fine fractions varied largely from one area to another, SOM was found generally more altered than in the coarse fractions. In fact, SOM from the UB fine fraction showed high proportion of alyl compounds and comparatively lower of carbohydrate- and lignin-derived compounds. In contrast, SOM from B fine

fraction did not show a high contribution of alkyl compounds, which may be due to a thermal cracking of alkane/alkene chains [3]. In addition, a high contribution of UAC and PAH was observed in this B fine fraction. Finally, the fine fraction of BR samples showed a high contribution from labile compounds, possibly due to topsoil mixing caused by tilling during rehab actions. The van Krevelen diagram applied to pyrolysis compounds differentiated among chemical processes caused by fire and rehab practices. Among the main processes identified are condensation (aromatization), demethylation (oxidation and dehydrogenation) and oxidation-reduction.

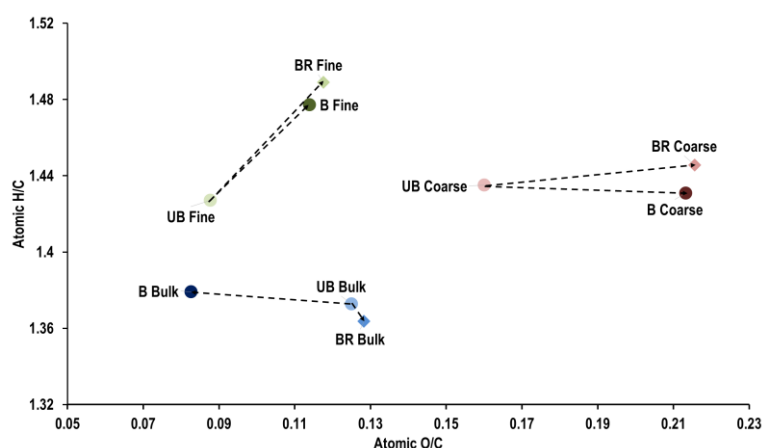


Figure: van Krevelen diagram based in the chemical formula of the pyrolysis compounds as inferred from their mass spectra. Atomic ratios are mean values of detected compounds

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**ACCURACY OF THE ROCK-EVAL METHOD ISO 5725-1-5725-6**R.S. Kashapov<sup>a</sup>, I.V. Goncharov<sup>a\*</sup>\*E-mail: [GoncharovIV@nipineft.tomsk.ru](mailto:GoncharovIV@nipineft.tomsk.ru)<sup>a</sup>Tomsk, 634027, Russia, JSC «TomskNIPIneft»

Rock-Eval pyrolysis gained immense popularity in geochemical research of the oil-and-gas content assessment, therefore the accuracy of the information obtained using this method became topical. In the instruction manual for the hardware metrological characteristics are given very briefly. Thus novice users, who are not thoroughly acquainted with the peculiarities of the method, can be mistaken when interpreting the data. We evaluated measurement errors of research results of determining the main parameters of sedimentary rocks pyrolysis ( $S_1$ ,  $S_2$ ,  $T_{max}$ , TOC) in accordance with the requirements of ISO 5725-1-5725-6. The measurement errors are repeatability, precision, trueness and accuracy.

For pyrolysis from the wells located on the territory of Western Siberia, were selected 13 core samples from the Jurassic-Cretaceous section. They all represented pieces of mudstone or siltstone, which weight was from 20 to 50 g. For each sample was obtained granulometric fraction with a particle size 0.25 mm or less.

The research conducted with Rock-Eval 6 Turbo in Bulk Rock cycle. Once a week (during 4 month) for each sample two parallel measurements were performed. Parallel measurements were carried out sequentially in the same conditions. Together with the prepared samples were analyzed a standard sample IFP160000. To avoid overloading of a flame ionization detector (FID) during the analysis of the samples with high generation potential ( $S_2$ ) the mass of the samples for analysis usually was about 20-40 mg. Every two weeks the adjusting of the FID, thermocouple and infrared (IR) cells was carried out. Two operators took part in the work. Thereby, for each sample were obtained 15 results of pyrolysis parameters measurements. For each pyrolysis parameter was determined a measurement range, based on its graphic dependence on the values of measurement errors. The maximum values of repeatability, precision and accuracy, represented in relative percentage ( $^{\circ}\text{C}$  for  $T_{max}$ ), were attributed for each range. The results are shown in the table.

Table

Values of measurement errors for main pyrolysis parameters

| Pyrolysis parameter | Measurement range  | Repeatability        | Precision            | Accuracy             |
|---------------------|--|----------------------|----------------------|----------------------|
| $S_1$               | 0.5–10.0<br>mg HC/g  | 10 %                 | 13 %                 | 25 %                 |
| $S_2$               | 1.0–200.0<br>mg HC/g                                       | 6 %                  | 9 %                  | 18 %                 |
| TOC                 | 1.0–30.0<br>% wt.  | 4 %                  | 5 %                  | 10 %                 |
| $T_{max}$           | 410–460 $^{\circ}\text{C}$<br>( $S_2 \geq 1.0$<br>mg HC/g) | 2 $^{\circ}\text{C}$ | 2 $^{\circ}\text{C}$ | 4 $^{\circ}\text{C}$ |

Rock samples with low values of the pyrolysis parameters ( $S_1 < 0.5$  mg HC/g,  $S_2 < 1.0$  mg HC/g, TOC < 1.0 % wt.) are not included in the measurement range due to the high error values, which is associated with a low intensity of signals from FID and IR cells. The signal intensity for 20-40 mg of poor samples did not exceed 1 mV. Therefore, when analyzing poor samples, it is recommended to select a sample weight so that the intensities of the FID signal in the areas of  $S_1$ ,  $S_2$  peaks integration and the IR cell signal of oxidation oven (both CO and CO<sub>2</sub>) were greater than 1 mV. This will lead to a substantial increase in measurement accuracy and bring the values of measurement errors closer to table values.

## PYROLYSIS PARAMETERS FEATURES OF THE RUSSIAN ARCTIC OUTCROPS

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From different areas of the Russian Arctic were selected 223 samples for research. The samples were rocks of different lithological composition with age from Cretaceous to Cambrian. The research conducted with Rock Eval 6 Turbo in Bulk Rock and Pure Organic Matter cycles.

The results of outcrops pyrolysis show a very wide range of pyrolysis parameter variation: TOC 0.4-81.1 % wt.;  $T_{max}$  420-640 °C; HI 0-245 mg HC/g TOC; OI 1-168 mg CO<sub>2</sub>/g TOC.

Among the results of pyrolysis are often found abnormally high  $T_{max}$  values (>500°C). Such values do not coincide with the maturity of these rocks, determined by certain other methods ( $R_o$ , TAI). In addition, the pyrolysis results of these samples significantly differ from the results of core analysis with the same level of catagenesis. The collection of our laboratory contains more than 25,000 results of core and cuttings samples studies. For samples of core and cuttings at  $T_{max}$  over 450°C the values of oxygen index (OI) usually do not exceed 10 mg CO<sub>2</sub>/g TOC. However, for these samples from outcrops even at  $T_{max}$  600°C the values of OI increase up to 50 mg CO<sub>2</sub>/g TOC (Fig.)

Organic matter of outcrops, depending on climatic conditions, mineralogical and lithological composition, may be susceptible in a great measure to physical weathering processes, chemical, photochemical and biochemical oxidation, which, like thermal effects, reduce the content of organic substance in rocks and reduce its generation potential ( $S_2$ , HI). At first, the weakest chemical bond is subjected to oxidation, then more and more durable. Therefore, in addition to a reduction the  $S_2$  value, a shift of  $T_{max}$  towards higher temperatures take place (pseudo catagenesis). In the case of pseudo catagenesis decreasing of OI is not happening. On the contrary, it may even increase due to formation of various oxygen-containing compounds with carboxyl groups. As can be seen from the figure, samples of outcrops in the diagram OI- $T_{max}$  differ from the General trend of natural thermal evolution.

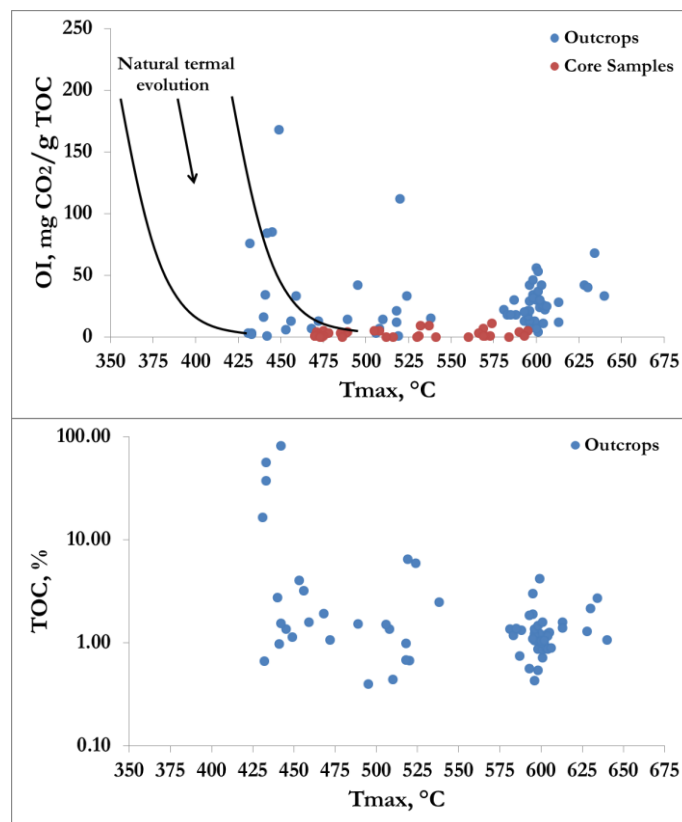


Fig. OI –  $T_{max}$  and TOC –  $T_{max}$  diagrams

## Suspended Particulate Matter from Moselle River (Lorraine, France): Organic characterization using Py-GCMS

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Suspended Particulate Matter (SPM) in rivers, are constituted of colloidal and particulate matter, and commonly described as heterogeneous aggregates of mineral, organic and biological phases. Due to their relative small size distribution, their high content in organic matter and amorphous (or poorly crystallized) solid phases, they display a high and reactive surface area. Thus, they play a crucial role in the fate, transport and partition of contaminants in aquatic media, including trace metallic element. Due to their composition complexity, these solids could provide various association modes for metals, determining their mobility and bioavailability and eventually fingerprinting the sources of trace elements. In order to better understand the reactivity of these particles towards metallic contaminants, it is necessary to characterize their organic fraction as this fraction has high affinity with metallic contaminants.

For that purpose, SPM were collected along the Moselle River (Lorraine, France) and four of its tributaries. The stations were chosen for their geological and land use specificities. The SPM were sampled using a continuous-flow field centrifuge, which can be used to obtain a more representative sample. The SPM were then gently recovered from the Teflon plates, immediately frozen and lately freeze-dried. After extraction of lipidic OM using an automatic extractor, the insoluble fraction was analyzed with on-line thermochemolysis coupled to a gas chromatograph-mass spectrometer (TMH-GC-MS) using TMAH.

The pyrograms showed differences of molecular composition according to the sites and the hydrology of the river. The anthropogenic OM (palmitic and stearic acids) was predominant downstream urban areas suggesting human inputs. The natural organic matter (lignin compounds, carbohydrates) was homologous through the catchment from upstream to downstream but did not show clear trend. The lignin ratios calculated revealed the predominance of non woody angiosperms in the catchment. However, seasonal variations were observed with strong autochthonous production during low flow level in summer. The regime flow increase resulted in the decrease of TOC content and evolution of the OM composition with the contribution of more degraded material as shown from lignin ratios. The leaching of deeper soils could explain these observations. The use of pyrolysis coupled with other techniques (GCMS) in order to isolate molecular tracers to investigate the origin of organic matter in SPM is a good tool when dealing with regime flow and SPM organic matter composition.



# CONJUGATED KINETIC EFFECT OF ALKYL BENZENES AND H<sub>2</sub>S ON ALKANES CRACKING

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## 1. Introduction

The chemistry related to H<sub>2</sub>S in hydrocarbon systems under geological conditions is of important concern to the petroleum industry. It provides background knowledge for instance to the formation of high sulfur oil fields, enhanced recovery of heavy oil, exploitation of sulfur rich petroleum or injection of H<sub>2</sub>S in depleted reservoirs. Studies have proved that Thermochemical Sulfate Reduction (TSR) is the main formation pathway for H<sub>2</sub>S under geological conditions. Yet little is known about the reaction pathways and kinetics of H<sub>2</sub>S-hydrocarbons systems. Interactions between hydrocarbons and H<sub>2</sub>S are studied through confined pyrolysis of model compounds which allows the construction of detailed kinetic models. Some binary mixtures, i.e. alkanes-H<sub>2</sub>S [1] and aromatics-alkanes [2, 3] have already been studied. The study of the n-octane-H<sub>2</sub>S mixture contributed to highlighting some formation pathways of organic sulfur compounds (OSC) and showed that H<sub>2</sub>S inhibits the thermal cracking of n-octane at 300-350°C and 700bar, but the modelling results also suggested that H<sub>2</sub>S accelerates n-octane thermal cracking at lower temperatures approaching geological conditions. Furthermore, the alkanes-aromatics system was modelled by n-octane and alkylbenzenes [2], [3]. These systems showed contrasted results. While long chain alkylbenzenes decrease the conversion rate of n-octane [2], toluene has almost no effect on the conversion of n-octane at 300-350°C [3]. Currently, the thermal cracking of alkyl-aromatic model compounds in presence of H<sub>2</sub>S is studied in order to highlight new genesis pathways for OSC and complete a detailed kinetic model capable to predict the composition and evolution of a sulfur crude oil.

## 2. Experimental

Confined pyrolysis of alkyl-aromatics (toluene, ethylbenzene, n-propylbenzene and n-butylbenzene) with H<sub>2</sub>S is carried out in gold cells (internal diameter: 5mm, lengths: from 50 to 100 mm). Gold is chosen to avoid catalytic effects on the cracking reactions and to warrant heat and pressure transfer to the reaction mixture [4]. Pyrolysis conditions range between 250°C-350°C under 700bar for 24h to 1 month. The pyrolysis products are extracted by thermal desorption in a volume of 28.8cm<sup>3</sup> at 0.17bar and 250°C. The quantification of hydrocarbons and OSC is made by coupled multidimensional gas chromatography (MDGC) while the identification of unknown molecules is made by GC-MS.

## 3. Results

Analysis of the pyrolysis products of alkylbenzenes with H<sub>2</sub>S shows an increase in the yield of derivate aromatic compounds and OSC proportional to the alkyl chain length of the initial reactant. The main hydrocarbon products are toluene, shorter alkylbenzenes and biaromatic compounds while benzylthiols, benzothiophenes and phenylthiophenes are the major sulfur products. The description of the products already allows highlighting new OSC formation pathways.

## 4. Conclusion and perspectives

The sulfur products obtained by pyrolysis of alkylbenzenes-H<sub>2</sub>S mixtures are similar to those encountered in sulfur oils. These compounds could be formed in reservoir oil by interactions between migrated H<sub>2</sub>S and the aromatic fraction. Moreover the results obtained at 300-350°C showed that H<sub>2</sub>S has an inhibiting effect on alkane thermal cracking which increases with temperature. Nevertheless, at temperatures below 300°C and closer to reservoir temperatures (investigated by modelling), H<sub>2</sub>S seems to have an accelerating effect on alkane cracking and leads to great amounts of OSC. On the other hand alkylbenzenes have an inhibiting effect on alkane cracking which increases when temperature decreases. The study of the conjugated kinetic effect of alkylbenzenes and H<sub>2</sub>S on alkane pyrolysis is now in progress.

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# THECP+TVWOOD DATA BASE (I): CAPABILITIES & APPLICATION SCOPE

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For a variety of applications, we are analyzing wood types by a standardized approach of Curie-Point pyrolysis (CP) and thermovaporization (TV), both coupled with gas chromatography-mass spectrometry in order to establish a chemical reference data base (CP+TV Wood Data Base). At the present stage, we can report the following criteria for qualitative and quantitative differentiations of individual wood types.

Generally, all wood types investigated exhibit very characteristic relative intensity patterns of individual compounds which enable a distinctive chemical diagnosis and biological assignment. Bark samples can easily be related to their corresponding heart wood, which means that bark is composed of the same wood type specific, principal chemical building blocks, but with different relative concentrations [1]. Even (bio-)degraded wood and even lichen covered barks exhibit characteristic, specific wood type compounds [1]. Comparisons between CP and microscopic analyses for pine wood embedded in a peat matrix of moss (Sphagnum, Polytrichum, Brown Mosses), grasses (Carex, Eriophorum) and blueberry (Vaccinium) reveal that down to less than 1% of wood can be verified [2], [3].

*Coniferous wood:* predominant compounds are fufural, guaiacol, ethylguaiacol, vinylguaiacol, isoeugenol, vanillin and benzenediol. These compounds are present in all coniferous woods with exception of fir (no fufural) and Kauri (no guaiacol). High concentrations of 1,4-benzenediol occur in pine, juniper, redwood, fir, spruce and yellowwood, of guaiacol in fir, of fufural and of vinylphenol in Kauri and of propiovanillone in one Rimu wood.

*Broadleaf wood:* the most prominent compound is (hydroxymethyl)phenoxy propane-2-one. Vinylguaiacol is strongly reduced in comparison to coniferous wood. Other compounds like syringol, 4-methylsyringol, syringaldehyde and 4-methylguaiacol are very prominent, too.

Based on the distinct differentiation potential of the CP+TV Wood Data base, we see a wide application range. Beside others, these are the fields of archaeology (e.g. artefacts, shipbuilding, restoration), ecology (e.g. environmental estimations by paleophytocoenosis reconstruction [3], paleobotany (e.g. genetic relationship of recent to fossil wood [1]), biology (e.g. recognition of tree diseases) and the differentiation of plantation wood and wood from primeval forest for various commercial users.

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# THE CP+TVWOOD DATA BASE (II): SELECTED CASE HISTORIES

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We present three selected examples from biochemical case histories for specific applications of the CP+TV Wood Data Base ([1], CP = Curie-Point pyrolysis, TV = thermovaporization). In detail, these are i) a detailed differentiation of particular birch species, ii) a documentation of wood identification for both non-degraded and degraded *Ginkgo biloba* bark and heart wood, and iii) a demonstration for the close genetic relationship between fossil and modern wood (*Taxodiioxylon*spp. and *Sequoia sempervirens*).

## - Case study species differentiation (birch)

Within the frame of an environmental study of a peat section (Haute Fagne, Belgium, 2900-300BC), we located 33 individual wood pieces of up to 6 cm length. It was possible to assign the specific wood type according to the biological family (*Betula*), but we failed to correlate them to a specific species of our modern wood reference samples (*Betula pubescens*, *Betula nigra*) or to the recent vegetation of this area (*Betula pubescens* *carpathica*) because all three species exhibit the same marker composition. Other birch species, like the Caucasian dwarf (*Betula raddeana*) from Georgia, can easily be verified due to two different compound ratios.

## - Case study degraded wood (ginkgo)

Bark exhibits the same chemical compounds as the corresponding heart wood type. For some major compounds, non-degraded bark exhibits about the same relative intensities as the corresponding heart wood, whereas for other major compounds, non-degraded bark exhibits different relative intensities. In addition, bark exhibits some further compounds in comparison to the corresponding heart wood. Very degraded bark even covered by lichens can still distinctively be assigned to the corresponding wood type, although the intensities of all major compounds are extremely reduced due to a dominating unresolved carbon mixture (UCM).

## - Case study palaeobotany (sequoia)

In the Lower Rhine Embayment (western Germany) the Miocene/Pliocene lignite bearing sequence is rich in large wood trunks most of which belong to the fossil wood genus *Taxodiioxylon* which is assigned to modern sequoia trees. *Sequoia sempervirens* ((D. Don) Endl.), the coast redwood, is the sole living representative of this genus. A chemical comparison of recent sequoia wood with Neogene *Taxodiioxylon* (open pit mine Garzweiler, Rhenish lignite district, Bedburg, Germany) from coal seam Morken (16 Ma) confirms the genetic relationship.

The above three case histories document the different application fields of the CP+TV Wood data Base.

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## PY-GC AS A USEFUL METHOD FOR GENERATED PRODUCT PREDICTION IN PALEOZOIC SHALE FORMATIONS IN POLAND

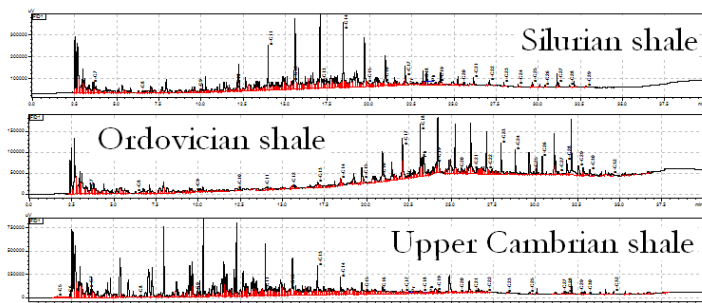
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In the last years over 50 wells have been drilled in Poland in order to identify technically recoverable shale gas resources. Lower Paleozoic formations (Silurian, Ordovician and Upper Cambrian) are most perspective source rocks for shale gas in Poland. Paleozoic shales in the Baltic Basin appear as excellent source rocks for hydrocarbon generation. They are rich in organic matter and are not deeply buried, so they are relatively low matured and could be considered as a source for both oil and gas generation due to high Hydrogen Index (approx. 300mg HC/g TOC). The aim of our research was to explain the differences between Silurian, Ordovician and Upper Cambrian shales for generation products prediction. The second goal of this research was to determine the activation energy of kerogen which can be applied in basin modelling. PY-GC experiments were used to identify the fluids constituents and quantify their percentage contribution. They were run on 6 shale samples representing 3 formations (2 samples for each) at various temperature ranges in order to develop an understanding of the molecular distribution at different thermal conditions. The low temperature pyrolysis can give us information about the producible light hydrocarbons. So we carried out the following experiments:

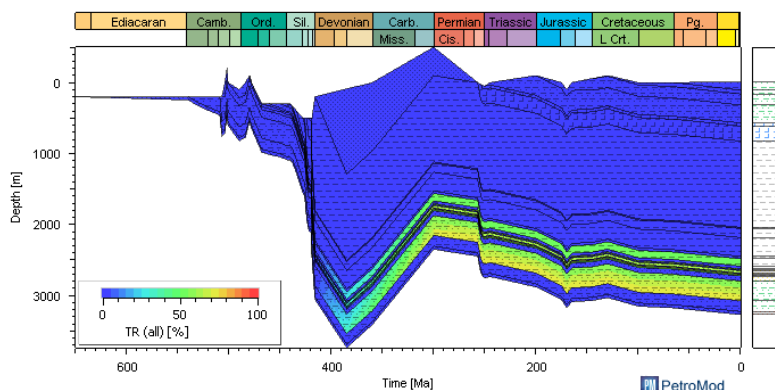
- Rock Eval pyrolysis for rocks samples,
- PY-GC (at 400°C and at 600°C) for rocks samples,
- Rock Eval pyrolysis for the residues after PY-GC.



As a result of pyrolysis at 600°C we received mainly light hydrocarbons (up to C<sub>9</sub>) and the whole pyrolytic carbon (PC) was converted into hydrocarbons for all samples. This distribution is the effect of primary and secondary cracking. PY-GC at 400°C differentiates Paleozoic shales, giving variable distributions of hydrocarbons which are illustrated on the chromatograms. Pyrolytic carbon content decreased only in the range from 24 – 35% which means an exhaustible generation potential. On the basis

of these investigations we can predict that Silurian shales can generate paraffinic low wax light oil, Ordovician shales are able to generate heavier waxy oil whereas samples from Upper Cambrian show a potential for gas - condensate generation.

All of the samples come from the same drilling area with very similar thermal and burial history proved in conducted 1D basin modeling. Based on the results from the experiments, the refined kinetic model had been applied in order to predict generated hydrocarbon components.



*This study was supported by The National Centre for Research and Development (Blue Gas project "MWSSSG" no BG1/MWSSSG/13 – Methodology to determine sweet spots based on geochemical, petrophysical and geomechanical properties in connection with correlation of laboratory tests with well logs and generation model 3D – DK-0601-6/13)*

## EVIDENCE FOR THE ROLE OF MINERALS ON THE GENERATION OF H<sub>2</sub>S AND CO<sub>2</sub> UPON AQUATHERMOLYSIS OF HEAVY OILS AND OIL SANDS IN CONFINED HYDROUS PYROLYSIS EXPERIMENTS: IMPLICATION FOR STEAM INJECTION PROCESSES FOR OIL RECOVERY

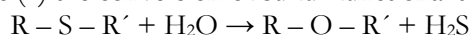
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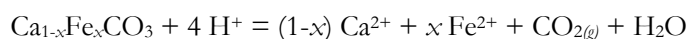
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In the industrial context of steam injection processes for enhanced heavy oil recovery, oil producers face the growing need to forecast the H<sub>2</sub>S and CO<sub>2</sub> production resulting from aquathermolysis reactions within the reservoir rock. Previous results from aquathermolysis experiments on heavy oil sands highlighted the relevancy to investigate the potential effect of minerals on H<sub>2</sub>S and CO<sub>2</sub> production [1]. The current study is an attempt to identify the minerals and the related reaction mechanisms affecting H<sub>2</sub>S and CO<sub>2</sub> production during steam injection. Aquathermolysis data on gas production and mineral composition were gathered from confined hydrous pyrolysis experiments at temperatures in the range from 240°C to 320°C, on oil sand samples and on heavy oil sand samples. The results indicate that the presence of the mineral matrix induced a significant decrease in H<sub>2</sub>S production and a significant increase in CO<sub>2</sub> production. The evolution of the composition of the mineral matrix upon aquathermolysis, characterized by both Rock-Eval and X-ray (powder) diffraction, suggests that Fe-bearing carbonates and clays, albeit present in low proportions in the mineral matrix, lead to the observed variations in H<sub>2</sub>S and CO<sub>2</sub> production. A possible combination of reactions include (1) the conversion of sulfur functionalities in the heavy oil to H<sub>2</sub>S,



(where the oxygen from H<sub>2</sub>O may be either incorporated into the asphaltene fraction of the heavy oil or consumed in a subordinate oxidation reaction), (2) the dissolution of iron-bearing carbonates releasing CO<sub>2</sub>,



and (3) the precipitation of pyrite, which consumes part of the H<sub>2</sub>S generated in (1) in accord with



Iron could also be provided by clay minerals. One implication of these results on the H<sub>2</sub>S and CO<sub>2</sub> production forecast in steam injection processes for oil recovery is that mineral interactions should be taken into account in the aquathermolysis numerical models, and that aquathermolysis experiments should be carried out not on oil samples alone but rather on the water-rock-hydrocarbon system.

This proposition needs to be substantiated by additional experiments, together with mineral and organic sulphur speciation characterization and thermodynamic simulations to improve our understanding of the nature and relative importance of the reactions involved in the overall process of aquathermolysis.

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## HONEY-LIKE SCENTED DEPOSITS IN A LAVA TUBE FROM LA PALMA ISLAND (SPAIN)

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Speleothems, or secondary mineral deposits in caves, are usually formed due to the dissolution of primary minerals from the host rock, such as in limestone and dolostone caves. In volcanic caves, the vast majority of speleothems are siliceous, formed in the initial stage of lava tube formation or due to leaching and subsequent precipitation of secondary minerals [1]. Among them, organic ooze deposits that coats the walls of lava tubes have been reported [2,3]. In a lava tube (*Llano de los Caños Cave*) from La Palma Island, in Canary Islands (Spain), black ooze with honey-like scent was collected from the wall and ceiling of the cave where sub-horizontal fractures occur (Fig. 1A,B). Field emission scanning electron microscopy (FESEM-EDS), X-ray micro-computed tomography (micro-CT) and mineralogical analyses were conducted for characterizing the surface morphology, 3D microstructure and mineralogical composition of these black organic deposits. Abundant microbial structures were found in close association with the organic ooze, including reticulated filaments (Fig. 1B), bacterial cells, platelet microorganisms and pollen grains (Fig. 1B). The overall volume of the sample showed low opacity or high transparency to X-rays according to micro-CT (Fig. 1C), with the exception of a superficial deposition of calcium carbonate in the form of calcite (whitish layer), as also observed by stereomicroscopy (Fig. 1B, white particles). The X-ray pattern showed a broad hump typical of non-crystalline material and some calcite, suggesting that the black ooze samples are mainly composed of amorphous material and calcite.

In an attempt to achieve an accurate characterization of the ooze deposits found in *Llano de los Caños Cave* in La Palma Island and unveil the nature of these unusual honey-like scented deposits, analytical pyrolysis (Py-GC/MS) and stable isotope analysis were performed. Py-GC/MS showed abundance of polysaccharides, plant lipids and specific terpenoids typical of the local vegetation (mainly *Erica arborea*). In addition, polycyclic aromatic hydrocarbons and N-containing heterocyclic compounds were detected, which probably derived from the leaching of charred vegetation resulting from a wildfire occurred in the area in 2012.

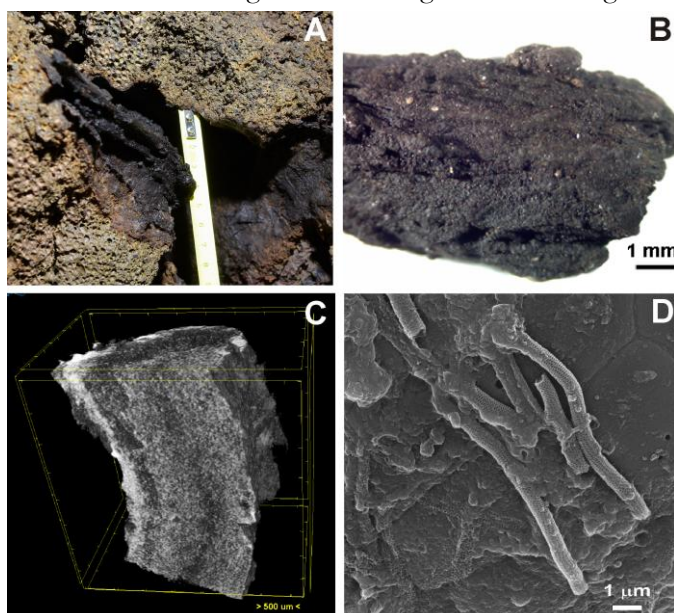
Stable isotope analysis of  $\delta^{13}\text{C}$ , performed on the cave black deposits, topsoil and *Erica arborea* collected from the area over the lava tube, confirmed that the organic fraction of the ooze deposits are a combination of partially charred vegetation and organic compounds from the andic soil located over the cave. Therefore, these cave deposits are the result of an input of plant organic matter and charred vegetation into the cave through rock fractures, which may constitute an important source of energy for cave organisms. The honey-like scent of the black ooze deposits is probably due to the thermal transformation of abundant plant polysaccharides during fire and their subsequent deposition on the cave wall.

**Acknowledgments:** AZM and JMR acknowledge the support from the Marie Curie Fellowships within the 7th European Community Framework Programme (Grants PIEF-GA-2012-328689-DECAVE and PCIG12-GA-2012-333784-Biocharisma respectively). The authors acknowledge the Spanish Ministry of Economy and Competitiveness (project CGL2013-41674-P) and FEDER funds for financial support.

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**Fig. 1.** Black honey-like scented deposits from *Llano de los Caños Cave*, La Palma Island, Spain. **A)** Photography of the black deposits in the lava tube. **B)** Stereomicroscopy image showing the texture and calcite particles deposited on the surface of the ooze material. **C)** Reconstructed micro-CT image of the internal 3D structure depicting several layers evidenced by differences in X-ray attenuation. Grayish regions are organic rich and brighter superficial areas are attributed to carbonate deposition. **D)** FESEM image showing bacterial filaments with reticulated ornamentation over a pollen grain.

## PYROLYTIC PARAMETERS SECTION BAZHENOV FORMATION OF WESTERN SIBERIA (RUSSIA)

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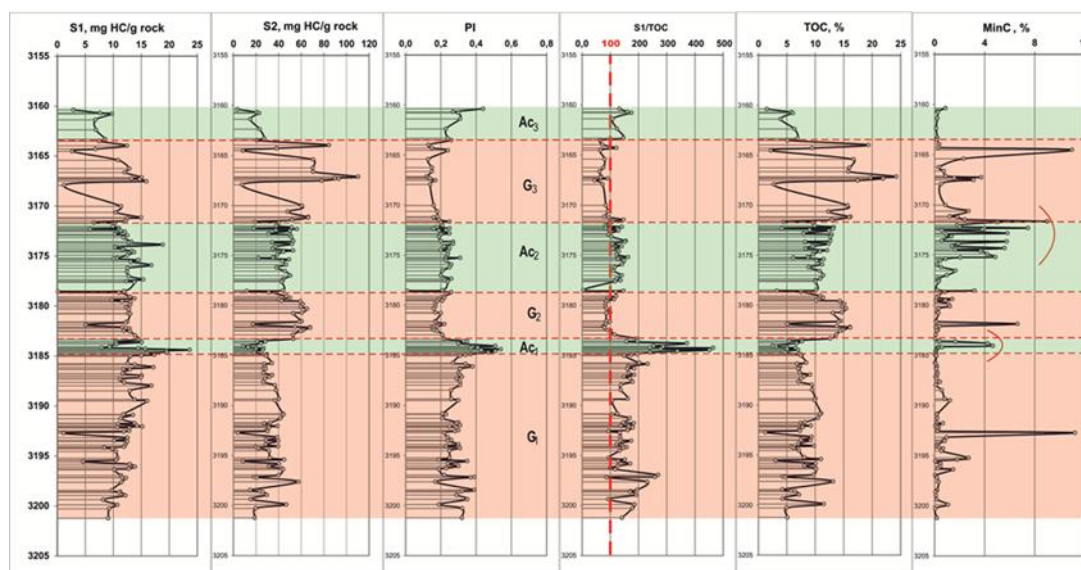
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With the organic matter of the Bazhenov Formation is related to 80% of total geological reserves of oil in Western Siberia. The unique properties of this source rock are under close study for more than half a century. It is one of the most promising targets for the development of shale oil in the world. Therefore, in connection with the development of new methods for the development of such deposits, the interest in rocks Bazhenov formation increased significantly.

The aim of this study was to investigate of variation of the Rock-Eval parameters of the Bazhenov Formation in one of the wells to identify it generation-accumulative properties. It located at the central part of Western Siberia.

A total of 40.5 meters section Bazhenov Formation has been investigated 142 core sample. Cut suite characterized by an excellent generational potential. Organic carbon content varies from 2.21 to 24.24% (average 9.56%). In most cases, low values of organic carbon content (1,24-2,5%) interlayers confined to the high mineral content of carbon. Tmax values of the parameter reflecting the degree of thermal maturity of kerogen, in the context of the Bazhenov Formation is 437-448 °C and meets the peak of the main phase of oil generation («Oil Window»). The values of hydrogen index (HI, mg HC / g TOC) range from 280 to 455, that the achieved level katagenesis can be attributed to the organic material suite the type II kerogen, generating oil. Also, on the excellent lasing properties of kerogen Bazhenov Formation indicate low values of oxygen index OI, that is, except the carbonate layers does not exceed 5 mg CO<sub>2</sub> / g TOC. Elevated values of productivity index PI (to 0.54), and the parameter S<sub>1</sub> / TOC (up to 465), evidence of active oil generation in the context of formation.

According to the pyrolysis can be seen that the content of free hydrocarbons (parameter S<sub>1</sub>), organic carbon, productivity index and parameter S<sub>1</sub> / TOC unevenly distributed and have a wide enough area separate minimum and maximum values (Figure 1). Thus, in the context of the suite, there are areas of large-scale oil generation (G<sub>1</sub>, G<sub>2</sub> and G<sub>3</sub>) - intervals section with a high content of organic carbon, and areas "discharge" (in the figure are Ac<sub>1</sub>, Ac<sub>2</sub> and Ac<sub>3</sub>) - the area of the cut with a low content of organic carbon, which also often corresponds to higher carbonate content. Obviously, the ranges with higher values of PI and S<sub>1</sub> / TOC can be considered as promising development objects after a set of special events (fracturing, etc.).





ABSTRACTS

# Waste / Reactors

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Oral presentations



## PYROLYSIS OF MULTICOMPONENT PLASTIC WASTE DERIVED FROM END-OF-LIFE VEHICLES

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According to The End of Life Vehicles Directive of the European Union “No later than 1 January 2015, for all end-of-life vehicles, the reuse and recovery shall be increased to a minimum of 95% by an average weight per vehicle and year. Within the same time limit, the re-use and recycling shall be increased to a minimum of 85% by an average weight per vehicle.” [1]. Although the recycling and pyrolysis of waste plastics of the vehicles have already been studied in the past few years [2,3], this directive makes plastic recycling studies even more urgent. Pyrolysis can provide good opportunity to obtain reusable products from waste materials taking into consideration of the environmental and economic factors, as well. The analytical pyrolysis of multicomponent plastic materials of the automotive industry gives information about the thermal properties of polymeric components, reinforcements and additives. Moreover, the analysis of the pyrolysis products can be useful to find the most beneficial recycling processes, which might produce valuable raw materials from these wastes materials. Therefore, this study aims at determining the thermal properties of multicomponent plastic samples derived from end-of-life vehicles.

The mixed plastic waste of end-of-life vehicles were analyzed by thermogravimetry/mass spectrometry (TG/MS) and pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). The waste samples were derived from wrecking yards. For comparison individual polymers were studied as well. The TG/MS experiments have revealed that the thermal decomposition of mixed plastic samples takes place in two or more distinct temperature ranges. The first stage begins at about 150 °C with the release of the volatile additives. The decomposition of the polymer components occurs between 380-520 °C. Further mass loss was observed between 540 and 1000 °C that can be attributed to the final charring process of the polymeric constituents. The yield of the remaining solid residue varies depending on the amount and type of the polymeric constituents, reinforcements and inorganic fillers.

Single step pyrolysis experiments at 500 °C and successive pyrolysis experiments at two temperature steps (350 °C and 500 °) have been carried out. Low-temperature pyrolysis experiments have revealed that plastic mixtures contain a wide range of volatile additives including fire retardants, plasticizers, lubricants and antioxidants. Pyrolysis at elevated temperature shows that the polypropylene (PP) has great importance among the polymers applied in vehicles, however several other polymers (polyethylene, polyesters, polyurethanes, polyamides, ABS) can be found in the mixtures.

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## PYROLYSIS – DECENTRALIZED RECOVERY OF HIGH-TECH METALS

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Waste Electrical and Electronic Equipment (WEEE) is a relevant source for nearly all kinds of metals, which are relevant for industry. However, the end-of-life recycling rates of a number of these metals are less than one percent [1]. As an example, composite materials like printed wiring boards, which contain both high-tech and base, precious as well as platinum group metals, are usually treated in pyrometallurgical processes [2]. Due to the chemically ignoble character of most high-tech metals, these metals, such as gallium, germanium and tantalum, get oxidized and become part of slag or dust, which have to be landfilled or end up being used as road construction material. Both cases show a loss of metals for the economic circuit.

In order to accumulate and recover high-tech metals from WEEE, Fraunhofer UM Sicht is currently developing a decentralized concept for treating selected components as well as residual fractions from the treatment of WEEE, based on a pyrolysis process in a pilot plant scale (30 kg·h<sup>-1</sup>). In combination with biochemical- and electrochemical processes, pure metals are planned to be recovered from the concentrated metal-coke-mixture. The produced pyrolysis oil and gas will be utilized in a combined heat and power (CHP) plant.

So far, a number of different shredder residues from the treatment of WEEE as well as selected components such as LCD-Displays, tantalum capacitors or photovoltaic panels got treated during extensive test series in a semi-continuous test plant for loads of 200 - 300 g. Figure 1 shows an exemplary mass and energy balance diagram for the treatment of 1000 kg shredder residues. The by-products oil and gas were tested concerning the energetic utilization in a CHP.

To demonstrate the ecological benefits of this technological approach, Fraunhofer UM Sicht developed an eco-balanced model according to DIN EN ISO 14040 / 14044 to compare different recycling-processes for metals and primary exploitation in a holistic approach. Furthermore, a business case was calculated to demonstrate economic benefits for a decentralized installation of the new processes on-site mechanical WEEE treatment plants.

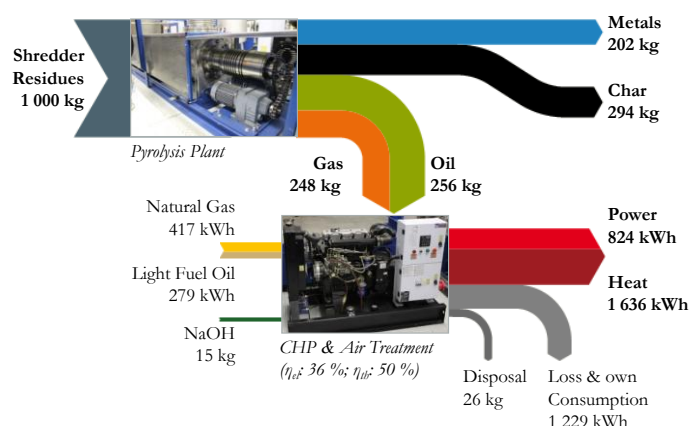


Figure 1: Mass and energy balance diagram for the treatment of 1000 kg shredder residues

At the 21<sup>st</sup> International Symposium on Analytical and Applied Pyrolysis further results especially from pyrolytic treatment of components containing critical metals can be presented. Special attention will be given to reactions between these chemically ignoble metals and reactive halogens from the thermal decomposition of flame retardants, which are contained in plastics from WEEE. Additionally, approaches for an upscale from the above mentioned semi-continuous plant to the pilot plant can be presented.

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## CO-PYROLYSIS OF MUNICIPAL PLASTIC WASTE AND DIFFERENT HYDROCARBONS: REDUCTION OF CONTAMINANTS

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Pyrolysis is one of the most widely investigated ways for waste plastic utilization, but the further utilization of products is significantly affected by their composition and contaminants. Contaminants from the structure of raw materials or even from their surface could be shifted into the products, which generates some disadvantages during their further transportation, storage and application. Large amounts of municipal plastic waste (MPW) was pyrolyzed in a batch reactor together with atmospheric gas oil and waste lubrication oil at 550°C using HZSM-5 and natural zeolite catalysts. The composition of gases and liquid products were investigated by gas-chromatography, while the contaminants were followed by EDXRFS and standardized methods. In this work different ratios of MPW and hydrocarbons (atmospheric gas oil or waste lubrication oil) were used during the co-pyrolysis. Regarding product hydrocarbons, it was found, that the presence of both atmospheric gas oil and waste lubrication oil could significantly affect their composition. E.g. higher yields of gases and lighter compounds in pyrolysis oil were found using higher portions of atmospheric gas oil and waste lubrication oil. Furthermore the catalytic effect of the used HZSM-5 and natural zeolite was also significantly higher in the case of co-pyrolysis. Regarding the product gases, higher yields of olefins and methane were found using catalysts. Catalyst, especially HZSM-5 also had a notable effect on the concentration of branched hydrocarbons. Owing to the PVC content of the raw plastic waste material, a high concentration of chlorine was measured in the product pyrolysis oils, which could be notably decreased by natural zeolite catalyst, especially in the case of co-pyrolysis. The products contained many contaminants, such as sulphur, nitrogen, calcium, bromine, antimony, zinc, molybdenum, phosphorous etc., which could be also decreased by the presence of catalysts. The positive effect of natural zeolite catalyst could be attributed to its chemical and physical sorption properties. It is important to note, that the contaminants were only partly sourced from the MPW, because atmospheric gas oil had significant sulphur and nitrogen content, while waste lubrication oil contained molybdenum, phosphorous, sulphur and zinc content. The olefin/paraffin ratio of pyrolysis oils were also significantly changed during co-pyrolysis of MPW and waste lubrication oil.

**Keywords:** co-pyrolysis, contaminants, MPW, atmospheric gas oil, waste lubrication oil

## Disintegration of metal-rich composite fractions from WEEE through pyrolysis

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### I. Introduction

The investigations presented focused on metal-rich fractions from waste of electrical and electronic equipment (WEEE), particularly with regard to consumer electronics. The objective was to achieve a high metal recovery rate through pyrolysis while minimizing the complexity of the necessary mechanical (pre-)treatment of these fractions. In this context, ferrous and nonferrous metals were designated as recyclable fractions. The composites were input to a rotary furnace and were pyrolyzed at 600 °C. Solid, liquid and gaseous products were sampled and analyzed.

### II. Materials and methods

The consumer electronic devices from WEEE were gathered at a local WEEE collection point in Aachen, Germany. Samples of the material (6.3 kg) were crushed and their composition was determined by manually separating different groups of materials: metal-plastic composites with and without printed circuit boards (PCBs, 12 weight-% and 24 weight-%), free plastics (47.5 weight-%), free ferrous metals (10 weight-%), free nonferrous metals (2.5 weight-%) and fines (4 weight-%). Organic contents, such as plastics and fibers, were analyzed. The high proportion of plastics in the consumer electronics accounted for a very high share of volatile components (totaling 49 weight-%) and an average gross calorific value of 24.7 MJ/kg. To assess the success of the disintegration process the ratio of free metals to metal compounds  $R$  is introduced, which indicates the pureness and marketability of the material regarding metal recovery. The  $R$ -value for the original material calculated to  $R = 0.35$ . After manual separation the material was mixed back together and was subsequently preconditioned mechanically using magnet and eddy current separation to enrich the metal composites prior to thermal decomposition. The respective metal products from these process steps were mixed back in, thereby, producing the feed material for treatment using pyrolysis. The enriched material showed a ratio of free metals to metal compounds of  $R = 0.98$ .

An electrically heated pilot-scale rotary kiln was used for the pyrolytic treatment. The oven's drum had a diameter of 162 mm and a length of 1,600 mm. Process parameters such as the rotational speed of the drum, the reactor's slope and the reactor's temperature could be set manually. The retention time of the material during each of the 4 trials was set to 30–60 min. A compressor extracted the process gases via appropriate piping, causing negative pressures of -500 to -2000 Pa. Downstream of the rotary kiln the produced gases passed a gas scrubbing line. Here condensable components were precipitated at -20 °C and solid particles were filtrated. A burner incinerated the remaining gases at the end of the process. After passing the drum, solid residues, mostly consisting of metals and coke from outgassed organic matter, fell into a container between the drum and the following gas scrubbing line. After treatment the solids were sieved shortly to separate the fine grained coke and the metals.

### III. Results

The product distribution of the thermal treatment of WEEE varied greatly over the series of trials. This was caused by the heterogeneity of the feed material. In spite of careful homogenization, the relative fraction of the organic components in the individual trials varied considerably, which had a direct effect on the gas and condensate production. Thus, condensates and non-condensable gases of all products varied from 5–10 weight-% and 1–10 weight-% respectively. Samples of these fractions mostly contained combustible components, e.g. hydrogen, carbon monoxide, methane, ethane, ethylene and other organic hydrocarbons. Furthermore, inert gases such as nitrogen and carbon dioxide were detected.

The chemical analysis of the coke showed a reduction of volatile components by 82 %. The coke comprehended high amounts of chlorine up to 5 weight-%, caused by plastics in the input material such as polyvinyl chloride. The solid residues contained no ferrous metal composite fractions. They were completely separated by pyrolysis and were present as free ferrous metals. However, in all trials nonferrous metal composites were still present. These composites primarily consisted of PCBs containing copper, which was interwoven in a thermally stable glass fiber matrix. Nevertheless, it was possible to completely release aluminum and other copper fractions, e.g. from electrical cables. The ratio of free metals to metal compounds  $R$  could be increased from  $R = 0.98$  to  $R = 9.2$ –25.0. The proportion of compounds dropped significantly for all ferrous and nonferrous metals, thus, proving a high process efficiency regarding metal recovery.

## Co-production of hydrogen and carbon nanotubes from catalytic pyrolysis of waste plastics on Ni-Fe bimetallic catalyst

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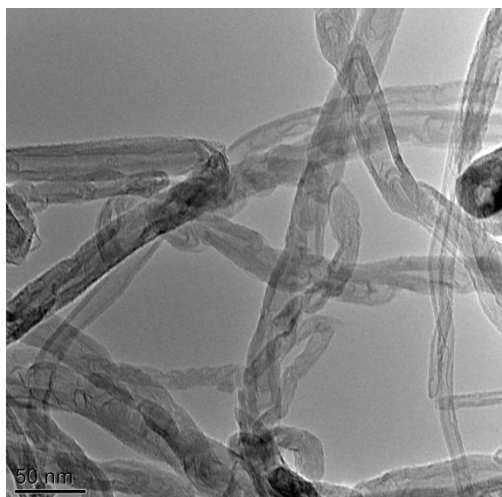
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### ABSTRACT

Producing high-value carbon nanotubes (CNTs) with clean hydrogen from catalytic gasification of waste plastic is a promising technology for management of plastic waste. Ni and Fe are usually used for CNTs production. However, there are limited data about using the combination of both metals for CNTs and hydrogen productions from waste plastics. In this work, a two stage fixed bed reaction system was used to obtain the effect of mixture of Ni and Fe with different molar ratios on hydrogen and CNTs productions. Various characterizations of fresh and used catalysts in addition to the produced carbons were carried out with temperature programmed reduction/oxidation, X-ray diffraction, scanning electron microscopy or/and Raman spectroscopy. Both the H<sub>2</sub> concentration and yield reached maximum values of 73.93 vol.% and 51.04 mmol g<sup>-1</sup> plastic, respectively, in the presence of NiFe13 catalyst. It is suggested that the productions of hydrogen and CNTs were influenced by the synergistic catalysis from Fe and Ni. The amount and quality of CNTs was found to be greatly influenced by the catalyst composition and crystal size. For example, the weak interaction between active sites and support produced more deposited carbon. The interaction between Ni and Fe was intensified and NiFe<sub>2</sub>O<sub>4</sub> crystal was found to dominate production of CNTs with a tip-growth mechanism in the presence of NiFe11, which contributed to the well-distributed filamentous carbon formation with low defects. The smaller size of crystal at a higher Ni/Fe molar ratio accounted for CNTs with thinner diameters.





ABSTRACTS

# Waste

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## Poster presentations

## PYROLYSIS-CATALYSIS OF WASTE PLASTICS TO METHANE FOR HIGH VALUE AROMATIC PRODUCTS

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Approximately 25 million tonnes of waste plastics are produced each year in the Europe, representing a major waste management issue. Conversion of the waste plastics to value-added products such as aromatic hydrocarbons represents a novel and alternative option for the processing of waste plastics. In this study the pyrolysis-catalysis of waste plastics has been undertaken to produce a high yield, methane rich syngas using a two stage fixed bed reactor in the presence of novel catalysts. The catalysed used were Y-zeolite, ZSM-5 zeolite and MCM-41 with added metal promoters, including ruthenium, platinum, nickel, iron and cobalt to enhance methane production. In further experiments a third stage catalytic reactor was added to the process to convert the product methane to high purity aromatic compounds. The influence of process parameters including catalyst temperature and plastics:catalyst ratio were also investigated in relation to maximising methane yield. The product gases were analysed using packed column gas chromatography and the used catalyst were characterised by temperature programmed oxidation using thermo-gravimetric analysis (TGA). The results show that manipulation of the process conditions and the use of different metal promoters, particularly ruthenium can markedly increase the yield of methane in the product gases.

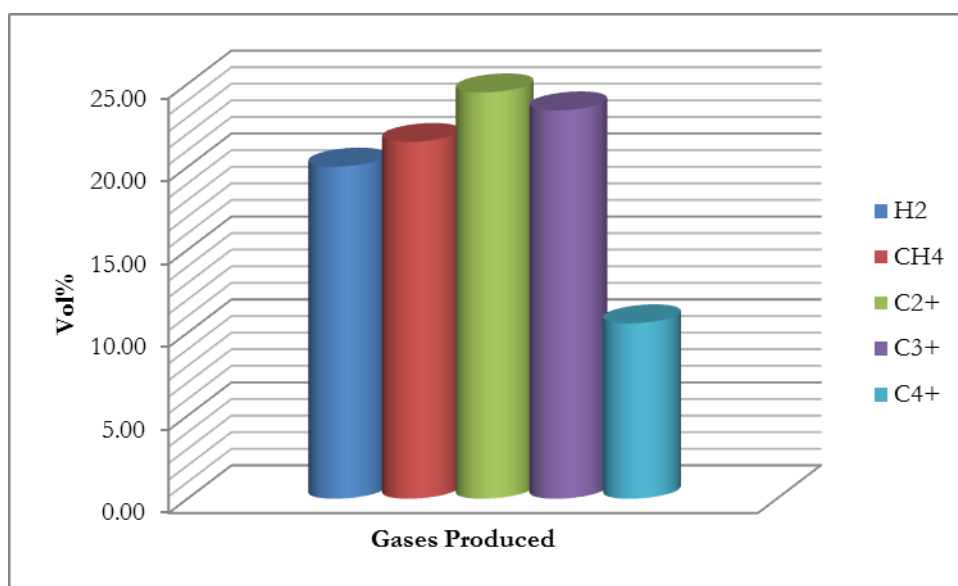


Figure 1 : Illustration of typical gas production from pyrolysis-catalysis of high density polyethylene (HDPE) in a two stage fixed bed reactor.

## Cracking of biomass tar model compounds using tyre pyrolysis char

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### Abstract

The effectiveness of tyre char for decomposing of biomass model tar compounds has been studied in a fixed bed reactor and at a bed temperature of 700 °C. Four model compounds were used including: phenol, furfural, toluene and methyl naphthalene to simulate typical biomass tar compounds produced during biomass gasification. The compounds were fed continuously for 60 min using methanol as a solvent, with a methanol and compound carbon molar ratio of 1. The reactivity of the tar compounds followed the order of furfural > phenol > toluene > methyl naphthalene. High carbon conversion (46-75%) and hydrogen yield (15-28 mmol/g) were obtained in comparison to the non-catalytic experiments. Further experiments were carried out with the use of 2-methylnaphthalene as tar model compound in terms of the effect of temperature, reaction time, the porous texture and the acidity of carbon on tar conversion. The carbon conversion increased from 46% at 700 °C to 51% at 900 °C. The formation of new by-products as a result of cracking of 2-methyl naphthalene over tyre char was determined using GC-FID. Naphthalene is the main formed compound and accounts for 50 % of the total products at a reaction temperature of 900 °C. The influence of porous texture and surface chemistry on tar conversion was compared using two commercial activated carbons with different porous texture with 2-methyl naphthalene. Neither the surface area nor the surface chemistry of the tested carbons had a role in enhancing the tar decomposition. However, activated carbon with microporous texture had a higher activity than the investigated mesoporous carbons. The waste tyre derived pyrolysis char was shown to be effective in reducing tar compounds produced during biomass gasification.



## CHEMICAL CHARACTERIZATION OF ORANGE JUICE WASTES FOR APPLICATION IN PYROLYSIS PROCESS

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The citrus fruits wastes represent an abundant, inexpensive and readily available source of renewable biomass and their utilization as raw material for the production of chemicals and fuels is increasing all over the world [1]. These wastes are composed of seeds, peels and pulp and they are the main by-product of the juices industry, representing about 50 wt. % of the raw processed fruit. In Spain, the average production of citrus wastes per year is near 500,000 t, being more than 60 % derived from orange juice squeezing [2]. The chemical composition of orange juice wastes mainly consists of insoluble carbohydrates such as pectin, cellulose, hemicellulose and lignin, however, other constituents like sugars, fats and proteins are also representative.

An alternative to improve the management of these residues is the implementation of new and environmentally friendly processes such as that of fast pyrolysis, which has been widely employed to convert biomass and organic residues into diverse products (bio-oil, gas and char). This technology is versatile, simple and has a low investment cost, which allow decoupling its deployment on a moderate scale in the regions where the raw material is available, from the further upgrading of bio-oil in large-scale bio-refineries [3].

This study focuses on a prior chemical characterization of the orange juice waste in order to obtain information on the feasibility of its valorization by pyrolysis. The main properties were determined by means of elemental analysis (LECO CHNS-932), bomb calorimeter (Parr 1356) and thermogravimetry (TGA Q500IR). Furthermore, the analysis of the data obtained by TGA enabled the determination of the main chemical constituents of this waste (pectin, hemicellulose, cellulose and lignin). The implemented kinetic model is based on the multi-component mechanism, which describes the volatile formation by means of four concurrent (independent and parallel) reactions corresponding to the decomposition of the four main biomass pseudo-components. A description of the model was reported in a previous work [3], where the authors successfully determined the concentration of each pseudo-component (hemicellulose, cellulose and lignin) of forestry residues from the Portuguese Central Inland Region. In this study, another component was included in the fitting of the experimental data: pectin.

The orange juice waste used in this study contained (on dry basis) 77.5 wt.% of volatiles, 19.9 wt. % of fixed carbon and 2.6 wt. % of ash, similar to typical woody biomasses. The contents of C, H, O were 48.6, 5.9 and 42.9 wt. %, respectively. Nitrogen and sulfur was not detected, indicating a good potential to obtain a low-emission bio-oil. The heating value of the orange juice residue was also relatively high (19.4 MJ kg<sup>-1</sup>).

As observed in the TG-DTG curves, the degradation occurs in a wide range of temperatures (100-700 °C). The kinetic model proposed in this work adequately fits the experimental results, although there are certain deviations at temperatures around 160 °C and in the 500-700 °C range due to the non-consideration of the additional peaks related to extractives, proteins or sugars. The decomposition peaks at the T<sub>max</sub> of 205 °C (30 wt. %), 270 °C (16 wt. %), 350 °C (22 wt%) and 380 °C (30 wt. %) are assigned to pectin, hemicellulose, cellulose and lignin, respectively. These results are consistent with those reported by Boluda-Aguilar et al. [2], who determined the mandarin peel chemical composition by thermogravimetry. Moreover, according to these authors, pectin decomposes between 120 and 300 °C, hemicellulose between 200 and 300 °C and cellulose between 315 and 430 °C, while lignin decomposes in a wide temperature range, 150–700 °C, due to its heterogeneous nature.

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## MODELLING THE COMPOSITION OF THE GAS OBTAINED BY GLYCERIN GASIFICATION

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### 1. Abstract -

As a result of the growing interest on the technologies based on biomass conversion processes, the spectrum of raw materials has widened; and any substrate with high carbon content can be of interest for thermal processing. In this way, nowadays, not only biomass wastes are investigated but also byproducts generated as a result of particular reactions can be regarded as potential materials for energy production.

This is the case of the glycerin obtained in biodiesel production factories. This material, if pure, has many applications in the manufacture of personal care products, leather, paints... However, if it is not pure (as it is the case when glycerine is obtained from transesterification processes) it becomes a waste and a contamination issue for the industries which cannot afford costly purification stages.

These reasons justify the need of looking for uses for this material, and, in this frame, several pieces of research have focussed on its thermochemical processing to obtain heat or a syn-gas. These studies have given evidence about the importance of the proper design of the experimental conditions (temperature, glycerine/water ratio, dwell time) in order to move the chemical equilibria towards the formation of energetic gases such as H<sub>2</sub>, CO or CH<sub>4</sub>. Usually, these works are based in “one variable at a time” approach and do not account for the interactions between variables.

In this work, and with the aim of complementing previous works on this field, a systematic study based in statistic methodology allowed to elucidate interactions between different variables, and their behaviour. The global effects and correlations can be isolated by this technique, and linked to the use of graphical plotting of equations obtained in this process, which extends the results exploitation and its uses, even allowing the forecasting of objective functions (power, or gas content), and letting the optimization of the number of runs carried out in the continuous pilot scale plant, with the subsequent saving of resources during the research or operative phase.

## STRUCTURE AND ACTIVITY OF ZSM-5 AND FLY ASH-DERIVED ZSM-5 CATALYS FOR SELECTIVE FORMATION OF AROMATICS FROM PYROLYTIC VAPORS OF RUBBER WASTES

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A large number of polymeric wastes including plastic, rubber and tyre wastes are produced causing the disposal and environmental problems. The recycling of these wastes is the alternative ways to solve the polymeric waste management. Thermal/catalytic degradation of these wastes which is known as pyrolysis technology seems to be of interest for liquid fuel production. In this work, rubber waste collected from bicycle brake industry was used as feedstock for pyrolysis process. The major element in the rubber wastes was carbon (43.4%) and oxygen (52.6%) with small amount of nitrogen (0.1%). Sulfur was found in low content (0.8%) compared to automobile tyre wastes, 1.6%. In term of proximate analysis, the volatile matter and fixed carbon were 48.5% and 11.9% with high content of ash (39.4%). As a result, the calorific value of this rubber was quite low as 15.2 MJ/kg. HZSM-5 zeolites synthesized from three different methods including conventional hydrothermal method (HZSM5-72h), metal loaded on HZSM-5 support (NiHZSM-5), and fly ash as raw materials (HZSM5-FA-3M) were introduced for examining the catalytic performance on fast pyrolysis of polymeric wastes by using an analytical Py-GC/MS technique. The catalytic fast pyrolysis of rubber waste was performed at 500°C with different rubber to catalyst ratios of 1:1, 1:5, and 1:10. Non-catalytic pyrolysis products consisted of mainly aliphatics and aromatics with small amount of aldehydes, alcohols, esters and nitrogen-containing compounds. After catalytic process, HZSM-5 catalysts remarkably promoted the increase in aromatic fractions, while the non-aromatic fractions tended to decrease significantly. The moderate catalyst content (1:5) showed the optimum catalytic result to improve aromatic selectivity. The levels of aromatic selectivity of HZSM-5 synthesized from three routes were in the order of HZSM5-72h > NiHZSM-5 > HZSM5-FA-3M, respectively. The aromatic formation increased up to 80.8-95.9%, while aliphatics were lessened to 2.8-18.7% with oxygenates and nitrogenates remained only approximately 2%. Overall results, HZSM-5 showed superior catalytic performance for upgrading pyrolytic vapors from rubber wastes in term of enhancing the aromatic production, especially BTX compounds. The improvement of aromatic compounds in pyrolytic vapors leading to high quality of pyrolysis oil derived from rubber waste.

## LEATHER CHARACTERISATION FROM DIFFERENT ANIMAL SPECIES AND TANNING PROCESS BY TGA AND Py-GC/MS

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The animal species is specified in the requirements established by some current legislation relative to the labelling of leather products. Although there is no labelling system regarding leather products in the majority of world countries, in some of them like USA (16 C.F.R., Section 24) and some EU countries, like France (Decree n°2010-29) or Spain, (RD 769/1984) there are national regulations for the labelling of leather goods, clothes, furniture and other products. Nowadays, the identification of the animal origin of leather is commonly carried out by means of visual observation with microscopy, since chemical analyses like MALDI-TOF Mass Spectrometry or DNA analysis imply many difficulties and high cost.

Pyrolysis is an analytical technique commonly used for material identification and discrimination. This study aims to characterise and discriminate the pyrolysis behaviour of leather from different animal species and tanning processes by means of the Thermogravimetric Analysis (TG) and the Pyroprobe pyrolyser connected online to a Gas Chromatograph-Mass Spectrometer (Py-GC/MS). Preliminary data in this field obtained by our research group has been published elsewhere [1].

In this study, five animal species were selected (bovine hide, horsehide, pigskin, sheepskin and goatskin) at different stages of the tanning process (pickled, tanned and crust leather) and with different tanning agents (chromium salts, glutaraldehyde and vegetable tannins). Principal component analysis (PCA) has been used to confirm statistical differences between leather samples.

The thermogravimetric analysis was carried out in a TGA/SDTA 851 Mettler-Toledo thermobalance. The temperature range selected for the study was from room temperature to 800 °C with a nominal heating rate of 10 °C min<sup>-1</sup>. The analysis was carried out in a nitrogen atmosphere with a flow rate of 50 ml min<sup>-1</sup>. The amount of sample analysed was around 7-8 mg, the sample was taken as several cylindrical portions of 2 mm diameter.

For the flash pyrolysis of the samples, a pyroprobe 5250 device was used. The products generated in pyrolysis were analysed using a gas chromatograph (HP-6890N) with a capillary column HP-5MS, provided with a mass spectrometer detector (HP-5973 MSD). The amount of sample pyrolysed in each experiment was approximately 150 µg, placed in a quartz capillary tube. The parameters used in this process were: nominal heating rate, 20 °C ms<sup>-1</sup>; pyrolysis time, 20 s; and process temperature, 500 °C.

According to thermogravimetric data, thermal stability of leather varies clearly with the type of tanning process followed by leather. The specific features of each tanning step are revealed in a similar way in all animal species studied. On the other hand, when the tanning process is fixed, differences between animal species are also highlighted with the thermogravimetric study.

Flash pyrolysis of tanned leather generates a wide distribution of pyrolytic compounds, heterocyclic aromatic compounds being the major group. Some peaks can be defined as representative of each treatment, thus 6-methyl-2,2'-bipyridine-1-oxide is characteristic of pickled samples, 1H-pyrrole of chrome tanned leather, phenol of glutaraldehyde tanned leather, 1,3-benzenediol of vegetable tanned leather and 9-octadecenoic acid of crust leather.

The results obtained from the multivariate analysis performed confirm the viability of the pyrolytic process to discriminate leather samples.

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## PYROLYSIS-CATALYTIC STEAM REFORMING OF POLYSTYRENE IN A TWO-STAGE REACTION SYSTEM

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The growing interest of the polymers recycling is related with their high production and consumption and with the environmental problems associated with their management. Plastics have a remarkable fraction of MSW, about 20 vol.%, representing one of the major fractions of post-consumer waste stream. Thermo-chemical processes can produce valuable products from plastics residue like chemicals, fuels or hydrogen.

Pyrolysis is considered one of the most suitable methods for plastics thermo-chemical recycling at large-scale, given that it is versatile, environmentally friendly and different plastics as well as residual materials can be treated jointly. The conical spouted bed reactor (CSBR) performs very well for plastics flash pyrolysis, since the vigorous cyclic movement of the particles, characteristic of this reactor, minimizes bed agglomeration problems caused by the fused plastics.

This study approaches the continuous steam reforming of polystyrene (PS) pyrolysis volatiles for the production of hydrogen. Pyrolysis has been carried out in a conical spout bed reactor and the volatile stream formed has been reformed in line in a fluidized bed reactor in which a commercial Ni catalyst has been placed. The volatile stream formed in the first step (using steam as fluidized agent) is mainly composed by styrene (70 wt.%).

The experimental conditions have been selected based on the previous studies on the flash pyrolysis of PS in the CSBR [1] and the reforming of HDPE pyrolysis volatiles using the same commercial catalyst [2]. The pyrolysis of PS (first step) has been carried out at 500 °C and the steam reforming (second step) at 700 °C. It has been fed 0.75 g min<sup>-1</sup> of PS and 3 mL min<sup>-1</sup> of water continuously, accordingly the steam/plastic ratio equal to 4. It has been studied two space times 4.1 and 16.7 g<sub>cat</sub> min g<sub>PS</sub><sup>-1</sup>.

With 16.7 g<sub>cat</sub> min g<sub>PS</sub><sup>-1</sup> of space time, pyrolysis-reforming strategy gives way to full conversion of pyrolysis volatiles, with yields being high for H<sub>2</sub> (82.6 %), CO<sub>2</sub> (60.2 %) and CO (39.8 %) and negligible for CH<sub>4</sub>, and C<sub>2</sub>-C<sub>4</sub> and C<sub>5</sub>+ fractions. By decreasing the space time, the yields of H<sub>2</sub>, CO<sub>2</sub> and CO decrease significantly whereas the yield of C<sub>5</sub>+ fraction increases considerably, given that the reforming reaction is disfavored. Regarding to the gas composition obtained using this strategy, the effect of the space time on gas product distribution is less pronounced. The H<sub>2</sub> concentration is around 66 % in both case and a little difference in CO and CO<sub>2</sub> concentration is obtained, i.e., CO concentration is slightly higher with 16.7 g<sub>cat</sub> min g<sub>PS</sub><sup>-1</sup> of space time (20.8 %), just as CO<sub>2</sub> concentration (13.8 %).

The pyrolysis in CSBR and in line reforming of PS in a fluidized bed reactor has been revealed as a feasible alternative for the production of H<sub>2</sub> from plastics.

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## Stepwise citrus waste pyrolysis. Carbon Footprint & LCA.

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### Abstract.

Citrus fruits are one of the most important agricultural products in some areas of the world, including developed countries. The world orange production reported by FAOSTAT (Organization of the United Nations for Food and Agriculture, in its Nations Statistics Division), ranks the top five producers of orange as follows: Brazil as the largest, followed by the United States, Mexico, India and China. [1]

The presence of hemicellulose, cellulose and lignin in biomass generate a product diversity during the pyrolysis process. If each component is submitted to thermochemical conversion it can be expected that the selectivity increases, for example, cellulose pyrolysis could achieve a high level of recovery of levoglucosan [2]. The presence of lignin in the biomass involves an increase at least 50% in the pyrolysis temperature, due to its wide range of decomposition. Despite the above, the intention of generating processes comprehensive utilization of waste in recent decades, we inclined to use the materials as they are generated.

The experiments were performed in a pyrolysis reaction system that consists in a tubular stainless steel reactor mounted over an electric furnace and a condensation train. The carrier gas was nitrogen and the sample was solar-dried orange peel waste from a juicemaker industry. The volatile products were collected in Tedlar bags and analyzed by GCMS. [3]

In step 2, the bio-oil has only one phase, the presence of levoglucosan as one of the main products of the decomposition of cellulose is evident and furfural, products of hemicellulose is recorded, indicating that activated the reaction temperature of step 1 and decomposition continues in Step 2.

Sequential pyrolysis allows a separation of products from the main components of the orange peel and the volatile content obtained in bench scale consistent with the expected laboratory scale with a standard deviation of 3.9.

A proportion of 25% of the lignin is decomposed in step 1 and 2 evidenced by the presence of phenolic compounds in the oil collected meaning that the pyrolysis of lignin comprises a wide temperature range that begins at 180 ° C and can reach up to 800 ° C according to lab scale pyrolysis.

The lignin decomposition proportion is 65% in step 3 in which a variety of aromatic compounds is obtained emphasizing the importance of comprehensive utilization of biomass components using the pyrolysis process.

The study creates the basis for subsequent application involving the gasification process as a comparative framework and study the process is recommended to use the discharge currents of the line as self-supply power.

The stepwise LCA was performed from cradle- to- grave using the SIMAPRO® software.

The carbon footprint in Kg of CO<sub>2</sub>/Kg of biodiesel is 1.13±0.64 for conventional orange peel pyrolysis.

From the results would be advisable to treat different types of biomass for products holocellulosic portion systematic way using the stepwise pyrolysis process according to the proportion and use the remaining fraction of lignin to treat it as one regardless of generation source.

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## INFLUENCE OF CLASSIC AND INNOVATIVE DRYING PROCESSES ON THE MOLECULAR CHARACTERISTICS OF SEWAGE SLUDGE

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Sewage sludges constitute an important by-product of municipal wastewater treatment plants. Their production has grown exponentially during the last decade and was estimated at more than 9 million tons of dry matter in Europe in 2013. Sustainable valorization or disposal options involve direct amendment for crop production or composting. A step of drying is commonly used before, which aims at sanitizing and at reducing the volume of sludge thus lowering the transportation cost. Drying pretreatment processes includes thermal drying, Advanced Oxidation Processes (AOP) or methanation which has the supplementary advantage to produce energy.

The objective of this study was to compare the influence of 3 different processes: thermal drying, electron beam (e-beam) irradiation and anaerobic digestion on the organic matter (OM) characteristics of wastewater sludge (WWS). Indeed the knowledge of the characteristics of this residual biomass is essential to improve their valorization. WWSs OM were investigated at the global scale using elemental analysis, attenuated total reflectance Fourier transform infrared spectroscopy, thermogravimetric analysis and OM fractionation. Double-shot thermochemolysis coupled with gas chromatography and mass spectrometry (GCMS) which has been demonstrated [1] to be an accurate and efficient method for characterizing WWS, was used to compare the diversity and distribution of the molecular contents.

A strong influence of thermal drying on lipid and humic-like substances contents was observed through OM fractionation, which traduced a weakening of the OM. The anaerobic digestion induced an increase in lipids for the hydrolysis phase followed by a decrease which correlates with the volume reduction of sludge by about 30%. E-beam induced a change in the distribution of the different pools of organic matter depending on the irradiation dose.

At the molecular scale, fatty acids, steroids and aromatics were the main thermochemolysis products in all the samples. The thermal drying induced an increase in fatty acids and steroids, probably released from the refractory OM. The anaerobic digestion modified exclusively the amount and distribution of fatty acids while e-beam induced a decrease in all the identified compounds including aromatics. Finally double-shot thermochemolysis-GCMS demonstrated the impact of 3 drying processes on the molecular contents of WWS, which can have consequences on its valorisation.

[1] Improved quantitative analysis of molecular constituents of wastewater sludge pellets using single- and double-shot thermochemolysis – GCMS. M. Collard, B. Teychené, L. Lemée\*. *Journal of Analytical and Applied Pyrolysis* (2015) 114,265-272.

## KINETIC STUDY AND THERMAL DECOMPOSITION BEHAVIOR OF VISCOELASTIC MEMORY FOAM

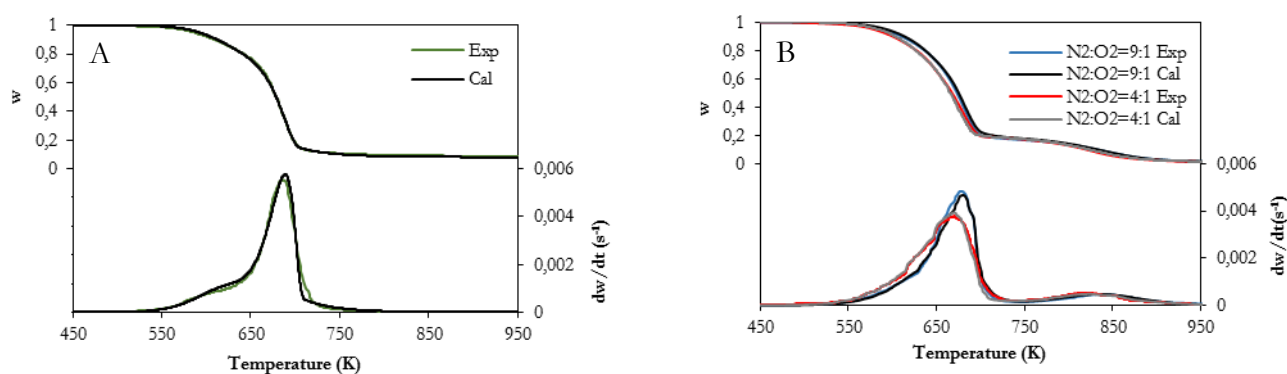
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Viscoelastic memory foams (VMF) are a variety of flexible polyurethane foams (FPUF) which show both viscous and elastic behaviour at same time [1]. These special foams were first developed in 1966 to absorb shock and improve protection and comfort in NASA's airplane seats [2]. The slow recovery after compression and the ability to distribute the body weight make that VMF are employed to manufacture high quality mattresses and pillows. Mattresses are not desirable material for landfilling due to their low density and the recycling presents economics deficiencies. These facts join with the increase in the demand for energy due to the economic growth make pyrolysis and combustion processes optimal routes for upgrading from waste [3], allowing the obtainment of combustible, gases and/or energy [4]. To develop these techniques, it is necessary to know the thermal decomposition and reaction kinetics during the combustion and pyrolysis of these wastes [5].

The thermogravimetric study was performed in Perkin Elmer thermobalance employing three different atmospheres: pyrolysis (N<sub>2</sub>), combustion (N<sub>2</sub>:O<sub>2</sub>=4:1) and oxidative pyrolysis (N<sub>2</sub>:O<sub>2</sub>=9:1) with a flow rate of 100 mL/min and using sample amounts close to 7.5 mg. Dynamic and isothermal runs were carried out at three different heating rates (5, 10 and 20 K/min). A kinetic model with two consecutive reactions has been chosen to describe the decomposition of the samples under pyrolytic atmosphere, obtaining the pre-exponential factor ( $k_0$ ), the activation energy ( $E$ ), the reaction order ( $n$ ) and maximum production of volatiles at infinite time for both reactions ( $v_\infty$ ). On the other hand, the twelve runs performed under the two oxidative atmosphere (N<sub>2</sub>:O<sub>2</sub>=4:1 and N<sub>2</sub>:O<sub>2</sub>=9:1) have been correlated with a four consecutive reactions model optimizing the same parameters mentioned previously plus the reaction order for oxygen (b). **Figure 1** shows the experimental and calculated TG and DTG curves for the dynamic run at 20 K/min in pyrolysis, combustion and oxidative pyrolysis.



**Figure 1.** TG and DTG experimental and calculated curves for the run performed at 20 K/min in: A. Pyrolysis and B. Oxidative atmospheres

Apart from the thermogravimetric study, the evolved products during the pyrolysis and combustion of VMF have been analysed by TG-MS and TG-FTIR.

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## DECOMPOSITION OF MATERIALS COMBINING BIOMASS AND WASTE FROM ELECTRICAL AND ELECTRONIC EQUIPMENT (WEEE)

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The disposal of waste from electrical and electronic equipment (WEEE) is an actual problem of industrialized countries. According to the report of the United Nations University (UNU), 41.8 million tonnes of waste electrical and electronic equipment were generated worldwide in 2014. It should be pointed out that these wastes are composed of many products considered potentially dangerous. The WEEE contain, between other contaminants, heavy metals such as cadmium, lead and nickel, besides mercury and brominated plastics. Therefore, these wastes are considered a serious threat to the human health and the environment.

In the present work, thermal decomposition of different materials (sawdust, electrical wires and printed circuit boards) has been studied under dynamic conditions in different atmospheres such as nitrogen and mixtures of nitrogen and oxygen (4:1 and 9:1) on a Thermal Gravimetric Analyzer. Nine dynamic experiments were carried out by combining three different atmospheres and three heating rates (5, 10 and 20°C min<sup>-1</sup>) from the room temperature up to 950°C for each material studied with a total flow rate of 100 mL min<sup>-1</sup>.

Kinetic models have been proposed for the pyrolysis, gasification and combustion of sawdust, electrical wires (EWs) and printed circuit boards (PCBs). In the case of sawdust, a model considering three independent first-order reactions gave very good correlations all the heating rates tested both in inert and oxidant atmosphere. The decomposition of synthetic materials (EW and PCB) was modelled by using n-th order kinetics. The kinetic fitting obtained is very satisfactory to describe the behavior of the pyrolysis and combustion runs for each material.

On the other hand, mixtures of these three materials have been prepared and tested for decomposition behaviour. A weighted sum of the curves simulated using kinetics of the materials separately gives a good concordance with the experimental curve in the case of PCBs, indicating that there is not chemical interaction between sawdust and PCBs when heated and decomposed. This would indicate that the production of pollutants in the decomposition will not be affected by the presence of the other material. Nevertheless, a strong interaction is found with the mixtures between biomass and EW in oxidant atmospheres. Fig. 2. shows the experimental and calculated TG curves at 10°C/min in combustion for all the mixtures.

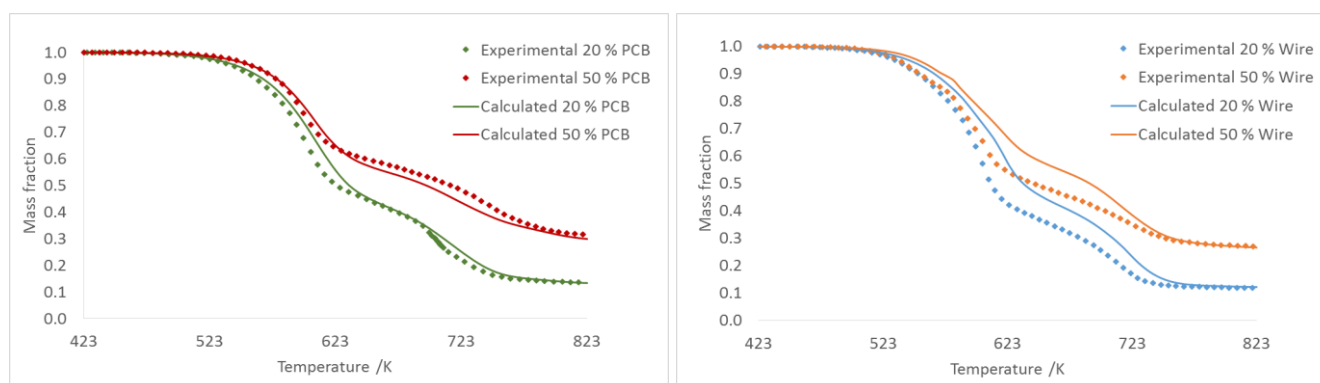


Fig. 2. Decomposition of the mixtures prepared at 10°C/min in the presence of 20 % oxygen: A. mixtures of PCB and B. mixtures of EW.

### Acknowledgements

Support for this work was provided by the CTQ2013-41006-R project from the Ministry of Economy and Competitiveness (Spain) and the PROMETEOII/2014/007 project from the Valencian Community Government (Spain).

## REVEALING THE STRUCTURE AND MECHANISMS INVOLVED IN THE PRODUCTION OF SEWAGE SLUDGE CHAR

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The increasing amount of sewage sludge (SS) demands sustainable recycling alternatives. The use of pyrochars for increasing carbon sequestration potential of soils and thus reducing the emission of greenhouse gases with a concomitant improvement of soil fertility is gradually being more recognized [1]. In addition, carbonization offers a sustainable approach for managing urban wastes and to produce added value products. Char properties is highly dependent upon feedstock and the carbonization process and therefore if the mechanisms involved in the transformation of biomass into pyrochars are known it will be possible to infer the process to functionalize the product according to the intended final use. De la Rosa et al. [2] demonstrated that a significant part of the organic nitrogen contained in pyrogenic organic matter (OM) from plant residues was bioavailable. A comparable behaviour for chars produced from other N-rich sources like SS is expected. This fact opens the possibility to use chars derived from SS as slow-release N-fertilizers in agricultural systems. The major aims of this work are: i) achieving a better understanding of the biochemistry involved in the formation of chars from SS and ii) evaluating the potential of N-rich SS chars as slow-release N-fertilizers.

We produced <sup>13</sup>C and <sup>15</sup>N-enriched biochar and hydrochar from labelled SS by applying dry pyrolysis (600 °C; 20 min) and hydrothermal carbonization respectively (200 °C, 30 min; p=10 psi) (samples called <sup>13</sup>C-<sup>15</sup>N-L-SS Py600 and <sup>13</sup>C-<sup>15</sup>N-L-SS-HTC200). After charring the SS, total C and N content decreased by c. 15% and 25 % respectively (TC and TN of SS were 29.3% and 4.3% respectively). The isotopic signature of light elements ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ) was determined to diagnose turnovers and dynamics of biomass transformation occurred during the pyrolysis process.

Furthermore, analytical pyrolysis (Py-GC/MS) was applied to <sup>13</sup>C & <sup>15</sup>N-labelled and unlabelled pyrochars (samples SS-Py600 and SS-HTC-200). This tool was useful to trail OM transformations that occurred during the pyrolysis process (dry and hydrothermal) at a molecular level. The pyrograms obtained for SS-HTC-200 were found similar to these for the original feedstock (SS). They consisted of aromatics including N-containing heterocycles, furans, fatty acids and esteranes (mainly cholestanes). Dry pyrolysis at 600°C removed the cholestanes and increased the presence of polycyclic aromatic hydrocarbons. These results were further confirmed by solid state Nuclear Magnetic Resonance Spectroscopy (<sup>13</sup>C CP/MAS NMR). Finally, direct pyrolysis  $\delta^{13}\text{C}$  compound specific isotopic analysis (Py-CSIA) was used to understand the dynamics of organic compounds during carbonization process and to discern the origin of the newly formed structures. This study is still in progress and we are confident that the use of this combination of techniques will be capable to discern the degradation pathways over time as well as the portioning and fate of C & N when SS chars are used as soil amendment.

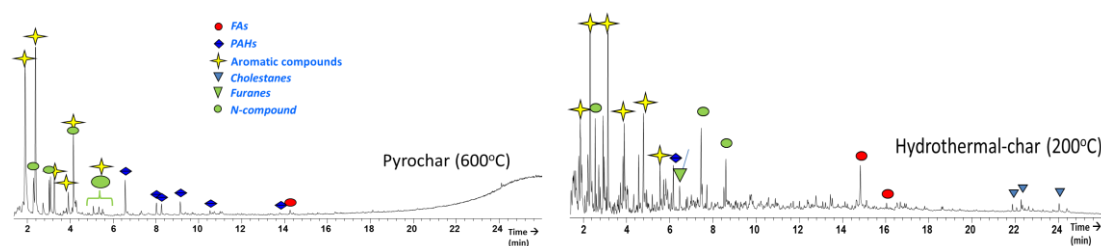


Figure 1. Analytical pyrolysis of SS-Pyrochar (600°C) and SS-HTC (200°C)

Acknowledgments: JMR acknowledges Marie Curie Fellowship within the 7<sup>th</sup> European Community Framework Programme (PCIG12-GA-2012-333784-Biocharisma project). The Spanish Ministry of Economy and Competitiveness and FEDER funds are thanked for financial support (projects CGL2012-37041 & CGL2012-38655-C04-01). MP and NJ acknowledge the funding of the FPU (FPU 13/05831) and FPI (BES-2013-062573) fellowships respectively.

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## Transformation behaviour of As during thermal treatment of *P. Vittata*, a As hyperaccumulator

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### Abstract

As contamination is a growing problem in China, affecting large area of farmland and causing human health concerns. *P. vittata* is a well-known hyperaccumulator that has demonstrated successful properties of arsenic phytoremediation in a number of large and small-scale field applications. Phytoremediation using *P. vittata* offers a promising and low-cost solution for arsenic contaminated site remediation, provided the residual arsenic laden biomass is properly disposed of. Thermal treatment is an efficient way to achieve biomass volume reduction, energy production and As recovery simultaneously.

In this study, the behaviour of contamination within *P. vittata* biomass was investigated by analysing the As content in the bottom ash, fly ash and flue gas following pyrolysis and combustion. The experiment was conducted in a N<sub>2</sub> and air atmosphere representing typical pyrolysis and combustion conditions, respectively. Four different temperatures (400, 500, 600 and 700 °C) were tested for both conditions, during the operation of the reactor.

Bottom ash, fly ash and flue gas were then collected and analysed by ICP-MS and XRF to characterize the As content and speciation. It was found that the volatilization of As was closely correlated with the reaction temperature and atmosphere. Results show that nearly 40%-70% of As retained in the bottom ash during pyrolysis and combustion, 30%-60% of As existed in the fly ash, as shown in Fig.1. Only a limited amount (about 0.5%) transferred into gas. The high retention of arsenic in the bottom ash is attributed to the source of alkaline metals such as Ca found in the biomass material. XRF is used to confirm these results. Figure 2 shows the soluble As content in the bottom ash and that this gradually decreased with increasing temperature during both the combustion and pyrolysis tests. The soluble As mainly presents as As<sup>5+</sup> in the bottom ash. As<sup>3+</sup> was not found in the bottom ash, now was it present in the combustion atmosphere. Whereas a small amount of As<sup>3+</sup> was found in the bottom ash during pyrolysis. This increased with temperature, largely due to the reduction of As<sup>5+</sup> to As<sup>3+</sup> during pyrolysis.

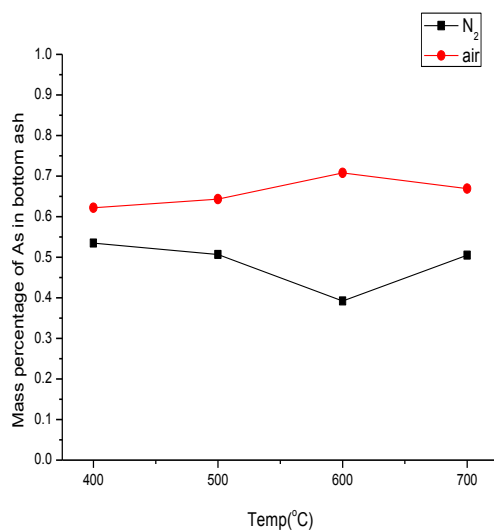


Fig.1 As retained in the bottom ash during pyrolysis and combustion

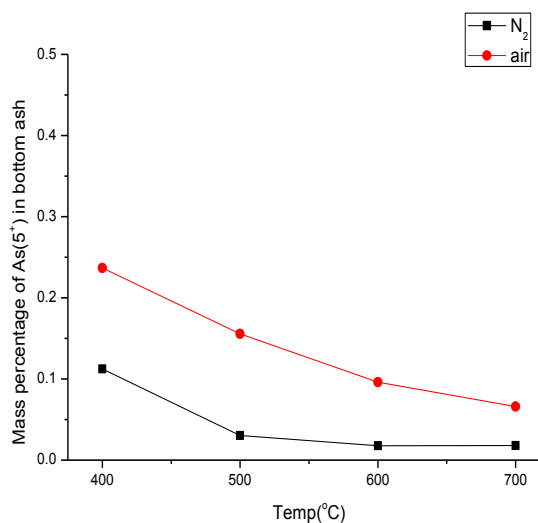


Fig.2 Soluble As<sup>5+</sup> in the bottom ash

## Thermal treatment of wood waste for particleboard production

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The production of wood particleboard from wood furniture waste could help to reach two objectives: Meet the new requirements (evolution of french regulation) concerning wood furniture waste enhancement and limit economic tensions in the wood industrial sector by providing a new resource able to partly replace wood raw material. To improve quality of particleboard produced from waste, a thermal pre-treatment is studied in this work which aims to remove inefficient urea-formaldehyde resin residues (used as glue) in waste (characterized by the nitrogen content) [1 - 2] and to decrease waste hygroscopicity and therefore improve dimension stability and natural durability of produced particleboard [3].

The thermal treatment tests have been performed at different temperatures (275 to 350°C) and for different duration (5 to 30 minutes) on three kinds of waste (particleboard, medium density fibreboard, laminated flooring) under pyrolysis conditions under nitrogen. Produced gases have been characterised and partly quantified through FTIR gas analysis. The mass of gas added to weighed solid and liquid fractions after pyrolysis tests allows matter balance estimation.

Treated and untreated samples have been characterised according to:

- Nitrogen content measured by Kjeldhal method. Some elemental analyses have also been performed to confirm accuracy of Kjeldhal method;
- Hygroscopicity evaluated by contact angle measurement between a water drop and the surface of a tablet produce from samples in a manual hydraulic press.

Thermal treatment performances have been evaluated according to different criteria (quantity of nitrogen removed in pyrolysis gases under ammonia (NH<sub>3</sub>) and isocyanic acid (HNCO) forms; quantity of nitrogen removed during thermal treatment calculated from nitrogen content in treated and untreated material taking into account the mass loss during test; level of degradation of sample during treatment; hygroscopicity of treated materiel) and optimal conditions for thermal treatment have therefore been determined.

It has been shown that, in the range of studied temperature (275 to 350°C), the optimum times of treatment vary from 15 to 5 minutes and that nitrogen removing efficiency is between 50 to 60 %, hygroscopicity of treated materials being lowered during treatment. Regarding results the lower temperature of treatment appears to be the best compromise between nitrogen removing and hygroscopicity lowering.

In addition, particleboard have been produced from different mixtures of laminated flooring treated at 275°C during 11 minutes and of fresh wood (100/0 % ; 50/50 % ; 30/70 % ; 0/100 %) and characterized according to mechanical properties (resistance to perpendicular traction in N/mm<sup>2</sup>) and dimensional stability. Results show that production of particleboard from pure treated waste is not possible. For other mixtures, the increase of treated material content conducts to an improvement of the dimensional stability and a decrease of the mechanical properties which remains above specciation for most of particleboard utilisations.

References added at the end of the abstract, after the figures (Garamond10 pt, justified, Line spacing: 1.0)

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# EFFECT OF CARBON NANOTUBES ON THERMAL AND CATALYTIC PYROLYSIS OF POLYOLEFINS

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The growing market of polymeric nanocomposites (PNCs) has raised a great interest thanks to the improvements in thermal, mechanical, electrical, and barrier properties, among others, that nanoparticles confer to the polymeric matrix at low loadings [1]. Within PNCs, those based on polyolefins are of great importance covering more than 50% of the world demand of plastics, being polyethylene and polypropylene the main exponents [2]. Among nanoparticles with the highest demand, carbon nanotubes (CNTs) are considered as an unique reinforcement for polymers. In particular, many studies have been carried out expanding the applications of PP and PE by adding CNT to improve the Young's modulus, tensile strength, gas permeability, flame retardancy, and electrical conductivity [3]. The thermal behavior is also important considering the great consumption of plastic polymers, more than 300 million annual tons, demanding novel strategies for feedstock recycling such as the pyrolysis. This kind of chemical recycling has become one of the most attractive method for waste polymer treatment allowing the attenuation of their environmental impact besides the recovery and valorization of its degradation products [4]. In this sense, the goal of this work is to analyze the effect of carbon nanotubes (CNTs) on the thermal and catalytic (employing H-Mordenite with Polymer/Catalyst = 70/30 wt%) pyrolysis of either high density polyethylene (PE) or polypropylene (PP) matrices by using both kinetic thermogravimetric analyses (TGA) under non-isothermal (at 5, 10, 15, 20 K/min) conditions and a fixed-bed reactor under isothermal conditions (450°C-40') [5].

Under non-isothermal conditions, for the case of thermal pyrolysis, CNTs increased the beginning of thermodegradation (BOT) for both matrices with differences as high as 30 °C and 22 °C as compared with neat PP and PE, respectively. This enhanced thermal stability in PP based composites was associated with an increase in the apparent activation energy whereas in PE based composites lower pre-exponential factors associated with reduced conformational entropy, are responsible for the enhanced thermal stability [5]. For the case of catalytic pyrolysis, the BOT increases ~ 20-30 °C for polymer-CNT composites as compared with neat matrices. The thermodecomposition processes were studied by assuming geometrical contraction and nucleation models. The invariant pre-exponential factor and apparent activation energy obtained were in good agreement with those obtained by isoconversional analyses allowing the prediction of the thermogravimetric behavior.

Results from isothermal (non-catalytic) pyrolysis confirmed the thermal stability by the presence of CNTs as higher condensable (C<sub>9</sub>-C<sub>40</sub>) and lower gas (C<sub>1</sub>-C<sub>4</sub>) yields in PP-CNTs composites, and a higher amount of unreacted polymer and a lower both condensable and gas yields for PE-CNTs, as compared with the pure matrix, were found. For isothermal (catalytic) pyrolysis, the yield of C<sub>1</sub>-C<sub>4</sub> and C<sub>1</sub>-C<sub>10</sub> compounds increases for PP-CNTs and PE-CNTs, confirming that these distributions depend on the polymer matrix.

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## Characterization of pyrolysis reaction of waste paper laminated phenolic printed circuit board

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Due to the increased demand generation for the electronics industry, the amount of waste printed circuit boards (PCBs) is also being increased with the growth of their production amounts. Although metallic components in PCBs can be recovered by physical separation, proper treatment for high amounts of non-metallic components in PCBs, occupying about 70% of total weight of PCB, is still remains as an issue for the recycling of PCBs. Among various kinds of treatment techniques, pyrolysis has a high potential for PCB treatment because pyrolysis can produce gas, liquid, and solid products which can be used as the fuel or chemical feedstocks. PCBs are divided into two categories, epoxy-PCB and phenolic-PCB. Although many researchers studied epoxy-PCB containing tetrabromo bisphenol-A (TBBA) as the flame retardant of PCB, there are few reports for the pyrolysis of a few studies have been conducted the pyrolysis reaction of the phenolic-PCB.

In this study, non-isothermal pyrolysis of paper laminated phenolic printed circuit board (PLP-PCB) was performed using thermogravimetric analyzer (TGA) and pyrolyzer-gas chromatography/mass spectrometry (Py-GC/MS). Combined interpretation of kinetic and multi-shot GC/MS analysis results revealed that the pyrolysis of PLP-PCB is consisted with four independent decomposition reactions of phosphate flame retardants, laminated paper, TBBA, and phenolic resin followed by char stabilization reaction. The large amounts of chemicals such as phosphate flame retardants, phenols, and cresols were also produced by the pyrolysis of PLP-PCB.

## AIR GASIFICATION STUDY IN FLUIDIZED BED REACTOR: COMPARISON OF WOOD AND WASTE FROM CITY OF ABOMEY-CALAVI

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### Abstract

One of the principle development issues for West African countries such as Benin is the development of the waste disposal sector. Previous studies considering waste coming from the city of Abomey-Calavi [1] show that the waste contains more than 50% of fermentable compounds making composting a promising solution. Nevertheless, regarding the market, this solution could not alone ensure the enhancement of the total resource. That is why thermochemical processes of waste enhancement should be studied and compared to provide solutions other than composting. This would respond to another important issue for the country's development; energy production.

This study aims to supply experimental data concerning waste gasification in fluidized bed compared to the study of wood in terms of matter balance, gas composition and flows, condensable composition and energy efficiency.

Gasification tests of the present study were performed on a fluidized bed with air as gasification agent at LERMAB (Laboratory for Study and Research on Wood Material). The tests were conducted at a set temperature equal to 800 °C in order to make comparisons with the previous studies on the subject [2-9], including the gasification of wood.

The tested fuels were pine wood pellets, and pellets made from a combustible mixture representative of household waste from the city of Abomey-Calavi in Benin. This fuel mixture is composed of 88% wood, 7% cardboard, and 5% plastic. The treated waste plastic is polyethylene because it is the most prominent plastic waste in Benin.

Various analytical devices were used to perform the characterization of the initial materials and solid, gaseous, and liquid products resulting from the reaction. Knowing that steady state cannot be reached during experiments, a simplified model has also been developed to predict energy efficiency in steady state for comparison with other thermochemical ways such as pyrolysis and combustion.

The model describes the evolution of the solid mass in the bed, the gas flow and composition in terms of permanent gas, tar and water contents, the energy released by the reaction and energy efficiency of installation in transient and steady state. The hypothesis and reactions are:

- The first stage of the reaction is drying and pyrolysis. This leads to the production of char, gas (CO, CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub> and C<sub>x</sub>H<sub>y</sub>) water and tars. From an energy perspective, Pyrolysis is considered athermal.
- The char produced during pyrolysis is then partially oxidized by oxygen (from air). This second reaction produced water vapor and CO<sub>2</sub>. From an energy standpoint, the reaction is considered exothermic.
- The residual char is reduced by steam gasification with water vapor. This reaction leads to the production of CO and H<sub>2</sub>. From an energy point of view, this reaction is considered endothermic.

Model predictions are thus compared to experimental data obtained after an experiment of two hours.

**Keywords:** Air Gasification, Fluidized Bed, Cellulosic Materials, Plastic

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# CO-PYROLYSIS BEHAVIORS OF BEECH WOOD AND POLYETHYLENE MIXTURES

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## Introduction

Pyrolysis behavior of woody biomass has been widely studied to reveal reaction mechanism and to improve products yield. For these purposes, the interactions of cellulose, hemicellulose, and lignin during pyrolysis have been studied in detail [1]. In similar, elucidation of the co-pyrolysis behavior of woods and plastics is an important to treat their composite wastes. There are several works reporting the interactions between woody biomass and plastics [2-4]. However, the mechanism of interactions is still not clear. Therefore, further investigation is necessary for achieving the above purposes. In this research, interaction between beech wood (BW) and polyethylene (PE) was investigated at ramp heating using a tube reactor.

## Experimental

Commercial BW was dried, extracted, and demineralized to prepare moisture-, extractives-, and ash- free BW. The pre-treated BW and purchased PE were crushed into powder with a particle size under 250  $\mu\text{m}$ . These were mixed to get certain weight ratio of samples (BW:PE = 100:0, 60:40, 40:60, and 0:100), which were pyrolyzed at ramp heating from ambient temperature to 650  $^{\circ}\text{C}$  with a heating rate of 10  $^{\circ}\text{C min}^{-1}$ . All pyrolysis experiments were carried out under 100  $\text{mL min}^{-1}$  helium flow using a horizontal tube reactor. The products were defined as (1) gas collected in gasbag; (2) tar that were tetrahydrofuran (THF)-soluble, derived from BW; (3) oil that were THF-soluble, derived from PE; (4) wax that were THF-insoluble, derived from PE; and (5) char remained in the sample holder.

## Results and discussion

The yields of gas, tar, oil, and some products are summarized in Figure 1. The lines written in the figures are connected with the yields obtained from 100% BW and 100% PE fraction. Therefore, on the lines mean calculation yields of each product. The gas compounds were mainly CO, CO<sub>2</sub>, and CH<sub>4</sub> derived from BW and C<sub>2</sub>-C<sub>4</sub> hydrocarbons derived from PE. The main compound in tar was levoglucosan (LG). In addition, LG decomposition products such as glycol aldehyde (GA), 5-hydroxymethylfurfural (5-HMF), and lignin decomposition products such as guaiacols and phenols were observed. Oil contained aliphatic hydrocarbons produced from PE.

Experimental gas yields from mixed samples are lower than those of calculation yields, while experimental yields of tar and oil are higher than those of calculation yields. Experimental yield of LG is higher than that of calculation yield when mixed samples are pyrolyzed. On the other hand, experimental yields of LG decomposition products such as CO<sub>2</sub>, CO, CH<sub>4</sub>, GA, and 5-HMF are lower than calculation yields of those. These results imply that fragmentation of LG is inhibited in the presence of PE, suggesting that hydrogen radicals from PE stabilize LG radicals at gas phase. Experimental yields of oil and tar produced from lignin are higher than calculation yield of those. Therefore, it suggests that radicals from BW and PE enhance homolysis of PE and lignin each other. Thus, this work implies that the presence of homolytic interactions in the products of BW and PE during co-pyrolysis of BW and PE.

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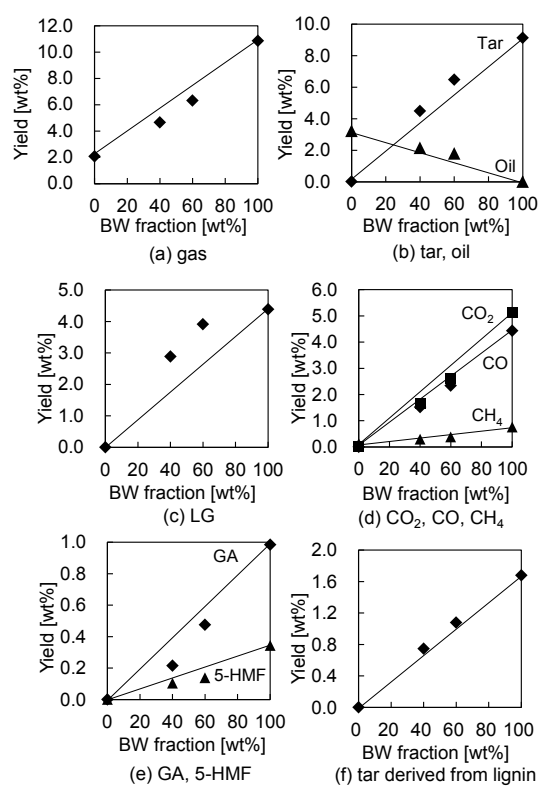


Figure 1 Yields of (a) gas, (b) tar and oil, (c) levoglucosan (LG), (d) CO<sub>2</sub>, CO, and CH<sub>4</sub>, (e) glycolaldehyde (GA), 5-hydroxymethylfurfural (5-HMF), and (f) tar derived from lignin.



# PRODUCING HYDROGEN AND HIGH VALUE CARBON NANOTUBES FROM PLASTICS WASTE USING Ni- AND Fe-BASED CATALYSTS

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For several decades, plastic materials have been key enablers for innovation and have contributed significantly to the development of society. However, large amounts of waste plastics have been produced due to the increasing consumption of plastic materials. Around 38 wt. % of waste plastics ended up as landfill in 2012 in the EU, causing large environmental problems and wasting the energy stored inside the waste plastics. In this work, we focus on converting plastic waste into clean hydrogen-rich synthesis gas and high value carbon nanotubes (CNTs). Catalyst development is one of the key factors for this process to improve hydrogen production and the quality of CNTs. Ni/SiO<sub>2</sub> and Fe/SiO<sub>2</sub> catalysts with controlled metal particle sizes will be reported in this work in relation to their performance for the co-production of hydrogen and CNTs from the catalytic gasification of waste polypropylene, using a two-stage fixed-bed reaction system. The influences of the types of metal and the size of the metal crystals on product yields and the quality of CNTs in terms of purity and homogeneity are also reported. The products are characterised by a range of techniques, including, gas chromatography (GC), temperature program oxidation (TPO), X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) etc. The results showed that, both carbon nanotubes and hydrogen gas were successfully produced in high yield using the Ni/SiO<sub>2</sub> and Fe/SiO<sub>2</sub> catalysts. The Fe-based catalyst produced a higher yield of carbons (up to 30 wt.% of the plastic sample) compared with the Ni-based catalysts. In addition, from the TPO and SEM analysis, catalysts with large crystal size produced higher yields of carbons. However, the CNTs produced with the Fe/SiO<sub>2</sub> catalyst with large metal particles showed a better uniformity (Figure 1), compared with the Ni/SiO<sub>2</sub> catalyst and the Fe/SiO<sub>2</sub> catalyst with small metal particles.

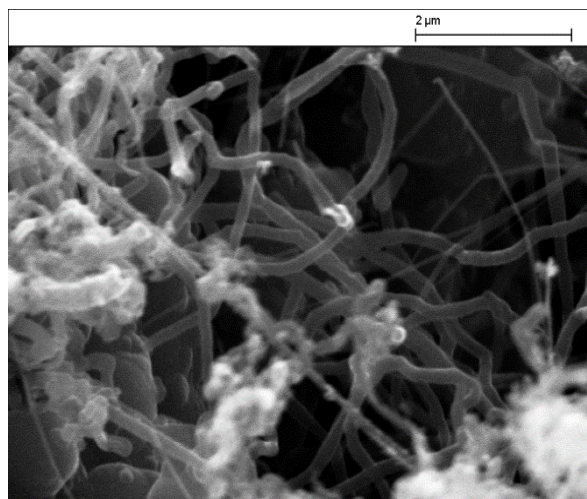


Figure 1 SEM result of the carbons formed on the surface of the reacted Fe/SiO<sub>2</sub> catalyst

## HYDROTHERMAL LIQUEFACTION OF ANIMAL BY-PRODUCTS: DIFFERENT EXTRACTION PROCESSES

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Slaughterhouses produce high quantities of animal by-products (ABP). Nowadays, the most common management of their wastes is the rendering process [1]. Hydrothermal liquefaction (HTL) can be proposed as a new alternative for the treatment of these residues. It is a high-pressure reaction under the presence of liquid water that maximizes the generation of liquid products vs. gas phase.

In this paper, different extraction processes to separate the fractions obtained in the HTL runs of ABP samples have been studied.

Batch HTL experiments have been carried out at two different process temperatures: 150 and 250°C, keeping constant the other conditions in all the runs: 80% water content, 5 min residence time at the maximum temperature and about 80g of sample (ABP and water). Solid, liquid and gas fractions were collected at room temperature.

For the separation of solid and aqueous and organic (biocrude) liquid fractions three methods were analyzed: centrifugation, use of dichloromethane (most frequently used solvent) and use of hexane as extraction solvents. When solvents are used, solid and liquid fractions are filtered and washed with the solvent. The liquid obtained is kept in a decanting funnel to separate both aqueous and organic phases.

In order to characterize the products, the following analyses were carried out: TGA to solid and liquid fractions, GC/MS to liquid products and GC/FID and GC/TCD to gas products.

The gas fraction generated in all the experiments was negligible comparing to the other phases and it was mainly composed of CO<sub>2</sub>.

The compounds detected in the liquid fraction were grouped according to their functional groups and five groups were established: heterocyclic organic compounds (HOC), nitrogenous compounds (NC), acids and esters (OAE), ketones, alcohols and phenol derivatives (OC) and aromatics (AR).

By analyzing the different extraction processes, it has to be indicated that the centrifugation led to a significant amount of interface, between aqueous and organic phases, difficult to be manageable. About the solvent extraction, it was found that hexane was a better extraction solvent of OAE group from the aqueous phase than dichloromethane, increasing the percentage of this group in the organic phase. Similarly, dichloromethane gave better results in the extraction of HOCs while higher yields of this group remained in the aqueous phase with the hexane extraction. Figure 1 shows, as an example, the composition (mass fraction) of the biocrude obtained at 250°C.

According to these results, a unique extraction solvent cannot be considered as optimum in this type of processes and it must be selected as a function of the composition of the liquid fraction obtained. In the experiments performed, two extreme process temperatures were selected. At 250°C, the highest yield of biocrude was obtained when dichloromethane was used. However, at 150°C, the liquid fraction was mainly formed by fatty acids and, in this case, the extraction with dichloromethane leads to poor results, hexane being a better choice.

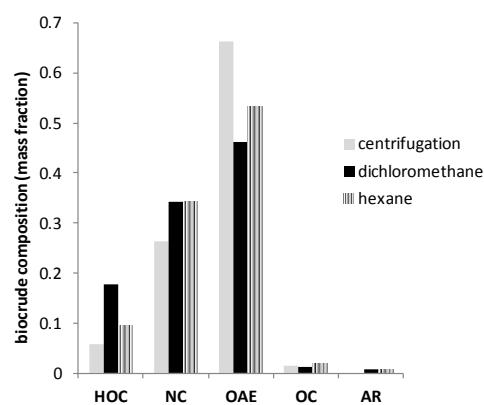


Figure 1

[1] M. Ortner, D. Wöss, A. Schumergruber., T. Pröll, W. Fuchs, Energy self-supply of large abattoir by sustainable waste utilization based on anaerobic mono-digestion. *Applied Energy* 143, pp. 460–471, 2015.

**Acknowledgements.** The research leading to these results has received funding from the European Community's 7th Framework Programme (FP7-2007-2013) under Grant Agreement No. 603986.

## EFFECT OF THE PROCESS TEMPERATURE ON THE PRODUCTS GENERATED BY HYDROTHERMAL LIQUEFACTION OF ANIMAL BY-PRODUCTS

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Animal by-products (ABP) are wastes from different origins (slaughterhouses, butcher's shops, restaurants or houses). Over 20 million tons are being generated annually in the European Union (EU) [1] that can be dangerous if they are not properly disposed of. The hydrothermal liquefaction (HTL) is presented as an alternative method for thermochemical conversion of wastes of animal origin, producing a liquid energy carrier (biocrude). The aim of this research is to evaluate the influence of temperature on the yield and composition of biocrude product.

The experiments were carried out with a real raw waste from porcine and bovine origin in a proportion 60/40 respectively. The experimental system used for carrying out the HTL batch runs was an electrically heated reactor made of stainless steel. Approximately 80 g of sample, with a humidity percentage of 80%, were placed in the reactor. After being purging, the reactor was pressurized with nitrogen at 28 bar. Then, outlet valves were closed, the reactor was heated up to set temperature and maintained for the residence time (5 min). The values of temperature analysed were 150, 175, 200, 225, 250 and 290°C. Afterwards, the reactor was cooled down and pressure decreased simultaneously. Solids, liquids and gas fraction were collected at room temperature. The solids were separated by vacuum filtration. Meanwhile, organic solvents were utilised to recover the biocrude from the liquid fraction. The gas composition was analysed by GC/FID and GC/TCD. Organic and aqueous fractions were analysed by GC/MS. Liquid fractions were also analyzed by TGA. The high heating value of biocrude was determined in a bomb calorimeter.

The results indicated that the yield of biocrude increases by increasing temperature from around 45% at 150°C and 65% at 175°C up to 70-80% at temperatures higher than 200°C. The complexity of the compound spectrum also increased with temperature. At 150°C only fatty acids were detected while the number of organic compounds in the spectrum increased at higher temperatures and acids, esters, heterocyclic organic compounds, nitrogenous compounds, ketones, alcohols and phenol derivatives were identified.

Differences in the composition of biocrude with temperature were also distinguished in the TG/DTG analysis of the samples since the DTG peaks detected show a clear evolution with temperature. Thus, as can be observed in Figure 1, the DTG peak located at around 280°C is increasing with temperature, being the main peak in the sample generated at 290°C. On the other hand, the DTG peak centred at around 400°C decreases with temperature, being almost negligible at the highest temperature value.

The high heating value of biocrude obtained in the experiments shows a clear trend to diminish with temperature, although the range of values obtained is narrow. Thus, the highest value was 39 kJ/g for the biocrude obtained at 150°C while the lowest value was 35 kJ/g for that at the highest temperature.

The yield of gases obtained in all the runs was very low (0.02 – 1.14%), obviously increasing with temperature. In all the experiments, CO<sub>2</sub> was the main compound in the gas fraction.

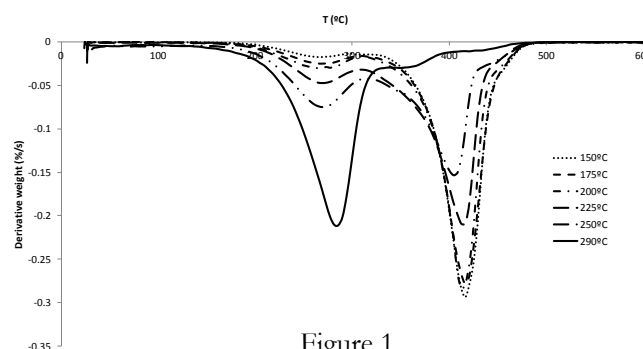


Figure 1

[1] European Commission website ([http://ec.europa.eu/food/food/biosafety/animalbyproducts/index\\_en.htm](http://ec.europa.eu/food/food/biosafety/animalbyproducts/index_en.htm)).

**Acknowledgements.** The research leading to these results has received funding from the European Community's 7th Framework Programme (FP7-2007-2013) under Grant Agreement No. 603986.

## NUMERICAL MODELLING OF THE PYROLYTIC DEGRADATION OF PLASTIC COMPOUNDS

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Pyrolysis is the most promising thermo-chemical process for thermal valorization of organic waste in order to protect the environment and to ensure the continuous supply of energy. Wastes that we will be interested in particular are synthetic plastic waste. To our knowledge, no complete scientific methodology has been developed to build pyrolysis of biomass models that predict the rate of formation and the composition of the product taking place in a tubular reactor.

The objective of this work is to develop a CFD computer code for the calculation of steady state, thermo-reaction behavior, of a closed-tubular reactor over a temperature range of 550 to 750 °C with various residence time. In fact, the design of these reactors requires detailed kinetics, based upon radical reaction schemes and a fine knowledge of hydrodynamics and heat transfer. CFD approach will predict the distribution and composition of the pyrolysis products in different geometric parameters and operating conditions, and provide a better selectivity of pyrolysis reactors, in particular for reducing the production of tars and to produce high-value compounds with a high liquid content.

Hence, in order to control the progress of the reaction pathway, the kinetic multi-lump models, reported in the literature, were integrated as source-sink terms in the species transport equations. The coupled momentum, species and energy balance equations were numerically solved using the finite-volume discretization method.

To conclude, the interest is to be able to conduct the numerical simulation of the behavior of the pyrolysis in a tubular reactor having internal agitation caused by helical ribbon to better control the multi-reaction system.

## EPOXY RESIN FAST PYROLYSIS STUDIED IN MICRO-FLUIDISED BED

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With the increasing amount of epoxy / carbon fibre composites used in aeronautic, aerospace and sport industries and due to the cost of carbon fibres, the end-of-life of these composites should be considered. Recycling of the scrap by pyrolysis could be a solution. This study concentrates on the degradation of the epoxy matrix of the composite. The main aim is first to determine which products will be formed during the pyrolysis of the epoxy resin and then to highlight the main reaction pathways of the thermal decomposition.

In our case a bisphenol A diglycidyl ether based epoxy resin was cured with an aromatic diamine, the 4-4' diaminodiphenylmethane (DDM). This mixture was heated for 1h at 110°C, 2h at 140°C and 1h at 170°C[1]. After the curing, the resin was pyrolysed at different temperatures ranging from 400 to 500°C.

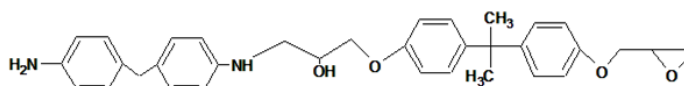


Figure 1: Chemical structure of the resin studied

The reactor used here is a micro-fluidised bed[2], with nitrogen as fluidising medium. The epoxy resin is contained in a quartz basket that is immersed in the hot fluidized bed at a given time. This procedure allows to achieve fast pyrolysis of the epoxy resin without any contact between the sample and the sand bed. The advantage is the possibility to weigh the char accurately in order to calculate the char yield. Two methanol traps at 0°C and a gas bag were employed to recover pyrolytic products. The liquid and gaseous products were respectively analysed by GC/MS and a micro-GC equipped with TCD detector. The gas yields were computed from these measurements, whereas the global vapour yields were obtained by difference. The main liquid products identified for this epoxy resin are: phenol, bisphenol A, N,N-dimethylaniline, p-isopropenylphenol. Possible degradation pathways are then presented, based on the calculated Bond Dissociation Energies [3][4] and the analysis of the products.

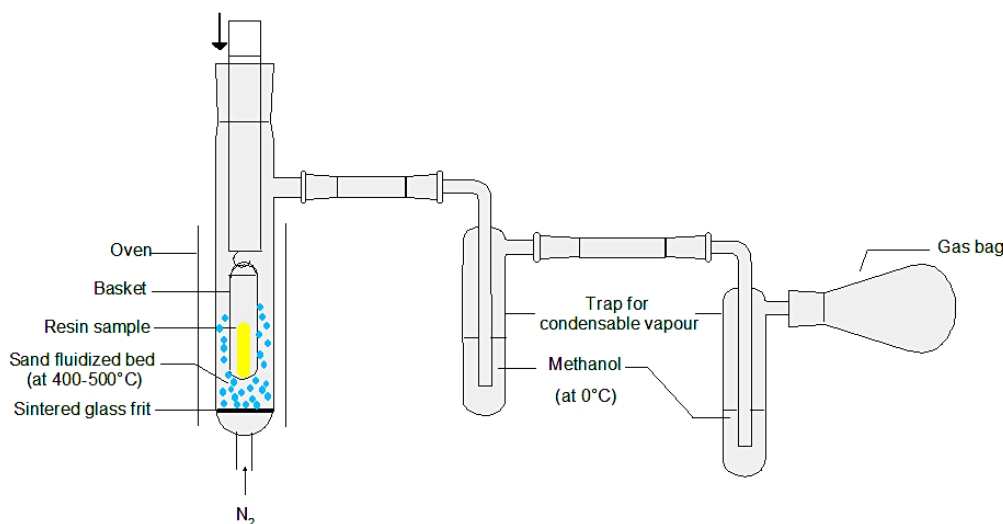


Figure 2: Scheme of the pyrolysis setup

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- [2] Liangyuan Jia, Yann Le-Brech, Binod Shrestha, Matthias Bente-von Frowein, Sven Ehlert, Guillain Mauviel, Ralf Zimmermann and Anthony Dufour, *Energy Fuel* 29, pp. 7364-7374, 2015.
- [3] Sydney W. Benson, *Thermochemical Kinetics Methods for Estimation of Thermochemical Data and Rate Parameters* (Second Edition), 1976.
- [4] Yu-Ran Luo, *Handbook of Bond Dissociation Energies in Organic Compounds*, 2003.

## ENHANCING SYNTHESIS GAS QUALITY FROM DRY REFORMING OF WASTE PLASTICS

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**Abstract:** The reforming reactions of a simulated mixture of waste plastics representative of those found in municipal solid waste with the aim of producing usable quality synthesis gases (syngas) comprised of H<sub>2</sub> and CO were investigated. The experimental process consisted of a two-stage fixed bed reactor system with pyrolysis of the plastics in the first stage and catalytic dry (CO<sub>2</sub>) and/or catalytic steam reforming in the second stage. The catalyst investigated were Ni-Co-Al and Ni-Mg-Al prepared by the rising – pH technique. Five different CO<sub>2</sub>/steam ratios were considered, namely 4:0, 4:0.5, 4:1, 4:1.5 and 4:2. The experimental results obtained from this study demonstrate that both catalysts and CO<sub>2</sub>/steam ratio are influence the syngas quality, as represented by the H<sub>2</sub>/CO molar ratio value. In the presence of the Ni-Co-Al catalyst, the H<sub>2</sub>/CO molar ratio was increased from 0.74 (no steam) to 0.94 (CO<sub>2</sub>:steam = 4:1) however the ratio decreased with further steam addition. Results using the Ni-Mg-Al catalyst showed a different trend, wherein the H<sub>2</sub>/CO molar ratio increased with the increase of steam addition into the system. From the evaluation of the gas composition, the steam addition with the Ni-Mg-Al catalyst promoted hydrogen production while the Ni-Co-Al catalyst showed good catalytic activity towards carbon monoxide production. The addition of steam to the dry reforming of waste plastics has the potential to manipulate the H<sub>2</sub>/CO molar ratio, hence the quality of syngas produced can be matched to the desired end-use industrial application.

Table 1. Influence of CO<sub>2</sub>/steam ratios on the pyrolysis-gasification of waste plastics using the two-stage fixed bed reactor with Ni-Co-Al or Ni-Mg-Al catalyst in the second stage at 800 °C

| CO <sub>2</sub> /steam ratio   | 4:0   | 4:0.5 | 4:1   | 4:1.5 | 4:2   |
|--------------------------------|-------|-------|-------|-------|-------|
| <u>Ni-Co-Al</u>                |       |       |       |       |       |
| H <sub>2</sub> /CO molar ratio | 0.74  | 0.88  | 0.94  | 0.85  | 0.84  |
| CO <sub>2</sub> conversion     | 51.53 | 48.14 | 48.96 | 56.55 | 51.04 |
| <u>Ni-Mg-Al</u>                |       |       |       |       |       |
| H <sub>2</sub> /CO molar ratio | 0.68  | 0.61  | 0.77  | 0.94  | 1.08  |
| CO <sub>2</sub> conversion     | 66.75 | 66.81 | 58.61 | 46.34 | 38.07 |

## EFFECT OF HIGH HEATING RATES ON THE PRODUCTION OF LIMONENE BY PYROLYSIS OF WASTE TYRES

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Pyrolysis of waste tyres to produce a liquid fraction (tyre derived oil or TDO) is a promising method to reduce waste tyre stockpiles which are currently polluting the environment. Although the TDO can possibly be used as a low-grade fuel, the competition with petroleum-derived fuels impedes the feasibility of waste tyre pyrolysis. To improve this feasibility, recovery of valuable chemicals (such as DL-limonene) from the TDO has been proposed[1-3]. Thermogravimetric analysis combined with mass spectrometry (TGA-MS) is employed to study the effect of high heating rates (up to 100 °C/min) on the limonene yield. Two ion current signals (67 and 93 amu, representing isoprene and limonene, respectively) are monitored in the MS. These signals (in combination with the mass loss data) can elucidate on the two competitive depolymerisation reactions of the allylic radicals of the polyisoprene (natural rubber) fraction of the tyre, i.e. depropagation (unzipping) to isoprene and intramolecular cyclisation followed by scission to limonene, see Figure 1[1]. The results show that, at the same heating rate, the maximum limonene production rate is at slightly higher temperatures than that of isoprene, which implies that the limonene reaction has a slightly higher activation energy. A higher activation energy for the limonene reaction seems reasonable, since this reaction includes both the formation of a bond (during cyclisation) and the breakage of a bond (scission), while the depropagation reaction only entails the latter. Furthermore, it is shown that the reaction temperature at maximum depolymerisation rate (both towards isoprene and limonene) of the tyre particles increases for increasing heating rates. It is concluded that the heating rate can be optimised to improve the production of specific valuable chemicals in waste tyre pyrolysis.

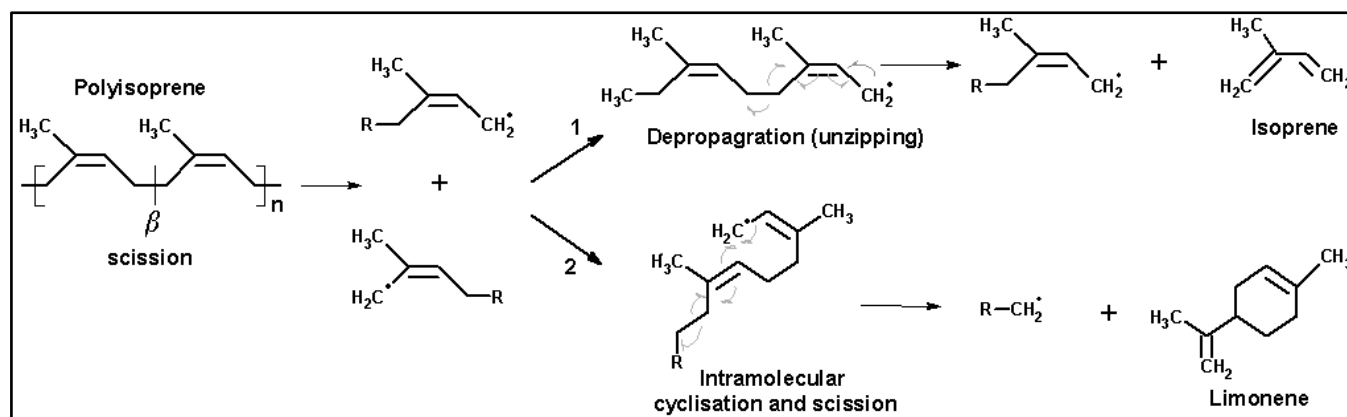


Figure 1: Polyisoprene depolymerisation by 1) depropagation to isoprene and 2) intramolecular cyclisation and scission to limonene.

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[3] P.T. Williams, S. Besler, D.T. Taylor, Fuel, 69, pp. 1474-1482, 1990.

## FUELS BY RECYCLING OF WASTE PLASTICS FROM END OF LIFE VEHICLES

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Owing to the strict regulations, the utilizations of constituents from end of life vehicles (ELV) is in the focus of nowadays waste management. This work is dedicated to the mixed waste plastics pyrolysis from ELV. Waste plastics were pyrolyzed using TG apparatus, while larger amount of waste polymers were also decomposed in a batch system in the temperature range of 400 and 600°C. Products of pyrolysis were analyzed by gas-chromatography, Fourier-transformed infrared spectroscopy and different standardized methods. Raw material contained lots of different polymers, such as polyethylene, polypropylene, polyamide, polyurethane, acrylonitrile-butadiene-styrene, polycarbonate, etc. The kinetic of pyrolysis reactions was followed by first order kinetic approach using Arrhenius equation. Synergetic effect was found among different constituents of waste plastics from ELV regarding the pyrolysis, which resulted e.g. elevated yields of volatiles and decreasing in activation energy. Gases contained hydrocarbons up to C<sub>5</sub>, while pyrolysis oil could be characterized as mixtures of C<sub>6</sub> and C<sub>35</sub> hydrocarbons. To ensure the higher degradation of raw materials, equilibrium fluid catalytic cracker catalyst was used in 5% concentration. Catalyst had a significant effect especially to the composition of pyrolysis oil, because the yield of naphtha boiling point range hydrocarbons was higher than without that. FCC catalyst had more significant effect to the products yields at moderate temperature, which was attributed to the catalyst deactivation at higher temperature. In case of thermo-catalytic pyrolysis higher yields of branched hydrocarbons was found at lower pyrolysis temperature, while the concentration of aromatics was higher at 600°C

**Keywords:** ELV, gas-chromatography, catalyst, pyrolysis oil



## THERMO-CATALYTIC REFORMING OF MUNICIPAL SOLID WASTE

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In order to tackle climate change and reduce the dependency of fossil fuels, the production of advanced biofuels from non-food competing biomass is today of paramount importance by all governments worldwide. The thermal conversion of the organic fraction of Municipal Solid Waste (MSW) via a Thermo-Catalytic Reforming (TCR®) process (pyrolysis with subsequent post catalytic reforming) is a promising method to achieve this. MSW refers to a heterogeneous mixture of everyday household rubbish which is thrown away by the general public and subsequently collected for disposal by local authorities. The current state of the art for the disposal of this type of waste is either by landfill or incineration; however both of these practices are unsustainable. Landfilling contaminates vast areas of land which could otherwise be used for arable farming and both landfilling and incineration are major contributors to greenhouse gas emissions. Furthermore, the enforcement of the EU landfill directive (CEC 1999) prohibits the disposal of all organic materials sent to landfill without prior treatment. The TCR process implemented at Fraunhofer UMSICHT is an alternative means of converting organic wastes and residues into sustainable energy carriers (H<sub>2</sub> rich synthesis gas, liquid bio-oil and solid char). This paper has investigated the use of the TCR technology to process the organic fraction of MSW at a 2 Kg/h throughput. The results revealed that MSW could be successfully pre-treated (sorted, dried and pelletised) and processed by the TCR under pyrolytic conditions. Approximately 24 wt% of the feedstock converted into liquids, made up of 19 wt% aqueous phase and 5 wt% organic phase (bio-oil). The liquids readily phase separated and the bio-oil fraction revealed superior fuel physical and chemical properties, higher heating value (HHV) approximately 37 MJ/Kg, oxygen content <7 wt%, water content <4 wt %, Kinematic viscosity <10 cSt and acid number <5 mg KOH/g. The oil produced was found to be directly miscible fossil crude oil and fossil diesel, which makes its application as a blended feedstock for conventional fossil fuel refineries an attractive prospect. Since, the liquid yields which could theoretically be obtained from processing the organic fraction of all MSW produced in Europe in this way, fit directly in line with EU targets to achieve a minimum of 2 % of all transportation fuels from advanced biofuels by 2020. The oils produced were further analysed by GC-MS and were found to be composed of mainly polycyclic aromatic hydrocarbons (PAHs) and mono-aromatic hydrocarbons (MAHs), while aliphatic hydrocarbons, phenols and fatty acid methyl esters were also identified but in lower concentrations. The closure of the mass balance revealed that 45 wt% of the feedstock converted into synthesis gas with a H<sub>2</sub> content of 36 vol% and HHV of 17 MJ/kg and 31 wt% converted into char with a HHV of 17 MJ/kg. The energy balance revealed that approximately 14% of the energy contained within the feedstock was required as heat input for the process itself. The production of high quantities of H<sub>2</sub> by the process makes downstream hydrogen separation and subsequent hydro-deoxygenation of the bio-oil a very promising future upgrading strategy to achieve drop in transportation grade liquid fuels from MSW. The methodology for the TCR process, the experimental results, as well as the economic feasibility of the process at smaller decentralised scales (<5 MW) will be presented. Future research plans to scale up the technology will also be discussed.

## Online study on the influence of thermal treatment of HUSY on the catalytic pyrolysis of polypropylene with photoionization mass spectrometry

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Calcination is a basic method of modifying zeolites. Thermal treatment at a certain temperature can change the amount of acid sites and the microstructure, clean up the micropores, and improve the performance of zeolites. Thus, the understanding of the influence of calcination on zeolites and catalytic pyrolysis is of particular importance[1].

Recently, a newly built online pyrolysis photoionization time-of-flight mass spectrometer (Py-PI-TOFMS) was utilized to investigate the catalytic pyrolysis process of polypropylene (PP) in the presence of HZSM-5[2]. Compared to traditional “hard” electron ionization (EI) method for the gaseous components analysis, photoionization produces little or no fragments, making the identification and interpretation of complex pyrolysis products in real time possible. In the present work, the influence of HUSY zeolite calcination on the catalytic pyrolysis behavior of PP was studied using online Py-PI-TOFMS as well as other conventional methods. Our results show that calcination can change the feature and catalytic activity of zeolite, and the yields and selectivities of products will also be significantly affected.

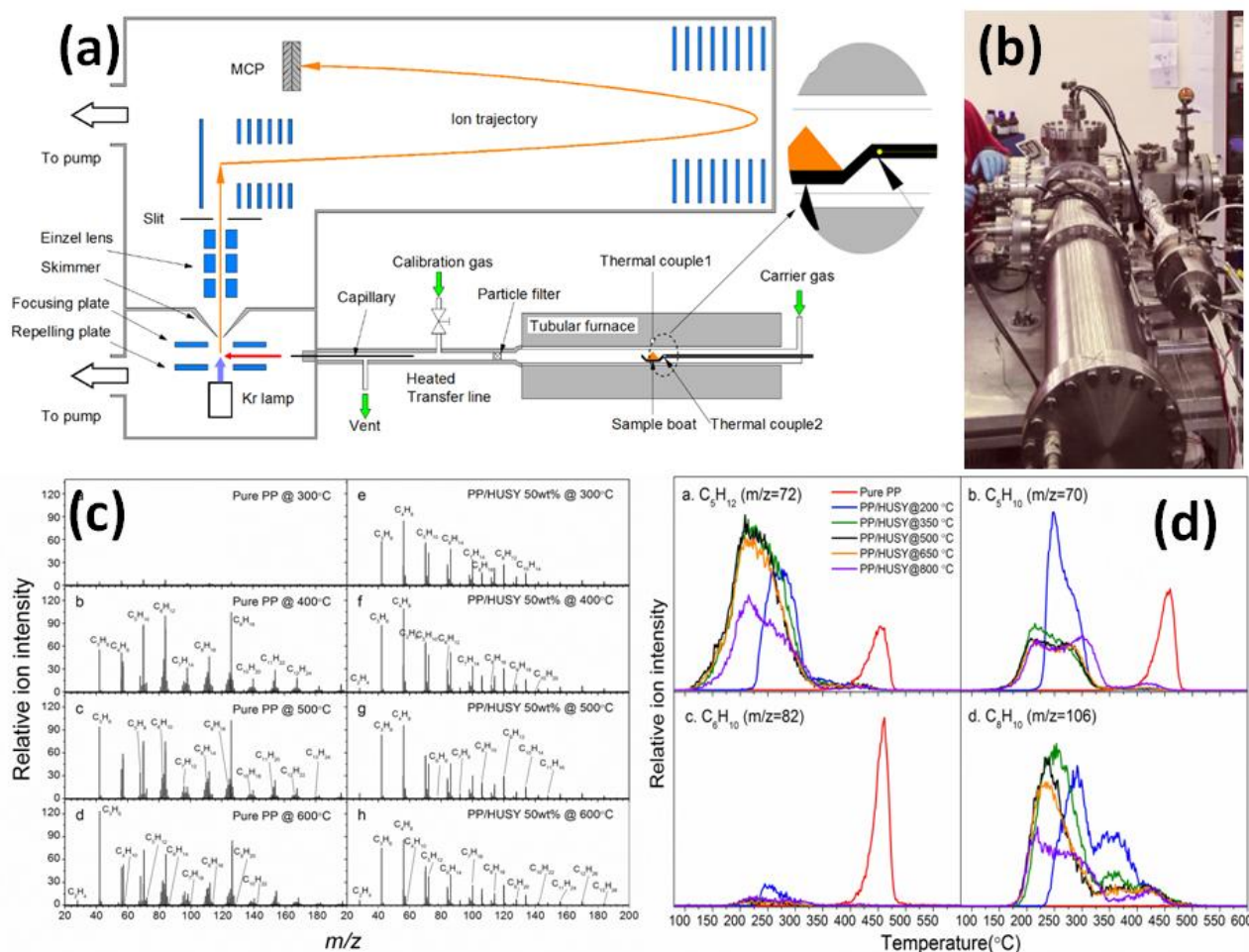


Figure 1. (a) Schematic of the Py-PI-TOFMS setup; (b) Photo of the Py-PI-TOFMS setup; (c) Photoionization mass spectra of pure PP and PP/HUSY at different pyrolysis temperatures; (d) Profiles for four typical pyrolysis products of PP, i.e. pentane ( $m/z=72$ ), pentene ( $m/z=70$ ), hexadiene ( $m/z=82$ ), and xylene ( $m/z=106$ ) as a function of temperature. HUSY calcined at five temperatures was used as catalyst.

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## Recycled polymers from WEEE in food contact articles on the European market: completing the story by pyrolysis GC-MS

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Food contact articles are an important group of consumer goods mainly made of polymeric materials which are regulated within Europe by the EC. Regulation No. 10/2011 having in its annex 1 a whole list of constituents which are allowed to be used.[1] However, recently in black polymeric food contact items traces of brominated flame retardants (BFRs) have been detected indicating the presence of recycled polymers, mainly coming from waste electric and electronic equipment (WEEE) as BFRs are a main additive in electric applications.[2] The presence of traces of BFRs in polymer food contact articles is prohibited in the EU as there are not approved within the EC. Regulation No. 10/2011, moreover, the BFR concentrations in the measured samples are too low to achieve flame retardancy. Another argument that WEEE might be used is the detection of multiple BFRs (both: older ones and more recent alternatives) in one polymer which indicate again that a mixture of several polymers has been used.

Multiple analytical techniques like off-line XRF combined with thermal desorption GC-MS measurement allow to measure the overall bromine concentration in polymer samples followed by an BFR identification step. In order to get more evidence that WEEE has been used, several black polymeric kitchen utensils were selected (n=10) and measured for their bromine content (XRF); BFR presence (thermal desorption GC-MS); additionally rare earth elemental content and antimony levels (ICP-OES). These WEEE precursors were confirmed for 7 of 10 samples. Moreover, for an elevated Sb content also a higher Br content was observed as both elements are used as a synergetic flame retardants system.[3],[4] Beside this measurement also FTIR has been performed in order to detect foreign polymer content. In some cases the absorption signals were strong enough to detect e.g. polycarbonate in ABS. However, in many cases pyrolysis GC-MS was used to confirm the FTIR measurements as well as to detect specific fragments in order to prove the presence of other ``foreign`` polymers. The main matrixes were based on styrenic polymers (ABS) or polyolefins (PP/PE) as they have advantages in the recycling process. In Table 1 results are shown from a selection of the results obtained by combining pyrolysis GC-MS, thermal desorption GC-MS, FTIR, ICP-OES and XRF. Due to the detection of several foreign polymer fractions by pyrolysis GC-MS the suspicion that WEEE fractions are added to consumer goods could be confirmed.

Table 1: selected results

| Sample           | Main polymer | Macromolecular contamination        | Bromine conc. (mg kg <sup>-1</sup> ) | Antimony conc. (mg kg <sup>-1</sup> ) | Detected BFRs                  |
|------------------|--------------|-------------------------------------|--------------------------------------|---------------------------------------|--------------------------------|
| Egg cutter       | PP/PE        | HIPS/<br>PBT or PET                 | 57                                   | < 2                                   | TBBPA,<br>decaBDE              |
| Thermo-cup cover | ABS          | PMMA<br>PC<br>PP                    | 1521                                 | 271                                   | TBBPA,<br>decaBDE,<br>decaBDPE |
| Thermo-cup cover | ABS          | PMMA/<br>PBT or PET                 | 504                                  | 113                                   | TBBPA,<br>decaBDE              |
| Thermo-cup cover | PP/PE        | PBT or PET<br>HIPS or ABS or<br>SAN | 62                                   | < 2                                   | TBBPA,<br>decaBDE              |

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## CATALYTIC PYROLYSIS OF WASTE PLASTICS USING STAGED CATALYSIS FOR PRODUCTION OF GASOLINE RANGE HYDROCARBONS

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**Abstract** - The increase in plastic materials consumption has led to a parallel rise in the generation of plastic wastes which are becoming a major stream in solid waste. Plastic waste generation imposes negative environmental effects, since these materials are usually non-biodegradable. Plastic waste recycling can provide an opportunity to collect and dispose of plastic waste in the most environmentally friendly way. A simulated mixture of plastic waste representative of the plastics found in municipal solid waste was processed in a two-stage pyrolysis-catalysis fixed bed reactor in the presence of staged catalysis in the form of Fluid Catalytic Cracking (FCC) catalyst as a mesoporous catalyst and ZSM-5 as a microporous catalyst. The aim of the research was to produce a premium grade, gasoline range hydrocarbon fuel. The quality of the liquid hydrocarbon products was evaluated in terms of research octane number and the yield of single ring aromatic compounds, which are the important characteristics of gasoline. The product gases were analysed using packed column gas chromatography. The liquid hydrocarbon product was analysed using gas chromatography and mass spectrometry (GC-MS), Fourier transform infrared spectroscopy (FT-IR) and the used catalysts characterised using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The results showed that a higher ratio of FCC in a catalyst bed produced the highest liquid fraction which consisted of C<sub>5</sub>-C<sub>20</sub>. More valuable chemical raw materials including benzene, toluene, and other condensed aromatic hydrocarbons were obtained.

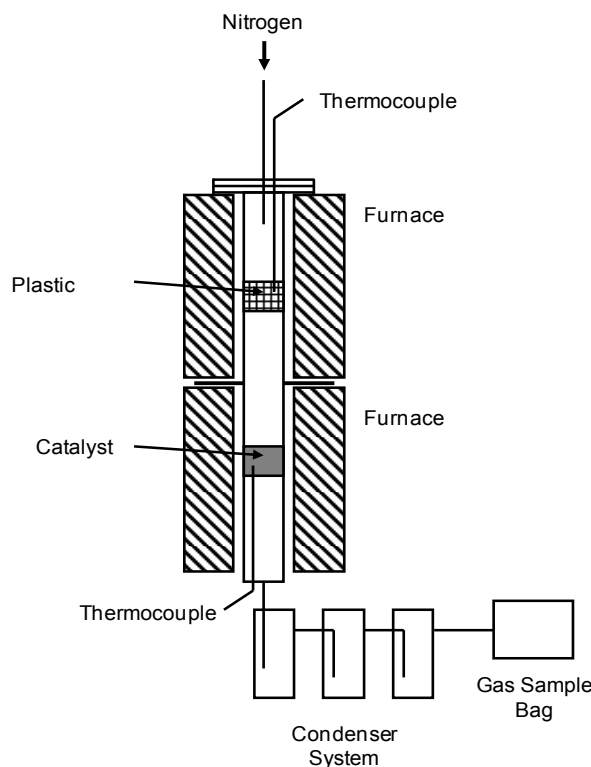


Figure 1. Schematic diagram of the two-stage pyrolysis-catalysis reactor.

## CATALYTIC PYROLYSIS OF REFUSED PLASTIC FUEL OVER ZEOLITES

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Because refused plastic fuel (RPF) has a great potential to produce valuable chemicals, catalytic pyrolysis of RPF was carried out. Zeolites such as ZSM-5, Ni/ZSM-5 and Ga/ZSM-5 were used as catalysts. Liquid product via catalytic pyrolysis mainly consisted of aromatic compounds and aliphatic hydrocarbons. HZSM-5 with 5wt% Ga impregnated had increased mono-aromatics in oil. Especially BTEX increased significantly. Among zeolites, Ga/HZSM-5 showed high selectivity to xylene. This is because strong acid sites of HZSM-5 still remained after Ga was impregnated. Also the optimum conditions between impregnated metal and acid sites were elucidated.

The detailed reaction mechanism of catalytic pyrolysis of RPF in terms of acidity will be suggested.

### Acknowledgement

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## INFLUENCE OF DEMINERALIZATION ON PYROLYSIS OF SUGARCANE BAGASSE AND TRASH

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Sugarcane bagasse (SCB) and sugarcane trash (SCT) are lignocellulosic materials that have attracted interest as potential feedstock for the thermochemical conversion into bio-oil, particularly by fast pyrolysis. However, their relatively high inorganic content, especially alkali and alkaline earth metals, affects the quality of the produced bio-oil. In order to overcome this problem, pre-treatment with demineralized water, or aqueous solutions of HCl, H<sub>2</sub>SO<sub>4</sub> and citric acid has been developed. The present study reports for fixed demineralization conditions (25 °C and 1 h of leaching time) the effect of the used liquid type on the pyrolysis yield and bio-oil characteristics. Both samples SCB and SCT exhibited similar trends in ash reduction after leaching: the degree of de-ashing depends on the nature of the leaching liquid. The untreated and leached biomass samples were subject to compositional analyses. Pyrolysis trials were conducted in a bubbling fluidized bed reactor at 500 °C in inert gas atmosphere (N<sub>2</sub>); 1.5 kg pure sand was used as the bed material. Approximately 100 g of pretreated biomass was used in each run and it was fed at a rate of 1.7 g·min<sup>-1</sup>. The resulting bio-oil was examined by ultimate analysis, chemical analysis (i.e. GC-MS), and the determination of its acid number and water content (i.e. Karl Fisher Titration). The HHV was calculated by using the Milne formula. Finally, the char was characterized by ultimate analysis and HHV calculation. As a result of this work the bio-oil yields for both biomass samples appeared to be higher when they were pre-treated with either organic or inorganic acids. For instance, the bio-oil yield obtained from citric acid-treated SCB was about 5 wt.% higher than from water-treated SCB and 10 wt.% higher than from untreated biomass. Correspondingly, the values of water content are 20.02, 30.39 and 24.52 wt.%. The acid number of bio-oils were 109.17, 115.23 and 110.78 mg KOH/g for citric acid-treated, water-treated and untreated SCB, respectively.

## USE OF SEWAGE SLUDGE AND MANURE ASH FOR H<sub>2</sub>S REMOVAL FROM THE PYROLYSIS GAS

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Pyrolysis of sewage sludge (SS) and manure have gained interest as a potential management of these wastes, reducing the waste volume, and at the same time, producing valuable byproducts. However, due to the sulfur presence in these materials, hydrogen sulfide is formed during these treatments. This gas impurity involves environmental problems related to acid rain, operational troubles in pipes, engines and turbines, or deactivation of catalyst in the tar cracking and gas reforming. Several materials have been studied in order to remove H<sub>2</sub>S from the off-gases of the pyrolysis process, such as wet scrubbing with selected solvents, activated carbons or metal oxides based sorbents. Zinc, copper, iron and calcium oxides are the most promising and the most studied oxides for the removal of H<sub>2</sub>S. SS and manure combustion ash present an important proportion of iron and calcium oxides, therefore they can be used as sorbent of H<sub>2</sub>S from the gases produced in the pyrolysis of these wastes.

The main purpose of this work is to evaluate the capacity of desulphurization of the SS and manure combustion ash. The variables studied are the kind of ash (SS ash, manure ash or ash from SS/manure mixture) and the desulphurization temperature (room temperature, 200°C and 550°C). Ashes were obtained by combustion in a heating muffle furnace at 900°C (heating rate 20°C·min<sup>-1</sup>) during two hours and were characterized before the tests. The techniques used were ultimate analysis, metal content by inductively coupled plasma combined with optical emission spectroscopy (ICP-OES), BET surface area, powder X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS).

The desulphurization tests were performed in a fixed-bed quartz reactor at atmosphere pressure, packed with 1 g of ash. The diagram of the installation could be found in a previous work [1]. To simulate the pyrolysis gases a synthetic pyrolysis gas was used, with a similar composition to the dry off-gas generated during the pyrolysis process in a fluidized bed reactor [2]. The flow rate was fixed at 50 mL<sub>STP</sub>·min<sup>-1</sup>. The length of the experiments was established in two hours. All the tests have been also theoretically simulated using HSC Chemistry® 6.1, which used the Gibbs energy minimization method to calculate the equilibrium amounts of each species in isothermal and isobaric conditions.

H<sub>2</sub>S breakthrough curves in the outlet flow have been represented in order to evaluate the removal of H<sub>2</sub>S from the pyrolysis gas. Sulfur content in the ash after the test has been also analyzed. Besides these analyses, XRD and XPS were carried out in order to know more about the desulphurization process and the species obtained in the ash. To fix the H<sub>2</sub>S breakthrough time, 100 ppmv of H<sub>2</sub>S has been used as tolerable level.

The characterization of the ashes before the test confirms the presence of metal oxides. In the case of SS ash, iron is the main metal present (192 mgFe·gash<sup>-1</sup>), followed by calcium (65 mgCa·gash<sup>-1</sup>) and magnesium (17 mgMg·gash<sup>-1</sup>). For the manure ash, the distribution is different, calcium is present in more proportion (191,67 mgCa·gash<sup>-1</sup>) followed by magnesium (32,55 mgMg·gash<sup>-1</sup>) and iron (27,46 mgFe·gash<sup>-1</sup>). Both ashes are able to remove H<sub>2</sub>S from the gas. Temperature has an influence in the H<sub>2</sub>S breakthrough time in the case of SS ash, obtaining a long time with the lower temperature. However, this variable hardly affects the H<sub>2</sub>S breakthrough time in the case of the manure ash. This effect could be explained by the different range of temperatures for the desulphurization of the metals present. During the experiments at temperature different from room temperature, a low proportion of COS has been detected. This gas can be formed due to the reducing atmosphere of the pyrolysis gas ( $\text{H}_2\text{S} + \text{CO}_2 \leftrightarrow \text{COS} + \text{H}_2\text{O}$ ).

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## BTEX FRACTIONS FROM THE CATALYTIC PYROLYSIS OF WASTE POLYMERS

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The aim of this research was to study the influence of different types of catalyst on the yields of benzene, toluene, ethylbenzene and xylenes (BTEX) fractions obtained during the catalytic pyrolysis of five different waste polymers (polypropylene, acrylonitrile-butadiene-styrene, styrene-butadiene rubber - automotive waste after moulding scraps, polyethylene terephthalate - municipal waste and pure non-vulcanised styrene-butadiene rubber from waste car tyres). Waste polymers used in this study were pyrolysed at four different conditions: (i) without catalyst, (ii) with non-impregnated ZSM-5, (iii) with ZSM-5 catalyst with ammonia groups and (iv) with ZSM-5 catalyst with 10% Ni added. Polymers were pyrolysed at 600°C in the pyroprobe close coupled with a GC-MS. The pyrolysis temperature was selected to target formation of aromatic compounds and olefins.

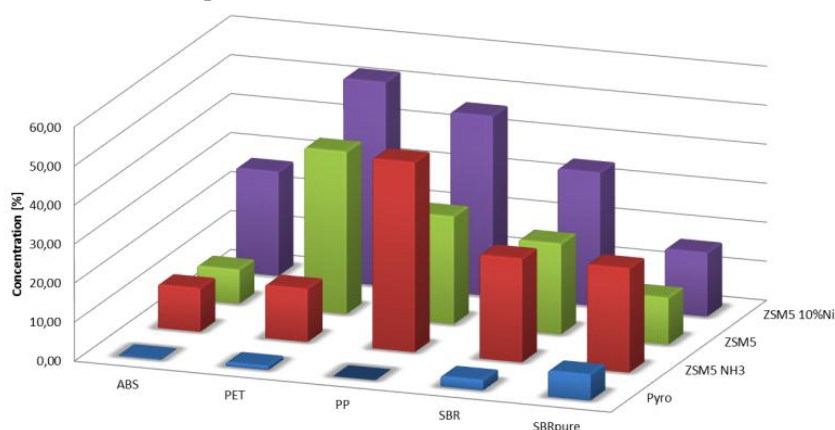


Fig.1. Concentrations of BTEX fractions from catalytic pyrolysis of waste polymers.

The highest yields of BTEX fraction were observed during the catalytic pyrolysis of polyethylene terephthalate with Ni-doped aluminosilicate (ZSM-5 + 10 wt.% Ni). With this catalyst over 52 wt.% of BTEX fraction was obtained, composed of: 24.4 wt.% benzene, 13.2 wt.% toluene, 13 wt % ethyl benzene and 1.6 wt.% xylene. High yields of BTEX fractions were observed during the polypropylene catalytic pyrolysis with two types of catalyst - aluminosilicate with ammonium groups (48.7 wt.% of BTEX fraction) and aluminosilicate impregnated with nickel ions (46.2 wt% of BTEX fraction).

Presented research was carried out at the European Bioenergy Research Institute (Aston University, Birmingham, UK) together with the Institute for Chemical Processing of Coal (Zabrze, Poland) and sponsored by the EU Biofuels Research Infrastructure for Sharing Knowledge (BRISK) project.



## Implementation of a New Pyrolysis Reactor in Linz

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In this paper we want to present the design of a novel large scale pyrolysis reactor. The setup is constructed to handle polymeric waste materials and other waste streams in the range of 10 to 30 kg per hour and transfer them into a gaseous feedstock and char. The gas (at above 400 °C) is monitored by quasi-online gas chromatography/mass spectrometry in order to qualify and quantify its components and then burned to create heat in the first place and then energy.

An important design feature of the pilot plant is that all steps can be monitored such as the gas and char composition, pollutants after the burner and the efficiency of the heat/energy transfer steps. The characterization of the char is performed by elemental analysis to estimate its heating value and icp MS to monitor the content of toxic metals. This work will present the first results on the pyrolysis of homogenous polymers which are used to optimize the basic reactor settings in terms of feed speed, temperature and residence time.

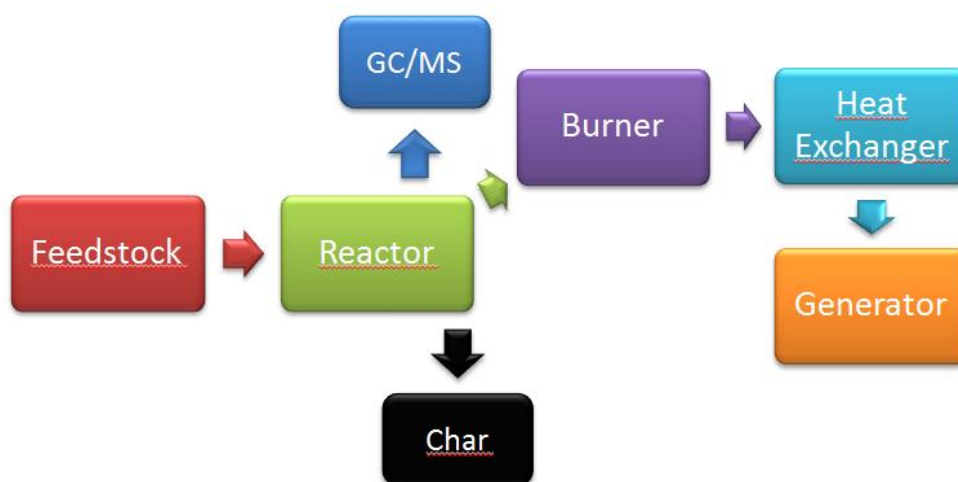


Fig. 1. Scheme of the pyrolysis unit.

# VALORISATION OF LOW QUALITY BIOFUELS BY HYDROTHERMAL CARBONISATION

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Hydrothermal carbonisation (HTC) is a process which uses hot compressed water to simulate natural coal formation producing a coal like product from biomass. Sometimes referred to as hydro-pyrolysis or wet-torrefaction; HTC aims to produce a fuel which is more energy dense, easily friable and more hydrophobic than the starting material, with increased combustion efficiency and reduced pollutant emissions during the combustion process [1, 2]. While the handling improvements of a range of biomass treated by HTC are well documented, until recently there has been little research into what influence HTC has on the inorganic elements within the biomass. These inorganic elements include the alkali metals which are particularly problematic during biomass combustion as they result in both slagging and fouling. Research into the leaching of salts using water, ion exchange solutions and acids have shown the partial removal of alkali metals is possible from biomass [3]. However the enhanced properties of subcritical water along with the modification of the biomass structure brought about during HTC has been shown to greatly improve the removal of problematic inorganic elements and heteroatoms greatly improving the combustion properties of the original fuel [4].

In this work a series of low value biomasses, including seaweed, miscanthus and willow, have been batch processed under HTC conditions using a range of temperatures. Results have shown that significant upgrading of energy density is possible with calorific value ranging from typically 24 MJkg<sup>-1</sup> at 200 °C to 28-31 MJkg<sup>-1</sup> at 250 °C for lignocellulosic material. A significant removal of alkali metals is observed and this in turn changes the ash chemistry. This change in ash chemistry has been shown to change the ash melting behaviour and the hemisphere temperatures (oxidizing conditions) which increase substantially. A number of tests via thermogravimetric analysis have been used to evaluate the influence HTC has on the fuel combustion behaviour along with tests on handling and milling properties of the fuel. This combined with the ash fusion testing has shown that HTC significantly reduces the potential fouling and slagging in problematic fuels while bringing about more coal like behaviour during combustion and improved handling and milling properties. This is particularly notable for the seaweeds and miscanthus which unprocessed had a high slagging and fouling propensity, low calorific value and high moisture content. A series of tests using varying sized blocks of willow has shown that the improvements in ash chemistry, handling and combustion properties of the fuel is still achieved even when processing blocks of wood greater than 4 cm<sup>3</sup>. Consequently HTC could be a promising pre-treatment in the valorisation of low quality, problematic biofuels, with minimal size reduction required.

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## CATALYTIC CRACKING OF NITROGEN CONTAINING PLASTICS USING SPENT FCC CATALYST

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### Introduction

Catalytic cracking of waste plastics is a promising way to obtain fuel oils. We have succeeded in producing diesel oil from waste polyolefins and polyvinylchloride with high yields using spent FCC catalyst. However, when this method is applied to nitrogen containing plastics, nitrogen atoms should transfer to the products, and would cause some problems such as NO<sub>x</sub> formation during combustion. In this study, cracking of several pure N-containing plastics (NCP) was examined to make clear the product distribution and fate of nitrogen.

### Experimental

Polyacrylonitrile-butadiene-styrene (ABS), polyurethane (PU) and Nylon 6,6 were used for the catalytic cracking. The plastic sample was charged in an agitated semi-batch reactor with spent FCC catalyst (7.5:1 by weight), and cracked at 430°C under atmospheric pressure. Vaporized products flew out with He carrier (100 ml/min), and they were cooled and collected with a condenser at 0°C in liquid or solid form. Gaseous products were analyzed by GC-TCD and GC-FID. Nitrogen contents in the solid samples and the product oils were analyzed by elemental analysis. HCN and NH<sub>3</sub> were analyzed by an ion-chromatograph and gas indicator tube. Nitrogen compounds in the oil samples were analyzed by GC-MS.

### Results and Discussion

Fig.1 shows product yield with NCP. ABS gave the highest oil yield because its chemical structure contains a large part of alkyl groups. A high yield of more than 30% of residue was observed in PU conversion. This would be because PU is a thermosetting resin. In the case of nylon 6,6 conversion, the major product was solid one which would probably be a mixture of its monomers. Fate of nitrogen in the polymers is shown in Fig. 2. The major part of N atoms in the parent polymer was transformed to the main product in each case. Gaseous HCN and NH<sub>3</sub> generated from all plastics, especially nylon 6,6 gave higher concentration. From GC-MS analysis, cracked oil from ABS was found to be composed of mainly single ring aromatic hydrocarbons and only 4-phenylbutyronitrile was detected as nitrogen containing compound. 3,3-Pentamethylenediaziridine was detected from the solid products from nylon 6,6.

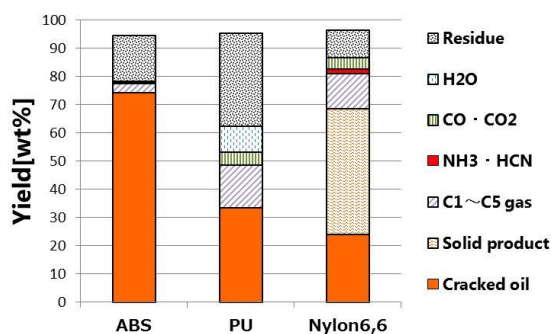


Fig.1 Carbon yield of product

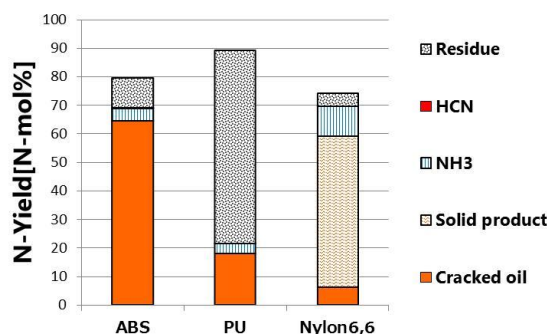


Fig.2 Nitrogen yield of products

### Conclusions

The major products from ABS, PU, and nylon 6,6 were oil, residue, and solid product, respectively. Large amount of nitrogen atoms in these plastics were found to transfer to the corresponding major products.

## INDUSTRIAL WASTE DERIVED CAO-BASED CATALYSTS FOR UPGRADING OF VOLATILES DURING JATROPHA RESIDUES PYROLYSIS

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The Cao-based catalysts for the catalytic pyrolysis of Jatropha residues were synthesized from Lime mud. Lime mud is the industrial waste from paper-making process (LMP) which obtained from a pulp and paper mill in Thailand. The chemical compositions of this waste measured by XRF consisted of a large fraction of CaCO<sub>3</sub> with small amounts of Na<sub>2</sub>O and MgO. Initially, lime mud was heated at 1000°C in air atmosphere and consequently transformed to active CaO catalysts. The CaO catalysts were modified by adding 5 wt% transition metals (Fe and Ni) using wet impregnation method. Phase analysis of synthesized catalysts was determined by using X-ray powder diffraction. The microstructure and surface area analyses were performed by scanning electron microscope and nitrogen absorption. Non- and catalytic fast pyrolysis of Jatropha residues using CaO, Fe/CaO and Ni/CaO were studied using an analytical pyrolysis-GC/MS at 500°C with Jatropha residues to catalyst ratio 1:1. Non-catalytic pyrolysis vapors contained mainly high acid levels (50.7%), N-containing compounds (20.3%), other oxygenated compounds including ketones, alcohols, esters, ethers, phenols and sugars (25.0%). The aromatic and aliphatic hydrocarbons were detected in small amounts (1-3%). The presence of CaO catalyst completely eliminated undesirable compounds involving acids and sugars and significantly decreased N-containing compounds. Moreover, it considerably promoted the formation of aliphatic hydrocarbons up to 35.3%. In case of metal/CaO catalysts, metal part contributed to increase the selectivity of aliphatic hydrocarbons, and reduced the aldehydes compared to that obtained from CaO support. Ni/CaO showed the highest hydrocarbon selectivity up to 48.9%. The formation of hydrocarbon compounds led to the high heating values of bio-oils. Thus, these CaO-based catalysts derived from industrial waste can be used as a potential catalyst for catalytic fast pyrolysis application.

**Applicable topic:** Application field---Waste

## **Conversion of earthworm manure into environmentally-friendly adsorbents through pyrolysis**

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**Abstract:** Earthworm manure (EM), an important part of biomass, is largely produced as earthworm is widely used in disposing organic solid waste, household garbage, municipal sewage and livestock manure. Technologies related to the resource utilization of earthworm manure thus have attracted numerous attentions. Thermal conversion (pyrolysis) is considered as an alternative and promising technology on the utilization of livestock manure (e.g., swine manure, dairy manure) due to it can immobilize the intrinsic contaminants (heavy metal, pesticide, antibiotic) in manure and produce a versatile product (biochar)<sup>[1]</sup>. In this work, EM as a biomass precursor was pyrolyzed at 400-600 °C to produce a series of biochar samples (EMBCs) which afterwards were employed to deal with dyeing wastewater. The difference of EM and EMBCs in physicochemical properties including surface area, pH, electrical conductivity, ultimate components and surface functional groups were determined. The adsorption capability and potential mechanisms of EMBCs to Rhodamine B (RB) were investigated as well. The surface area and pH of EM was significantly enhanced after pyrolysis treatment and positively related to pyrolysis temperature. The decrease of H/C and O/C suggested that pyrolysis process could increase the aromaticity and hydrophobicity of EM. FT-IR spectra showed that the surface functional groups dramatically reduced during pyrolysis, especially the aliphatic functional groups (CH<sub>3</sub> and CH<sub>2</sub> at 2915-2851 cm<sup>-1</sup>). Langmuir isotherm model and pseudo-second-order kinetic model could be well described the adsorption of RB by EMBCs. The maximum adsorption capacity of EMBCs were 14.49~21.60 mg g<sup>-1</sup>, which were superior to some other commercial adsorbents<sup>[2]</sup>. Surface functional groups (-NH/-OH and aromatic C=C) and surface area were responsible for the effective adsorption of EMBCs. These results indicated that EM can act as a feedstock to prepare an environmentally-friendly material through pyrolysis.

**Key words:** Earthworm manure; Pyrolysis; Adsorption; Rhodamine B

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## **SLOW PYROLYSIS OF ORGANIC FRACTION OF MUNICIPAL SOLID WASTE AND USING THE AQUEOUS PHASE PRODUCT IN ANAEROBIC DIGESTION**

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There are approximately 50 million tonnes of municipal solid waste (MSW) produced in the UK each year. This waste is currently disposed of by either incineration or landfill, both of which are unsustainable practices as they are costly, lead to an increase in greenhouse gas emissions and use up land which could be otherwise used for arable farming. The current research is aiming to develop a sustainable and societally acceptable means of recovering value from the non-source segregated organic fraction of MSW through the synergy between thermal (slow and intermediate pyrolysis) and biological (anaerobic digestion) conversion processes.

The feedstock used in the present work is densified shredded (<10 mm) MSW particles that have been segregated from processed refuse. The material contains approximately 45 wt.% moisture and 30 wt.% ash, as supplied by a commercial MSW treatment plant. Slow pyrolysis of MSW is initially carried out in a bench-scale auger reactor (300 g/h) under a range of different pyrolysis processing conditions, with furnace temperatures from 450 to 850°C and feedstock moisture contents from 12 to 45 wt.%. Both the organic and aqueous fractions of the phase-separated pyrolysis liquid are collected and characterised. The aqueous phase products from pyrolysis are tested through anaerobic inhibition toxicity assays and batch screening tests in order to study their anaerobic biodegradability. Preliminary results from the current work have shown that the concentration of organics in the aqueous fraction (expressed as Chemical Oxygen Demand - COD) is dependent on feedstock moisture content and temperature of the pyrolysis experiment. The inhibition of methanogenic *archaea* increases considerably with increase of pyrolysis temperatures. These results indicate that acclimatisation of the microbial population may be required for successful digestion. Larger scale pyrolysis tests will be carried out on a 20 kg/h intermediate pyrolysis reactor for production of large quantities of aqueous phase samples, which will be tested in long-term continuous anaerobic digestion experiments. Mass balances over the different pyrolysis conditions and process are reported with preliminary anaerobic digestion results.

# CARBON NANOTUBES AS VALUE ADDED PRODUCTS ALONG WITH HYDROGEN PRODUCTION BY PYROLYSIS CATALYTIC-GASIFICATION OF WASTE TIRES

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Currently, around 96% of hydrogen is produced from fossil fuels. For the development of a projected future hydrogen economy, hydrogen should be produced from alternative sources. In 2011, there was around 3.27 million tonnes of used tires arising in the Europe [1]. Among the current technologies being investigated for the treatment of waste tires, pyrolysis/gasification has shown great potential. The use of pyrolysis/gasification for hydrogen production would solve a waste problem and also generate an energy carrier for fuelling the future [2, 3].

One of the most important factors in maximising the yield of hydrogen from waste tires is the presence of a catalyst. From previous studies by many researchers, nickel-based catalyst are the most common catalysts used for hydrogen production from various waste materials by thermal processing because of their high thermal stability, surface area and hydrogen selectivity etc. [2, 4, 5]. However, adding a catalyst in the thermal decomposition process can result in catalyst deactivation by coke deposition on the surface of catalysts and cannot be avoided. Furthermore, research on the type of carbon deposited on the catalyst surface has shown that the carbon can be both amorphous and filamentous in character. Recently, the filamentous carbons have been shown to include carbon nanotubes (CNTs). Carbon nanotubes have been reported to present particular characteristic, chemical and physical properties which are linked to high value applications in electronics [6], biosensors [7], energy storage and reinforced composites etc. [8]. Therefore, production of CNTs as value added products can effectively increase the economic feasibility of hydrogen production from waste tires by the process of pyrolysis catalytic-gasification.

High-valued carbon nanotubes (CNTs) and hydrogen production have been investigated through the pyrolysis catalytic-gasification of waste tires using a two stage fixed-bed reactor in the presence of nickel based catalysts under a range of different process conditions. The influence of catalyst temperature, steam injection rate, and catalyst:tire ratio were investigated in terms of the yield of hydrogen and the yield and quality of the carbon nanotubes. The composition of the gaseous products was determined using gas chromatography (GC). Temperature programmed reduction (TPR) and X-ray diffraction (XRD) were used to characterize the fresh catalysts. The product CNTs and the reacted catalysts were analysed by a range of techniques, including temperature programmed oxidation (TPO), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Raman analysis.

The research shows that the development of a process to utilise waste tires to produce CNTs and hydrogen have great potential to turn a problematic formation of catalyst coke into an opportunity to recover high value carbon nanotubes in addition to the production of hydrogen from a source feedstock that is a problematic waste.

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AUTHORS'  
LIST

# Authors' list

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|                              |                      |                          |   |
|------------------------------|----------------------|--------------------------|---|
| Abbott Geoffrey              | p 298                | Boateng Akwasi           | p 105, 187, 238                                   |
| Abdelli Ghizlane             | p 301                | Bockland Roger           | p 227   |
| Adrados Aitziber             | p 191                | Bonaduce Ilaria          | p 34, 62  |
| Agnes Lattuati-Derieux       | p 302                | Boscagli Chiara          | p 224   |
| Aht-Ong Duangdao             | p 338                | Bostyn Stéphane          | p 254   |
| Akubo Kaltume                | p 334                | Bouchez Marc             | p 267   |
| Al Hussein Amelène           | p 301                | Bounaceur Roda           | p 256, 272, 275, 304, 320                         |
| Alarcon Salinas Sebastian    | p 56                 | Bozi Janos               | p 328, 359  |
| Alejandro Serguei            | p 206                | Bradley Jonathan         | p 298   |
| Al-Farraj Abbas              | p 186                | Bramer Eddy              | p 136, 211  |
| Allavena Audrey              | p 342                | Brazdausks Prans         | p 88  |
| Almeida Streitwieser Daniela | p 173                | Brem Gerrit              | p 136, 211  |
| Almendros Gonzalo            | p 300, 310, 315      | Bridgwater Anthony       | p 90, 101, 126, 142, 143, 148, 163, 234, 241, 373 |
| Alpermann Theodor            | p 270                | Briens Cedric            | p 178, 226, 261                                   |
| Al-Rahbi Amal                | p 335                | Brilhac Jean-François    | p 162   |
| Alvarez Ana M.               | p 315                | Brodin Fredrik           | p 231, 232  |
| Alvarez Jon                  | p 100, 336, 340      | Broust Francois          | p 228   |
| Alvarez-Murillo Andres       | p 171, 337           | Brzuszek Pawel           | p 323   |
| Amghizar Ismaël              | p 264                | Buffi Marco              | p 233   |
| Amutio Maider                | p 100, 336, 340      | Bulfaro Maria            | p 63  |
| Anastasakis Konstantinos     | p 282                | Burklé-Vitzthum Valérie  | p 256, 272, 304, 314, 320, 356                    |
| Anca-Couce Andres            | p 154                | Buss Wolfram             | p 202   |
| Anderson Ingeborga           | p 81                 | Bustos-Martinez Diana    | p 341   |
| Andersons Bruno              | p 81                 | Caballero Blanca Maria   | p 191   |
| Ando Daisuke                 | p 79                 | Cai Liang                | p 252   |
| André R.                     | p 290                | Calavia Alejandro        | p 366   |
| Aneke Mathew                 | p 194                | Capron Mickael           | p 53  |
| Anjorin Malahimi             | p 350                | Cara Jorge               | p 172   |
| Anquetil Christelle          | p 302                | Carr Andrew              | p 308   |
| Antuskova Vaclava            | p 57                 | Carral Pilar             | p 315   |
| Anu                          | p 58, 71             | Carré V.                 | p 236   |
| Apfelbacher Andreas          | p 182, 239, 240      | Carrier Marion           | p 143, 163  |
| Aragon Carlos                | p 345                | Carstensen Hans-Heinrich | p 173, 181  |
| Arias M. Enriqueta           | p 59                 | Cartoixa Bruno           | p 228   |
| Arregi Aitor                 | p 100, 336, 340      | Casal M                  | p 251   |
| Arshanitsa Alexandr          | p 60                 | Castello Daniele         | p 179   |
| Artetxe Maite                | p 100, 336, 340      | Castro Diaz Miguel       | p 208   |
| Asami Kenji                  | p 370                | Catala Lucia             | p 353, 354  |
| Ascough Philippa             | p 307                | Catteloin Delphine       | p 314   |
| Asmadi Mohd                  | p 203                | Ceamanos Jesus           | p 366   |
| Atienza-Martinez Maria       | p 366                | Celaya Javier            | p 231, 232  |
| Atong Duangduen              | p 112, 128, 338, 371 | Cerda Cristian           | p 206   |
| Aubriet F.                   | p 236                | Cersoy Sophie            | p 46  |
| Auret Lidia                  | p 163                | Chahen Ludovic           | p 225   |
| Azeez Akeem                  | p 78                 | Changsui Zhao            | p 252   |
| Azular Manuel                | p 198                | Chaouki Jamal            | p 283, 291  |
| Baccar Mounir                | p 355                | Charon Nadege            | p 225   |
| Bakos Gabriella              | p 328                | Chejne Farid             | p 127, 169, 260, 294                              |
| Balitskaya Ludmila           | p 306                | Chen Hanping             | p 164, 332  |
| Balitsky Vladimir            | p 306                | Chen Shangtao            | p 98  |
| Banks Charles                | p 373                | Chen Yingquan            | p 164   |
| Banks Scott                  | p 101, 142, 148      | Cheng Zhanjun            | p 253   |
| Banon Elena                  | p 339                | Cheon-Kyu Park           | p 244   |
| Barbarias Itsaso             | p 100, 336, 340      | Chetehouna Khaled        | p 267   |
| Barbiero Chiara              | p 110                | Chiaramonti David        | p 233   |
| Barres Odile                 | p 306                | Choi In-Gyu              | p 120, 242  |
| Barriocanal Carmen           | p 160, 208, 250, 251 | Choi Jae-Wook            | p 192   |
| Barta-Rajnai Eszter          | p 199, 207, 328      | Choi Joon Weon           | p 117, 120, 125, 210, 242                         |
| Bartley Laura                | p 139                | Chong Katie              | p 234   |
| Bartoli Mattia               | p 61, 230            | Chrubasik Maciej         | p 89  |
| Battin-Leclerc Frédérique    | p 253, 273, 279      | Chunfei Wu               | p 330   |
| Bauer Alan                   | p 319                | Cirule Dace              | p 81  |
| Béhar Françoise              | p 272                | Colin Baptiste           | p 347, 350  |
| Belandria Veronica           | p 254                | Collard Francois-Xavier  | p 213   |
| Bensabath Tsilla             | p 271                | Collard Marie            | p 342   |
| Bente Von Frowein Matthias   | p 67                 | Colmenares Juan          | p 276   |
| Berruti Franco               | p 226, 261           | Colombano Stéfan         | p 299, 311  |
| Biache Coralie               | p 299, 311           | Colombini Maria Perla    | p 62, 63, 80, 83, 124, 170                        |
| Bianchini Emma               | p 111                | Commandre Jean-Michel    | p 200   |
| Bikovens Oskars              | p 60                 | Conesa Juan A.           | p 343, 344  |
| Bin Li                       | p 161, 166           | Conrad Stefan            | p 235   |
| Binder Janos                 | p 78, 246            | Conti Roberto            | p 182, 360  |
| Binder Samir                 | p 182                | Costa Mario              | p 156   |
| Blanquez Alba                | p 59                 | Cozzani Valerio          | p 64  |
| Blazso Marianne              | p 328                | Crossley Steven          | p 105, 174  |

|                               |                          |                              |  |
|-------------------------------|--------------------------|------------------------------|--|
| Custodis Victoria             | p 102                    | Ghalibaf Maryam              | p 144                                  |
| Czégény Zsuzsanna             | p 199, 207, 328, 359     | Ghidotti Michele             | p 69                                   |
| Da Silva Perez Denilson       | p 201                    | Girods Pierre                | p 347, 350                             |
| Daheur Ghizlene               | p 46, 65                 | Giudicianni Paola            | p 156                                  |
| Dahmen Nicolaus               | p 134, 188               | Glaude Pierre-Alexandre      | p 271, 274                             |
| Danon Bart                    | p 358                    | Gley Renaud                  | p 319                                  |
| Daschner Robert               | p 182, 239, 240          | Gokalp Iskender              | p 254                                  |
| Dauenhauer Paul               | p 155                    | Gomez Natalia                | p 172                                  |
| De Bruycker Ruben             | p 264                    | Goncharov Ivan               | p 317, 318, 326                        |
| De Jong Wiebren               | p 282                    | Gong Xun                     | p 157                                  |
| De La Rosa José M.            | p 70, 300, 310, 325, 345 | Gonzalez Gonzalez Juan Félix | p 171, 337                             |
| De Luca Daphne                | p 82                     | Gonzalez Martinez Maria      | p 201                                  |
| De Marco Isabel               | p 191                    | Gonzalez-Pérez José A.       | p 59, 70, 300, 310, 315, 316, 325, 345 |
| De Wild Paul                  | p 180                    | Gonzalez-Quiroga Arturo      | p 181                                  |
| Debal Matthieu                | p 350                    | Gonzalez-Vila Francisco J.   | p 59, 70, 300, 310, 315, 316           |
| Degano Ilaria                 | p 62                     | Gorgens Johann               | p 213, 358                             |
| Derenne Sylvie                | p 302                    | Gourdon Christophe           | p 201                                  |
| Descamps Cédric               | p 265                    | Goyal Himanshu               | p 138                                  |
| Di Primio Rolando             | p 36                     | Graham Margaret              | p 202                                  |
| Diaz-Faes Elvira              | p 160, 208, 250, 251     | Grandl Robert                | p 134                                  |
| Dizhbite Tatiana              | p 60                     | Granged Arturo J. P.         | p 316                                  |
| Dobele Galina                 | p 81, 88, 151            | Grasset Laurent              | p 301, 312                             |
| Domke Anna-Maria              | p 246                    | Greenhalf Charles            | p 226                                  |
| Donar Yusuf                   | p 219                    | Grinins Juris                | p 81                                   |
| Doucet Jocelyn                | p 283                    | Gronli Morten                | p 199                                  |
| Dowling Jennifer              | p 92                     | Grottola Corinna             | p 156                                  |
| Duan Lunbo                    | p 252, 346               | Grunwaldt Jan-Dierk          | p 224                                  |
| Duan Yuanqiang                | p 252                    | Gueissaz Line                | p 47                                   |
| Duarte Shirley                | p 209                    | Guerrini Franca              | p 111                                  |
| Duce Celia                    | p 62, 82                 | Guilhaume Nolven             | p 123                                  |
| Dufour Anthony                | p 66, 67, 356            | Guizani Chamseddine          | p 135                                  |
| Duman Gozde                   | p 103, 130, 131          | Gupta Munish                 | p 58, 71                               |
| Dumarcay Stephane             | p 68                     | Gutierrez Omar               | p 348                                  |
| Dupont Capucine               | p 201                    | Gyotoku Koji                 | p 370                                  |
| Ege Paul                      | p 226                    | Ha Jeong-Myeong              | p 192                                  |
| Eidem Per                     | p 220                    | Ha Jong Han                  | p 146, 244                             |
| Elkasabi Yaseen               | p 105, 187               | Hakola Maija                 | p 264                                  |
| Fabbri Daniele                | p 111                    | Hall Keith                   | p 36                                   |
| Fagla Benoît                  | p 350                    | Hamzehlouia Sepehr           | p 291                                  |
| Fang Yan                      | p 196                    | Han Bin                      | p 46, 65                               |
| Faravelli T.                  | p 35                     | Han Jeong Sik                | p 121                                  |
| Faure Pierre                  | p 299, 311               | Han Tae Uk                   | p 72, 349                              |
| Fernandez Ana                 | p 251                    | Haussener Sophia             | p 168                                  |
| Fernandez Octavio             | p 325                    | Hauteville Yann              | p 313, 314                             |
| Ferreira Deyanira             | p 53                     | Hawangchu Yotwadee           | p 112                                  |
| Ferreiro Ana                  | p 156                    | Hayato Horii                 | p 73                                   |
| Fladung Matthias              | p 78                     | Heaven Sonia                 | p 373                                  |
| Florentino Laura              | p 160, 250               | Heeres H.j.                  | p 104, 113                             |
| Font Rafael                   | p 343, 344               | Heginbotham Arlen            | p 50                                   |
| Fonts Isabel                  | p 366                    | Hemati Mehrdji               | p 137                                  |
| Fournet René                  | p 265, 274               | Hemberger Patrick            | p 102                                  |
| Frassoldati A.                | p 35                     | Heng Lijun                   | p 189                                  |
| Freire Fabio                  | p 336                    | Hense Peter                  | p 329                                  |
| Frottier Ophélie              | p 273                    | Herbinet Olivier             | p 253, 273, 279                        |
| Frye John                     | p 241                    | Hernandez Manuel             | p 59                                   |
| Fujimoto Kaoru                | p 370                    | Hertzog Jasmine              | p 236                                  |
| Fujita Kohei                  | p 351                    | Heydenrych Mike              | p 237                                  |
| Fujita Osamu                  | p 97                     | Hirasawa Masahiro            | p 370                                  |
| Fukutome Asuka                | p 165                    | Hochenauer Christoph         | p 154                                  |
| Funke Axel                    | p 134, 188               | Ho-Jeong Choi                | p 116                                  |
| Gambineri Francesca           | p 80                     | Honda Takayuki               | p 74, 95, 292                          |
| Gamma Fausto                  | p 267                    | Hong Yeojin                  | p 364                                  |
| Garcia Angela                 | p 339, 353, 354          | Hornung Andreas              | p 182, 239, 240, 329, 360              |
| Garcia-Perez Manuel           | p 294                    | Horsfield Brian              | p 36                                   |
| Garcia-Ramos Francisco Javier | p 198                    | Horst Thomas                 | p 331                                  |
| Garcia-Sanchez Angela         | p 325                    | Hosaka Akihiko               | p 77                                   |
| Garrido Maria                 | p 343, 344               | Hou Xu                       | p 258                                  |
| Gascoin Nicolas               | p 267                    | Howe Dan                     | p 294                                  |
| Gasson James                  | p 182, 360               | Hu Guo-Hua                   | p 356                                  |
| Gastelu Naia                  | p 191                    | Huamei Yang                  | p 280                                  |
| Gaudry Grégoire               | p 228                    | Husson Benoit                | p 253                                  |
| Gauthier-Maradei Paola        | p 53                     | Huyghe J.                    | p 106                                  |
| Gea Gloria                    | p 366                    | Hwang Byeonga                | p 72, 349                              |
| Geantet Christophe            | p 123                    | Hwang Hyewon                 | p 117, 120, 210                        |
| Gérardin Philippe             | p 68                     | Hwang Kyung-Ran              | p 121                                  |

|                             |                                   |                             |                                |
|-----------------------------|-----------------------------------|-----------------------------|--------------------------------|
| Hyung Ju Kim                | p 116                             | Lauberts Maris              | p 60                           |
| Idei Soichiro               | p 75                              | Laurenti Dorothée           | p 123                          |
| Iiguni Yoshinori            | p 49                              | Le Brech Yann               | p 66, 67, 236                  |
| Iisa Kristiina              | p 38                              | Le Masle Agnès              | p 225                          |
| Im Soo Ik                   | p 259                             | Le Meur Mathieu             | p 319                          |
| Ingenito Antonella          | p 267                             | Le Naour Bruno              | p 267                          |
| Isler Daniel                | p 37                              | Le Thanh Kim                | p 200                          |
| Ito Koichi                  | p 77, 285, 295                    | Lebourleuxa G.              | p 290                          |
| Jae Jungho                  | p 115, 118, 119, 192              | Leclerc Philippe            | p 283                          |
| Jäger Nils                  | p 182, 239, 360                   | Ledesma Cano Beatriz        | p 171, 337                     |
| Jakab Emma                  | p 207, 328                        | Lee Heejin                  | p 119, 364                     |
| Janos Soja                  | p 359                             | Lee Hyung Won               | p 119                          |
| Jayaraman Kandasamy         | p 254                             | Lee Jae Hoon                | p 117, 120, 125                |
| Jeon Jong-Ki                | p 115                             | Lee Jin-Hyuk                | p 121                          |
| Jeong Rang Kim              | p 116                             | Lee Jin-Suk                 | p 121                          |
| Jiaxiao Cai                 | p 166                             | Lee Ki Bong                 | p 259                          |
| Jimenez-Gonzalez Marco A.   | p 315                             | Lee Kyong-Hwan              | p 121                          |
| Jimenez-Morillo Nicasio T.  | p 59, 70, 300, 310, 315, 316, 345 | Lee Yejin                   | p 364                          |
| Jin Hanfeng                 | p 287                             | Lee Yunhee                  | p 349                          |
| Jonsson Helena              | p 76                              | Legros Robert               | p 291                          |
| Jordan Antonio              | p 316                             | Leguizamon Guerra Nestor Ca | p 320                          |
| Jung Sang-Chul              | p 115                             | Leibold Hans                | p 183, 188, 193                |
| Jun-Ichiro Hayashi          | p 280                             | Leijenhorst Evert           | p 243                          |
| Junk Rene                   | p 94                              | Leistner Franz              | p 36                           |
| Jurado Valme                | p 325                             | Lemee Laurent               | p 342                          |
| Jurkjane Vilhelmine         | p 60, 81, 151                     | Lemonon Jérôme              | p 347                          |
| Kaluza Stefan               | p 235                             | Leng Erwei                  | p 157                          |
| Kameda Tomohito             | p 351                             | Lenzi Francesco             | p 184                          |
| Kamiya Yoshimi              | p 292                             | Leon Milagros               | p 339, 353, 354                |
| Kaneko Asako                | p 84                              | Li Tian                     | p 195                          |
| Kano Ryota                  | p 91                              | Li Xiaoqiang                | p 303                          |
| Karakashov Blagoj           | p 201                             | Li Yuyang                   | p 287                          |
| Karpel Vel Leitner Nathalie | p 342                             | Liangliang Wu               | p 36                           |
| Kashapov Roman              | p 317, 318, 326                   | Liangyuan Jia               | p 67                           |
| Kawamoto Haruo              | p 145, 165, 203                   | Limarta Susan               | p 118                          |
| Ke Zhang                    | p 161, 166                        | Lin Fan                     | p 139                          |
| Kern Jürgen                 | p 345                             | Lindstrom Heidi             | p 284                          |
| Kersten Sascha R. A.        | p 179                             | Lisowski Pawel              | p 276                          |
| Khalil Roger                | p 199                             | Littke Ralf                 | p 303                          |
| Khandavilli Muralikrishna   | p 167                             | Liu Chao                    | p 48                           |
| Kierat Maria                | p 323                             | Liu Guozhu                  | p 257, 258, 266                |
| Kim Beom-Sik                | p 115                             | Liu Xiaotong                | p 129, 352                     |
| Kim Chul Ung                | p 116                             | Liu Ying                    | p 98                           |
| Kim Jae-Kon                 | p 146, 244                        | Liu Yunquan                 | p 147                          |
| Kim Jae-Young               | p 117                             | Lizardo Huerta Juan Carlos  | p 274                          |
| Kim Seungdo                 | p 72, 77, 115, 119, 349           | Lobban Lance                | p 139, 174                     |
| Kim Sin                     | p 244                             | Lopez Gartzen               | p 100, 336, 340                |
| Kim Young-Min               | p 72, 77, 115, 119, 349           | Lopez Rojas Luis            | p 356                          |
| Kitagawa Shinya             | p 49                              | Lopez-Urionabarrenechea Ale | p 191                          |
| Kittelsen Helge             | p 226                             | Lorgeoux Catherine          | p 299, 304, 311, 314, 319      |
| Kiura Masaaki               | p 84                              | Lorreyte Clarisse           | p 168                          |
| Kleine-Benne Eike           | p 284                             | Louwes Alexander            | p 136, 211                     |
| Klingbeil Sophie            | p 94                              | Lovas Terese                | p 195                          |
| Klingberg Andreas           | p 78, 246                         | Lu Pin                      | p 209                          |
| Knicker Heike               | p 70, 345                         | Lu Rong                     | p 79                           |
| Knoetze Hansie              | p 163                             | Lucejko Jeannette           | p 57, 80, 83                   |
| Konath Tim                  | p 193                             | Ma Hao                      | p 122                          |
| Koyo Norinaga               | p 280                             | Maduskar Saurabh            | p 155                          |
| Kple Melhyas                | p 350                             | Mahmood Nubla               | p 226                          |
| Kramer Jurjen               | p 114                             | Mallinson Richard           | p 139, 174                     |
| Kristianto Ivan             | p 118                             | Mangin Patrice              | p 261                          |
| Krooss Bernhard M           | p 303                             | Mann Ulrich                 | p 321, 322                     |
| Krumm Christoph             | p 155                             | Manso José Antonio          | p 198                          |
| Kruse Andrea                | p 214, 215                        | Mansuy-Huault Laurence      | p 319                          |
| Kuc@rova Irena              | p 57                              | Manya Joan                  | p 198                          |
| Kumagai Shogo               | p 351                             | Marcilla Antonio            | p 339, 353, 354                |
| Kutzke Hartmut              | p 80                              | Margeriat Alexandre         | p 123                          |
| La Nasa Jacopo              | p 62, 82                          | Marin Guy                   | p 173, 181, 264                |
| Laduranty Joelle            | p 342                             | Marquaire Paul-Marie        | p 256, 265, 272, 275, 304, 320 |
| Laiwang Bin                 | p 255                             | Marrugo Escobar Gloria      | p 169                          |
| Langston Paul               | p 217                             | Marrugo Gloria              | p 260                          |
| Lannuzel Frédéric           | p 256, 320                        | Marsan Olivier              | p 137                          |
| Lars-Ove Jonsson            | p 76                              | Martin Eric                 | p 200, 228                     |
| Latifi Mohammad             | p 291                             | Martinez Isabel             | p 353, 354                     |
| Lau Kornelia                | p 94                              | Martinez Olegario           | p 172                          |

|                                |                                     |                            |                              |
|--------------------------------|-------------------------------------|----------------------------|------------------------------|
| Masek Ondrej                   | p 202, 216, 276                     | Oh Shinyoung               | p 242                        |
| Masmoudi Amal                  | p 355                               | Ohtani Hajime              | p 49, 84, 91, 285, 295       |
| Massaro Arianna                | p 124                               | Ojha Deepak                | p 149                        |
| Massoli Patrizio               | p 111                               | Okamoto Shun               | p 85                         |
| Masson Amandine                | p 356                               | Okamoto Takahiro           | p 49                         |
| Massonnet Geneviève            | p 47                                | Olazar Martin              | p 100, 336, 340              |
| Mattonai Marco                 | p 170                               | Orsini Sibilla             | p 82                         |
| Matyasik Irena                 | p 323                               | Osmaa Anja                 | p 227                        |
| Mauss Fabian                   | p 195                               | Osorio Velasco Jessi       | p 127                        |
| Mauviel Guillain               | p 67, 356                           | Ostertag-Henning Christian | p 305                        |
| Mayoux C.                      | p 290                               | Otto Stefan                | p 286                        |
| Mcbeath Anna                   | p 307                               | Ouadi Miloud               | p 182, 360                   |
| Mcgrath Thomas                 | p 64                                | Ozaki Ryo                  | p 293                        |
| Md Saad Juniza                 | p 357                               | Pala Mehmet                | p 243                        |
| Mehrabian Ramin                | p 154                               | Palencia Cristian          | p 53                         |
| Mei Lei                        | p 346                               | Palza H.                   | p 348                        |
| Meier Dietrich                 | p 78                                | Pan Yang                   | p 287, 361                   |
| Meija-Feldmane Anete           | p 81                                | Paneque Marina             | p 345                        |
| Meile Kristine                 | p 88, 151                           | Park Cheon-Kyu             | p 146                        |
| Melkior Thierry                | p 212                               | Park Jo Yong               | p 146, 244                   |
| Mengerink Ynze                 | p 114                               | Park Shin Young            | p 117, 125                   |
| Merckel Ryan                   | p 237                               | Park Young-Kwon            | p 72, 77, 115, 119, 349, 364 |
| Mercy Michel                   | p 356                               | Paterson Nigel             | p 176                        |
| Meredith Will                  | p 307, 308                          | Paul T Williams            | p 300                        |
| Meyer Michel                   | p 200                               | Paze Aigars                | p 88                         |
| Meyer Xuan Mi                  | p 201                               | Pecate Sébastien           | p 137                        |
| Michael Soll                   | p 77                                | Pecha Brennan              | p 294                        |
| Michel Pauline                 | p 324                               | Pentelei Svetlana          | p 306                        |
| Michels Raymond                | p 256, 304, 306, 314, 320           | Pepiot Perrine             | p 138                        |
| Mignard Dimitri                | p 216                               | Pereira Manuel             | p 325                        |
| Millan Marcos                  | p 176                               | Perlman Cathleen           | p 195                        |
| Miller Ana Zelia               | p 300, 325                          | Perré Patrick              | p 209                        |
| Min Zhao                       | p 161, 166                          | Peyrot Marine              | p 135                        |
| Mirodatos Claude               | p 123                               | Philip Longhurst           | p 346                        |
| Miskolczi Norbert              | p 300, 359                          | Pieters Jan                | p 218                        |
| Miskolczi Norbert              | p 328                               | Pironon Jacques            | p 306                        |
| Miyakoshi Tetsuo               | p 79                                | Pistocchi Rossella         | p 111                        |
| Mkhize Ntandoyenkosi           | p 358                               | Plavniece Ance             | p 151                        |
| Modugno Francesca              | p 57, 62, 80, 82, 83                | Prins W.                   | p 106, 107, 243, 365         |
| Moliere Michel                 | p 247                               | Pritchard Colin            | p 216                        |
| Mommers John                   | p 114                               | Pron Herve                 | p 168                        |
| Momose Hikaru                  | p 84                                | Prussi Matteo              | p 233                        |
| Monnier Hubert                 | p 271                               | Puke Maris                 | p 88                         |
| Montagne Pierre                | p 247                               | Puype Franky               | p 86, 87, 362                |
| Montargès-Pelletier Emmanuelle | p 319                               | Qi Fei                     | p 67, 122, 253, 287          |
| Montecinos Adan                | p 206                               | Quicker Peter              | p 331                        |
| Monteiro Gonçalo               | p 209                               | Quignard Alain             | p 227                        |
| Montiano Maria                 | p 160                               | Rabaçal Miriam             | p 156                        |
| Montoya Jorge                  | p 260, 294                          | Raffelt Klaus              | p 224                        |
| Moon Jaegwan                   | p 117, 125                          | Ragucci Raffaele           | p 156                        |
| Morin Mathieu                  | p 137                               | Rakotoalimanana Darwin     | p 272                        |
| Mos Michal                     | p 148                               | Randhawa B.s.              | p 58, 71                     |
| Moss-Hayes Vikki               | p 308                               | Randi Aurélien             | p 304, 306, 314              |
| Mudsainiyan R.k.               | p 58, 71                            | Randrianalisoa Jaona       | p 168                        |
| Mullen Charles                 | p 105, 187, 238                     | Ranzi E.                   | p 35                         |
| Mundike Jhonnah                | p 213                               | Ratel Gilles               | p 135                        |
| Murakami Yayoi                 | p 370                               | Ratnasari Devy             | p 363                        |
| Muzyka Roksana                 | p 89                                | Raulf Martin               | p 246                        |
| Nagai Yoshitaka                | p 292                               | Ravikrishnan Vinu          | p 149                        |
| Nahil Mohamad                  | p 129, 190, 332, 334, 352, 357, 363 | Resasco Daniel             | p 174                        |
| Naifar Fahmi                   | p 355                               | Rho Nam Sun                | p 259                        |
| Nan Deng                       | p 161                               | Riasat Selma               | p 367                        |
| Navarro Rosa                   | p 353, 354                          | Ribechini Erika            | p 63, 124, 170               |
| Neumann Johannes               | p 182, 239, 240                     | Richter Frank              | p 183, 193                   |
| Ngamyng Chatri                 | p 214                               | Rizhikovs Janis            | p 88                         |
| Nielsen Henrik                 | p 220                               | Rizzo Andrea Maria         | p 233                        |
| Nimlos Mark                    | p 38                                | Ro Donghoon                | p 364                        |
| Nobuhiko Kitano                | p 74                                | Rodriguez Anne             | p 253                        |
| Noda Shuji                     | p 370                               | Rodriguez Correa Catalina  | p 214, 215                   |
| Noritake Sato                  | p 74                                | Rodriguez Juana            | p 59                         |
| Nowakowski Daniel              | p 90, 101, 126, 142, 148, 241, 367  | Rodriguez Nélide           | p 191                        |
| Nyman Tomi                     | p 264                               | Rodriguez-Machin Lizet     | p 365                        |
| Oblasov Nikolay                | p 318                               | Rogaume Yann               | p 347, 350                   |
| Oevering Henk                  | p 114                               | Rolon Juan                 | p 209                        |
| Oh Chang Ho                    | p 146, 244                          | Roman Juan                 | p 260                        |

|                            |                           |                      |                      |
|----------------------------|---------------------------|----------------------|----------------------|
| Roman Suero Silvia         | p 171, 337                | Strahan Gary         | p 238                |
| Rombola Alessandro         | p 111                     | Streibel Thorsten    | p 94, 286            |
| Ronsse Frederik            | p 106, 107, 218, 243, 365 | Suarez Sergio        | p 172                |
| Rosas Mayoral J. Guillermo | p 172                     | Suh Dong Jin         | p 115, 118, 119, 192 |
| Ross Andrew                | p 369                     | Surup Gerrit         | p 220                |
| Rotheut Martin             | p 331                     | Suwelack Kay         | p 215                |
| Rovira Pere                | p 301                     | Swain Eleanor        | p 298                |
| Roy-Poirier Audrey         | p 216                     | Szelewski Mike       | p 50                 |
| Ruiz Bailon Miguel         | p 228                     | Taddeo Lucio         | p 267                |
| Ruiz-Gomez Nadia           | p 366                     | Tae Wan Kim          | p 116                |
| Ruiz-Matute Ana I.         | p 310                     | Takahashi Shinichi   | p 95                 |
| Russell Scott              | p 217                     | Takayuki Honda       | p 73, 85, 293        |
| Saada Alain                | p 299, 311                | Takeuchi Kaoru       | p 84                 |
| Saari Pia                  | p 227                     | Tamburini Diego      | p 57, 80, 83         |
| Sabio Rey Eduardo          | p 337                     | Tani Haruki          | p 370                |
| Sablier Michel             | p 46, 65                  | Tavera Claudia       | p 53                 |
| Saenz Carlos               | p 282                     | Telgheder Ursula     | p 246                |
| Sahin Olga                 | p 210                     | Telysheva Galina     | p 60                 |
| Saiz Eva                   | p 198                     | Teramae Norio        | p 77, 285, 295       |
| Saiz-Jimenez Cesareo       | p 325                     | Tetsuo Miyakoshi     | p 96                 |
| Sajdak Marcin              | p 89, 90, 126, 367        | Teychene Benoit      | p 342                |
| Saka Shiro                 | p 145, 165, 203           | Thiery Sébastien     | p 201                |
| Sakai Shun                 | p 91                      | Tina Maria Rosaria   | p 62, 82             |
| Salvador Sylvain           | p 135                     | Tomasi Morgano Marco | p 183, 188, 193      |
| Sam Karen                  | p 92                      | Toraman Hilal        | p 173                |
| Samoilenko Vadim           | p 318, 326                | Torri Cristian       | p 111                |
| Sanchez Marta              | p 172                     | Toven Kai            | p 231, 232           |
| Santamaria Laura           | p 100, 336                | Tritz Audrey         | p 275                |
| Santosa Miki               | p 241                     | Trushkov Pavel       | p 318, 326           |
| Sanz Jesus                 | p 310                     | Tschentscher Roman   | p 103                |
| Sauer Jörg                 | p 134                     | Tumiatti Vander      | p 184                |
| Scacchi Gerard             | p 256                     | Turrion Juan         | p 217                |
| Schaffer Mark              | p 105                     | Ubaldi Vanessa       | p 82                 |
| Schaller Jean Pierre       | p 64                      | Uguna Clement        | p 208, 308           |
| Scharler Robert            | p 154                     | Ulbrich Anne         | p 286                |
| Schilling Michael          | p 50                      | Valdes Carlos        | p 169, 200           |
| Schmitt Nina               | p 240                     | Valin Sylvie         | p 135                |
| Schulzke Tim               | p 235                     | Van Bokhoven Jeroen  | p 102                |
| Schümann Ulrike            | p 94                      | Van De Beld Bert     | p 227                |
| Schuurman Yves             | p 123                     | Van Der Gryp Percy   | p 358                |
| Schwarzinger Bettina       | p 93                      | Van Geem Kevin       | p 173, 181, 264      |
| Schwarzinger Clemens       | p 93, 284, 368            | Van Keulen Henk      | p 50                 |
| Scova Alessandro           | p 184                     | Van Loo Tom          | p 235                |
| Sebestyen Zoltan           | p 207, 328                | Vane Christopher     | p 308                |
| Seidel Lars                | p 195                     | Vargas Diana         | p 173                |
| Seifert Helmut             | p 183                     | Varhegyi Gabor       | p 44, 199            |
| Shao Shanshan              | p 196                     | Vega Maria           | p 251                |
| Shen Dekui                 | p 372                     | Vehus Tore           | p 220                |
| Shi Xiaogang               | p 218                     | Venetsaneas Nikolaos | p 373                |
| Shin Sangcheol             | p 259                     | Vercruysse Jop       | p 106                |
| Shinji Kudo                | p 280                     | Verdier Laurent      | p 274                |
| Shinyoung Oh               | p 117                     | Verstraete Jan       | p 40                 |
| Shoji Taeko                | p 145                     | Vichaphund Supawan   | p 338, 371           |
| Simcock Kerry              | p 298                     | Villemont Clément    | p 178, 261           |
| Simon Yves                 | p 275, 277, 278           | Vilmont Léon-Bavi    | p 65                 |
| Sinag Ali                  | p 219                     | Vin Nicolas          | p 279                |
| Singh Sarisha              | p 51                      | Viteri Fausto        | p 268                |
| Sirjean Baptiste           | p 274                     | Wang Daqian          | p 332                |
| Sithole Bruce              | p 51, 52                  | Wang Duo             | p 147                |
| Skreiberg Oyvind           | p 199                     | Wang Liang           | p 199                |
| Smith Aidan                | p 369                     | Wang Meihong         | p 194                |
| Smith Maurice              | p 64                      | Wang Peng            | p 157                |
| Snape Colin                | p 208, 217, 301, 307      | Wang Yanfang         | p 98                 |
| Snieg Malwina              | p 142                     | Wang Yizun           | p 287                |
| Solantausta Yrjo           | p 39                      | Wang Zhandong        | p 253, 372           |
| Solar Jon                  | p 191                     | Wang Zhaocheng       | p 98                 |
| Soler Aurora               | p 343, 344                | Warchol Gerd         | p 368                |
| Soll Michael               | p 285, 295                | Watanabe Atsushi     | p 77, 285, 295       |
| Soon Yong Jeong            | p 116                     | Watanabe Chuichi     | p 285                |
| Soongprasit Kanit          | p 128                     | Waters Christopher   | p 139, 174           |
| Spepi Alessio              | p 82                      | Weber Kathrin        | p 195                |
| Sricharoenchaikul Viboon   | p 112, 128, 338, 371      | Weng Wu              | p 287                |
| Stapf Dieter               | p 193                     | Wenig Philip         | p 78, 246            |
| Stevens Lee                | p 208                     | Weniger Philipp      | p 303                |
| Stolarski Mariusz          | p 142                     | Westmoreland Phillip | p 158                |

|                        |   |
|------------------------|---|
| Williams Paul T.       | p 129, 190, 332, 334, 335, 352, 357, 363, 374 |
| Wilson Karen           | p 101   |
| Wirth E.               | p 290   |
| Worasuwannarak Nakorn  | p 175, 221                                    |
| Wu Chunfei             | p 129, 332, 352                               |
| Wu Rongcheng           | p 41  |
| Xiao Rui               | p 48, 189, 196, 372                           |
| Xiaole Li              | p 346   |
| Xu Charles             | p 226   |
| Xu Guangwen            | p 41  |
| Xu Minghou             | p 157   |
| Yamabuki Midori        | p 79  |
| Yan Hui                | p 97  |
| Yang Haiping           | p 164, 332                                    |
| Yang Jiuzhong          | p 287   |
| Yang Rui               | p 98  |
| Yang Yang              | p 373   |
| Yanik Jale             | p 130, 131                                    |
| Yao Dingding           | p 332   |
| Yildiz Guray           | p 107, 243                                    |
| Yin Xin                | p 150   |
| Ying Jiang             | p 346   |
| Yoo Kyung-Seun         | p 115   |
| Yoshioka T.            | p 42, 351                                     |
| Younes Khaled          | p 312   |
| Yu Jie                 | p 176   |
| Yuki Furutani          | p 280   |
| Zacher Alan            | p 241   |
| Zavala Lorena M.       | p 316   |
| Zazzo Antoine          | p 46  |
| Zeng Dewang            | p 196   |
| Zeng Jimin             | p 196   |
| Zhang Fengbo           | p 98  |
| Zhang Huiyan           | p 189   |
| Zhang Yang             | p 157   |
| Zhang Yeshui           | p 332, 352, 374                               |
| Zhao Long              | p 287   |
| Zhou Mengmeng          | p 189   |
| Zhou Zhongyue          | p 122, 287                                    |
| Zhu Cheng              | p 155   |
| Zhu Shenjia            | p 147   |
| Zhurinsh Aivars        | p 88, 151                                     |
| Ziegler-Devin Isabelle | p 265, 275                                    |
| Zimmermann Ralf        | p 94, 286                                     |
| Zuber Gerard           | p 64  |

Friday 13<sup>th</sup> – 8:30 :

ENSIC (Room Wahl)

Sunday 8<sup>th</sup> – 14:00:

Musée Lorrain

Monday 9<sup>th</sup> – 17:00:

Fine Arts Museum

Tuesday 10<sup>th</sup> – 19:30:

Opéra

Wednesday 11<sup>th</sup> – 18h45:

Place Stanislas (in front of  
the Tourism Office)

Thursday 12<sup>th</sup> – 20:00:

City Hall

Congress location:

Faculty of Pharmacy

Railway Station



Bus stop (line T2):

Hôpital Central - Maternité

Bus line T2

