



Soirée in honour of Prof. Michael J. Antal, Jr

Fine Arts Museum – Nancy May 9, 2016

By Dr Jacques Lédé, Emeritus Research Director, CNRS, Nancy (France) E-mail : jacques.lede@univ-lorraine.fr Ladies and Gentlemen, Dear friends of Pyrolysis, Dear friends of Michael, Dear Ann,

First of all, I want to warmly thank Ann Antal who agreed to be with us during this evening.

Last year, during the planning period of Pyro 16, Prof. Michael Antal suggested that we arrange a special soirée linking together Science, Art and history. He agreed to present an invited speech entitled : "The Art, Archeology and History of Wood Pyrolysis". Full of genious imagination, Michael suggested also that we write a play (in the form of theater like Molière) where Violette (middle of the 19th century) would have discussions and debates with current experts in Pyrolysis !

Michael vas delighted at the thought of attending Pyro 16, and on October 14, he wrote us : "I have looked forward to your meeting more than any other in my life". At that time, he hoped to send us his presentation by the end of last December.

Unfortunately, one week later, Michael died.

So, we have decided to keep the idea of a session in this Museum and to devote the full soirée to the memory of Michael.

Organization of the soirée : Programme

18h00-18h30 : Keynote

Analytical Pyrolysis as a tool for the characterization of organic materials in cultural heritage. Dr Ilaria BONADUCE

18h30-18h40 : In remembrance of Prof. Michael J. ANTAL. Dr Jacques LEDE

18h40-19h00:

Towards a realistic kinetics in non-isothermal studies. 30 years of a US-Hungarian cooperation in biomass research. Dr Gabor VARHEGYI

19h00-19h20 :

Towards the maximum theoretical yields of charcoal from biomass pyrolysis. Dr Morten GRONLI, Dr Wang LIANG and Oyvind SKREIBERG

19h20-21h00 : Cocktail





In remembrance of

Pr. Michael J. Antal, Jr

Last October, the world of research lost an outstanding scientist and the community of biomass and pyrolysis, his most renowned specialist.

During several decades, Michael has been and continues to be THE reference in the field of biomass pyrolysis/gasification. He worked on practically all areas of biomass research and development, without respite during about 40 years, from 1976 (3 years after he got his PhD at Harward University) until last year. During his outstanding career, Michael published about 175 papers with about 10 700 citations ! His publications are among the most heavily cited of the engineering literature. The record is a paper co-authored with Gabor Varhegyi and cited 613 times ! Still more amazing is the number of his conferences presented all over the world. We shall never forget his extraordinary clean lectures : science seemed so easy !

However besides these often cited papers, other ones reporting also pioneering works are less known.

When I met him for the first time in Albuquerque (NM) in 1979, he had top interests with the use of solar energy for driving chemical reactions such as biomass fast pyrolysis.



RADIANT FLASH PYROLYSIS OF BIOMASS

-71-

Michael J. Antal, Jr. Assistant Professor Department of Aerospace and Mechanical Engineering Princeton University Princeton, New Jersey 08544

ABSTRACT

The pyrolysis of biomass is a three step process: (1) pyrolysis of the solid material producing gaseous volatile matter and char, (2) higher temperature gas phase pyrolysis (cracking) of the volatile matter producing permanant gases, (3) and gasification of the char at still higher temperatures. Products, rates and mechanisms of the primary, solid phase pyrolysis step are reviewed in references 1-3, and the products and rates of the gas phase pyrolysis step are reviewed in references 4-6.

The use of solar heat for biomass gasification has been under development at Princeton for the past five years. Because the char byproduct of step 1 is less valuable than the gaseous products, and because flash pyrolysis reduces char formation and enhances gas production, the use of solar heat to achieve flash pyrolysis of the biomass feedstock appears to be especially attractive. The general scientific and technological aspects of solar biomass gasification are reviewed in references 7-14. A case study of solar biomass gasification, including very detailed economic projections, is given in reference 15. The potential impact of solar biomass gasification on New Jersey and developing countries is discussed in references 16 and 17. Finally the results of recent experiments on solar flash pyrolysis, involving a team of U.S. and French scientists, are described in reference 18.

These references may be obtained from the author if they are not otherwise

available.

One year later in 1980 at the Specialist's workshop on fast pyrolysis held in Copper Mountain (Co), he described several experiments performed at Princeton University with solar simulators. This meeting was a top event and each one should have the proceedings on his desk.



BENCH SCALE RADIANT FLASH PYROLYSIS OF BIOMASS

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The results of continuing research at Princeton University on the radiant flash pyrolysis of biomass as a source of fluid fuels, industrial feedstocks and chemicals is described in this paper. Bench scale sources of intense, visible radiant energy have been used to simulate the concentrated solar flux available at the focus of solar towers. Windowed transport reactors have been developed, which act as cavity receivers for the focused radiant energy and provide a means for direct use of the radiation to rapidly pyrolyze the entering biomass. Detailed results of bench scale experiments are presented, which suggest the use of concentrated radiant energy as a selective means for the production of sugar related syrups from biomass by flash pyrolysis.

INTRODUCTION

The flash pyrolysis of biomass requires a source of high quality heat. Early work at Princeton [1-7] identified concentrated solar radiation as an attractive means for rapidly heating the biomass and thereby achieving flash pyrolysis. When used in this fashion the solar heat input is effectively stored in the form of a fluid fuel. This storage aspect overcomes some of the problems associated with the intermittent nature of solar heat. The energy of the biomass feedstock is preserved by the use of an external heat source for pyrolysis, so that the product energy leaving the reactor is equal to or greater than the feedstock energy entering the reactor. Because the solar heat input is only about 10% of the biomass energy throughput, the cost of the solar concentrator plays only a small role in the overall economics of the system. Thus the useful energy output of a solar concentrator system is magnified by about a factor of ten when the solar heat is used to pyrolyze biomass; in contrast with electric power production which reduces the useful energy output of the concentrator by a factor of three. Experimental work at Princeton suggests that the yields of valuable chemicals such as ethylene may be enhanced through the use of



33 years ago, **Michael already** pointed out the numerous interests of solar fast pyrolysis. In this table, he already anticipated the advantages of so called "sirups" that could be compared to current bio oils. He was also among the first to mention the idea of biomass central refinery.

Solar Energy, Vol. 30, No. 4, pp. 299-312, 1983 Printed in Great Britain. 0038-092X/83/040299-14\$03.00/0 Pergamon Press Ltd.

DESIGN AND OPERATION OF A SOLAR FIRED BIOMASS FLASH PYROLYSIS REACTOR

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and

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(Received 23 November 1981; accepted 7 June 1982)

Table 1. Advantages of a solar-fired biomass flash pyrolysis reactor

- Solar heat is stored in the form of a useful fluid fuel; thus overcoming the intermittent nature of solar energy.[2]
- The energy of the biomass feedstock is preserved or even magnified by the use of a solar furnace for gasification.[2]
- Solar furnaces enjoy few economies of scale; consequently the solar furnace can be sized to the modest scale of a biomass resource without economic penalty.[2]
- The system does not require an expensive oxygen plant to gasify biomass; moreover the gaseous fuel product is low in carbon dioxide and nitrogen, making it a high quality fuel.[3]
- Because the solar heat input is only about 10% of the biomass energy throughput, the cost of the solar concentrator plays only a modest role in the overall economics of the system. [8]
- 6. Valuable byproduct chemicals, such as ethylene, can be produced by the flash pyrolysis process. $\left[5\right]$
- The ability of the system to rapidly heat and flash pyrolyze biomass results in a very large throughput with reduced capital costs per unit of fuel produced.[9]
- 8. The system has negligible thermal mass and the biomass resides in the reactor for about 1 second; consequently the reactor adapts well to partly cloudy day situations when it must "warm up" and "shut down" almost instantaneously. [2]
- Extraordinary yields of liquid fuels (sirups) can be obtained from biomass processed by the reactor, when two temperatures are effected within it. [10]
- Liquid sirups are easily stored; thereby serving as a buffer between the intermittent availability of solar energy and the continuous operation of a central refinery.
- Liquid sirups can also serve as an interface between the inherently small scale of biomass conversion facilities and the large scales of central refineries.
- The sirups are an exciting new chemical feedstock with more potential uses than petroleum.

Table 2. High value uses for sirups produced from ligno cellulosic biomass using a solar fired flash pyrolysis reactor

- Polyurethane foam from polydiethylene glycol levoglucosan [29]
- Pharmaceutical products based on a chloral ester of levoglucosan [30]
- Ethanol or other products by enzymatic or microbial fermentation of levoglucosan
- Levulinic acid from levoglucosan as a basic chemical raw material [31]
- Glucose by hydrolysis of levoglucosan as an edible material derived from wood
- Surfactants produced from levoglucosan and related anhydrous sugars
- Gas phase pyrolysis of the sirups as a source of olefins

Michal worked in several solar furnaces (including the big facility of Odeillo, France) and built more than 5 solar simulators. He also designed and operated a very original fast thermogravimetric analyser (the most powerful in USA).

These works performed at Princeton and Hawaii Universities lasted about 13 years until 1989 with the publication of more than 10 papers and numerous conferences full of valuable informations. Michael had also numerous activities in the field of supercritical water with many collaborations all over the world with a great number of papers. The objectives were biomass gasification (H_2) and also ethanol or chemicals preparations. Here is the result of a discussion we had on the design of a supercritical water reactor.



A not enough cited paper was published 20 years ago. The paper clearly points out the important mistakes that can be made in the definitions of the actual reaction temperature and heating rate of a pyrolysing biomass particle (even very fine), submitted to severe heating conditions, with important consequences in the determination of Arrhenius kinetic constants, and bringing also an explanation to the "compensation effect".



Dean Jarques. it was great to see your marsel in Range Howard few extra cogness of the pagen. Maybe give one to Villermeux? Have 9 great Summer. Ravt agards michael

Thermal Lag, Fusion, and the Compensation Effect during Biomass Pyrolysis

Ravi Narayan and Michael Jerry Antal, Jr. Hawaii Natural Energy Institute and Department of Mechanical

Engineering, University of Hawaii at Manoa, Honolulu, Hawaii 96822 However, and until last year, the main interests of Michael were focused on charcoal. Gabor Varhegyi and Morten Gronli will report full details on these central topics in their two following presentations.

Michal was THE reference in the fields of fundamental chemistry, thermodynamics and kinetics. He was also a pioneer in engineering, modelling. For example, he was among the first to publish detailed mathematical models representing the pyrolytic behavior of a biomass particle. Also, he designed, operated and modeled different types of high temperature reactors.





... and also the tubular reactor in laminar flow : he pointed out the important errors that can be made in assuming simple plug flow ; also flash carbonization reactor : etc.

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Evaluation of Systematic Error Incurred in the Plug Flow Idealization of Tubular Flow Reactor Data

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When the plug flow idealization is used to treat tubular flow reactor data, systematic error can be introduced into calculated values of the reaction rate constant K and apparent activation energy E. In the worst case (when the plug flow idealization is (mis)used to evaluate data taken from an ideal, laminar flow reactor), the magnitude of the systematic error in K and E can be evaluated in closed form. In all cases the systematic error reduces the calculated values of K and E below their true values. For single-step, irreversible reactions of order 1/2, 3/4, 1, 3/2, and 2 at moderate conversions, the fractional systematic error in K does not exceed 20% of its true value, whereas the fractional systematic error in E remains below 10%. Thus, in the worst case the fractional systematic error in K and E due to a misuse of the plug flow idealization is comparable in magnitude to random errors introduced into K and E from uncertainties in analytic techniques and the measurement of residence time at reaction conditions.

Introduction

Tubular flow reactors are used by many chemists and engineers to make kinetic studies of combustion,1 pyrolysis,² and photolysis³ chemistry. Bench scale, tubular flow reactors usually operate in the laminar flow regime. In spite of the fluid's parabolic velocity profile within the tubular reactor, chemical kinetic parameters are almost always obtained from tubular flow reactor data by use of the plug flow idealization. Many experimental and theoretical examinations of the validity of the plug flow idealization have appeared in the literature.4-18 The re-

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sults of these examinations were recently summarized¹⁹ in the form of criteria (based on characteristic times describing the operating conditions of the flow reactor) that ensure the validity of the plug flow idealization. In our experience, it is usually possible to design a tubular flow reactor intended for kinetic studies that satisfies these criteria.²⁰ Such reactors may be used in research concerning homogeneous catalytic, pyrolytic, photolytic, or solvolvtic phenomena.

Although a tubular flow reactor may be initially designed to operate in the plug flow regime, it is not unusual for researchers to extend its use to regimes beyond those originally envisaged. Under such circumstances, significant departures from the intended plug flow regime may occur. This possibility prompts the question: In the worst possible case, how much systematic error will be introduced into kinetic parameters when the plug flow idealization is used to treat laminar flow reactor data? The purpose of this brief paper is to answer this question for single-step, irreversible chemical reactions of order 1/2, 3/4, 1, 3/2, and 2. Methods outlined here can be used to evaluate the magnitudes of this systematic error for any other reaction order that may be of interest.

27. 691-697.

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Every one looking at the list of references of his papers İS impressed by the number Of And citations. he could comment on every one ! Last but not least, he liked to cite and comment on very old works. For example, those performed in France during the 19th century as we can see here in the Introduction of his last paper where he described and commented the results of Mollerat (1808) during the Napoleonic wars and also those of Violette in 1853.

energy&fuels-

Biomass Pyrolysis in Sealed Vessels. Fixed-Carbon Yields from Avicel Cellulose That Realize the Theoretical Limit

Sam Van Wesenbeeck,**[†] Charissa Higashi,[†] Maider Legarra,[†] Liang Wang,[‡] and Michael Jerry Antal, Jr.[†]

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INTRODUCTION

in 1808, Møllerat presented a "Memoire" 1 to the Institute of France which newly invented an efficient method for the production of charcoal that he asserted would "... enable the forests of France to produce double the quantity of carbon that they give today; and France, would no longer be obliged to purchase 100 million [sic] of iron from its neighbors, would be able to sell, each year, a similar quantity of its surplus." This Memoire is noteworthy because the availability of iron in France was a lynchpin of Napoleon's military juggernaut (e.g., on 5 June 1808 the French army defeated the Austrian forces at Wagram). Unfortunately, to the best of our knowledge no engineering record remains of Møllerat's invention. Today mankind finds itself at war with climate change, and the production of charcoal for use as a reductant (e.g., to smelt iron ore²⁻⁵ or produce silicon^{6,7}) has regained the importance it enjoyed during the Napoleonic Wars.

As Mollerat emphasized in his Memoire of 1808, the efficiency of the carbonization process is the critical element of charcoal production. Remarkably, astounding research on this topic surfaced less than half a century later: **41853**, Volence described to the French Academy his legendary studies¹⁰ of wood pyrolysis that attained unprecedented charcoal yields. The following are highlights of Violette's findings:

- Dry wood (1 g) was carbonized from "150" to "350 °C" in sealed glass tubes (4 at each temperature with little void volume); each tube was held in a metal safety container because carbonization created "enormous" gas pressures.
- Violette reported a charcoal yield of 78.7% at 320 °C with %C = 65.6% (vs a comparable yield of 29.7% at 0.1 MPa)!
- Charcoal at 180 °C was said to resemble ordinary "red" charcoal at 280 °C.
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Charcoal at 300 °C was said to resemble coking coal having undergone melting: glossy, shiny, brittle, and bonded to the glass tube.

Article

pubs.acs.org/EF

5. Violette measured ash contents of 3-4% vs 0.5% in the case of ordinary charcoal.

Unfortunately, in the 1850s, the temperature scale was not well defined (for example, Violette believed that antimony melted at 432 °C, whereas its true melting point is 631 °C); consequently, in some cases the temperatures mentioned in Violette's papers were underestimates of the true temperature. The promise of pyrolysis in sealed vessels languished for 140

reported differential scanning calorimetry (DSC) studies of the pyrolysis of small (<22 mg) samples of cellulose, hemicellulose, woody, and herbaccous species in sealed crucibles that revealed unexpected phenomena.

- The char yields were greatly enhanced by pyrolysis in sealed vessels.
- The pyrolysis reactions were exothermic for all cases studied.
- The reaction rates were greatly enhanced in sealed crucibles, and further enhanced by high moisture contents.

The enhancement of the char yield for cellulose (Avicel) pyrolysis was particularly striking as thermogravimetric analyses of cellulose reveal the extreme difficulty in achieving high yields of charcoal from pure cellulose. For example, Gronli et al.¹² reported char yields of 3.3 wt% from a 0.94 mg sample of Avicel cellulose heated to 400 °C in flowing nitrogen, that fell to 2.2 wt% for a 0.11 mg sample. Some researchers believe that the

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DOI: 10.1021/acs.energyfuels.5b02628 Energy Fuels 2016, 30, 480-491 On this example, you can see how Michael analyzed historical papers even written in French (here is a report of Violette of 1851).

Uhy is the dated (304) En partant des principes qui viennent d'être déduits de (305) l'expérience, il m'a été possible de léterminer expérimen-L'étude de chaque série se composera des recherches talement les lois de la distribution de l'élasticité dans les suivantes : corps à plusieurs axes rectangulaires, et même dans des 1º. Préparation des charbons; plaques présentant des axes obliques, pourvu que ces axes 2º. Analyse élémentaire des charbons; soient égaux. Cette dernière étude, qui est terminée, et 3º. Propriétés physiques et chimiques des charbonn dont j'aurai l'honneur de soumettre très-prochainement les résultats au jugement de l'Académie, a pu être applitelles que pesanteur spécifique, dureté, hygrométricité, conductibilité pour la chaleur, inflammabilité, etc. (ces quée à divers corps cristallisés, et, enfin, il m'a été posdernières recherches, non encore terminées, feront l'objet sible de construire artificiellement des verges et des plaqu d'un Mémoire faisant suite à celui-ci). élastiques se comportant comme celles qui sont cristallisées et qui pourront rendre quelques services à l'ensei-PREMIÈRE SÉRIE. 3. gnement, attendu qu'il est presque impossible de se procurer des plaques cristallines d'une grande dimension. Charbons d'un même bois préparés à des tem croissantes de 150 à 1500 degrés. meaning MÉMOIRE SUR LES CHARBONS DE Préparation des charbons d'un même bois à des températures croissantes. - Le bois de bourdaine a été coupé PAR M. VIOLETTE, en fragments cylindriques de om, of de longueur et om, or alpêtres, ancien Elève de l'Écol de diamètre, de manière à fournir des petites bottes cylin-Mémoire présenté à l'Académie des Sciences, le 12 mai 1851. driques composées de vingt brins, pesant 130 à 140 grammes l'une : ces brins ont été pris sur la même baguette autant que possible, ou sur des baguettes de grosseur et d'âge sem-Dans ce Mémoire, je comprends l'étude des quatre ries survantes des charbods de bois. blables. On a disposé autant de bottes qu'il a été nécessaire Premiere série. - Charbons d'un même bois (le bour-150°C1 de préparer d'échantillons. Ces bottes ont été, l'une après danne & préparés à des températures croissantes depuis l'autre, séchées à la température de 150 degrés centigrades. 150 degrés jusqu'au dels de 1 500 degrés centigrades. A cet effet, on les a soumises pendant deux heures à un-Deuxième série. - Charbons d'un même bois (le bourcourant de vapeur d'eau surchauffée à 150 degrés, dans le daine), préparés à des températures croissantes, en vase même petit appareil qui m'a servi à faire mes premières expéotea riences sur la carbonisation du bois par la vapeur d'eau surentièrement clos. Troisième serie. - Charbons de bois différents, provechauffée. Cet appareil est décrit dans mon Mémoire en date nant de la fabrication courante des poudreries de France. du 15 mai 1848, que j'ai lu à l'Académie des Sciences dans la Quatrième série. - Charbons de soixante-quinze espèces séance du 19 juin 1848, et qui a été publié en entier dans de bois, tant indigènes qu'exotiques, préparés à la tempé-. les Annales de Chimie et de Physique, 3º série, 1. XXIII. page 475. Je rappelle qu'il se compose d'un peut serpen rature constante de 300 degres. en fer surmontant un foyer, et communiquant, d'une pe THIS MATERIAL MAY BE PROTECTED Ann.de Chim. et de Phys., 3º série, v. XXXII. (Julitet 1851.) 20 BY COPYRIGHT LAW (Title 17 U.S. Code) this poper?! 8-p= 63074°C; not 432°C

See also his brilliant conference at Pyro14.



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Plenary speaker abstracts

The Fundamentals Biocarbon Formation at Elevated Pressure: From 1851 to the 21st Century

Antal MJ Jnr.

Higashi C, Phothisantikul P, Van Wesenbeeck S, Williams S

University of Hawaii, USA mantal@hawaii.edu

Most residents of Silicon Valley would be surprised to learn that their prosperity, reflecting the worldwide demand for iPhones, E-books, laptop computers, and photovoltaic panels, is built upon a foundation of wood charcoal. Silicon is produced in electric arc furnaces where carbon serves to reduce quartz (SiO₂) to molten silicon according to the idealized reaction: SiO₂ + 2C = Si + 2CO. Because of its extraordinary reactivity and unusual purity, charcoal is the only carbon reductant capable of forming the key intermediate (SiC) in the transformation of quartz to Si. This insight unveils wood charcoal (i.e. biocarbon) to be a keystone of modern civilization.

In this presentation I trace the evolution of mankind's scientific knowledge of biocarbon production. In 1851 Violette reported studies of wood carbonization in sealed glass tubes which endured considerable pressure at elevated temperatures and evoked unusual pyrolysis chemistry that led to very high charcoal yields. Despite the priority and promise of Violette's work, his experiments were never reproduced and his findings forgotten. More than a century later, research at Princeton University, and subsequently at the University of Hawaii (in collaboration with the Hungarian Academy of Sciences and the Norwegian University of Science and Technology) again pointed to the key role of elevated pressure in improving the yields of biocarbon from biomass. Research involving thermogravimetry, differential scanning calorimetry, muffle furnaces, pressurized laboratory and commercialscale carbonizers - combined with thermochemical equilibrium calculations - led to definitions of the theoretical, limiting fixed-carbon yield of charcoal that can be obtained from a biomass feedstock, and the attainment of experimental yields that exceeded 80% of the theoretical yield.

Now we report experiments that closely reproduce those of Violette and confirm many of his prescient observations. We employ small steel tubing bomb reactors rated to pressures above 13.9 MPa (2000 psig) at 300 °C that are heated quickly in a fluidized sandbath. Gas analysis is accomplished by an Agilent micro-GC and the charcoal product is subject to proximate analysis. The yield of tar is small. Carbonization occurs at much lower temperatures than customary at atmospheric pressure. In the case of Avicel cellulose, the experimental fixed-carbon yield of charcoal reaches the theoretical value attained when thermochemical equilibrium is established. To the best of our knowledge, this is the first time that a pyrolysis process has produced a cellulosic char whose vield attained its theoretical fixed-carbon "limit".

He found several of these old references at the Bibliothèque Nationale de France in Paris. Unfortunately, illness prevented him to visit the library of Chateau de Vincennes. His oldest described works date 38 000 years ago : in a paper co-authored with Morten Gronli and cited 510 times, he showed, on the basis of the drawings of Grotte Chauvet (France), that charcoal was the first material produced by man.

With such comprehensive knowledges, Michael could rapidly detect which researches performed all over the world were genious or not. A problem was that, when we thought to have a good idea, we rapidly discovered that he already published the same one 10 or 20 years before !

The Art, Science, and Technology of Charcoal Production[†]

Michael Jerry Antal, Jr.*

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Morten Grønli

SINTEF Energy Research, Thermal Energy, 7465 Trondheim, Norway

In this review, we summarize the knowledge of the production and properties of charcoal that has been accumulated over the past 38 millenia. The manipulation of pressure, moisture content, and gas flow enables biomass carbonization with fixed-carbon yields that approach—or attain— the theoretical limit after reaction times of a few tens of minutes. Much of the heat needed to carbonize the feed is released by vigorous, exothermic secondary reactions that reduce the formation of unwanted tars by augmenting the charcoal yield in a well-designed carbonizer. As a renewable fuel, charcoal has many attractive features: it contains virtually no sulfur or mercury and is low in nitrogen and ash; it is highly reactive yet easy to store and handle. Carbonized charcoal can be a good adsorbent with a large surface area and a semimetal with an electrical resistivity comparable to that of graphite. Recent advances in knowledge about the production and properties of charcoal presage its expanded use as a renewable fuel, reductant, adsorbent, and soil amendment.

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Introduction

Magnificent charcoal drawings in the Grotte Chauvet (see Figure 1), which are over 38 000¹ years old, bear witness to Cro-Magnon man's artistic creativity and native chemical engineering talents.^{2,3} The antiquity of this breathtaking artwork suggests that charcoal was

[†]This review is dedicated to the memory of Dr. John W. Shupe, founding Director of the Hawaii Natural Energy Institute of the University of Hawaii at Manoa.



Figure 1. Charcoal mounds on the floor of the Grotte Chauvet with charcoal drawings on the wall above. Similar drawings have been dated at $\sim 30~000^2$ to 38 000^1 years B.P. Photo courtesy of Prof. Jean Clottes.

the first synthetic material produced by man.^{2,3} Many millennia thereafter, but still before the dawn of recorded history, man employed shallow pits of charcoal

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nf. Jean Clottes. e first synthetic material produced by man.^{2,3} Ma

^{*} To whom correspondence should be addressed.

I had the great pleasure and honour to meet Michael several times since 1979 in various international meetings : last one at Pyro14, here with Ralph Overend, ...



... and also in France where he liked to spend some holidays in the south, in Paris and also in Nancy : we visited together this museum 5 years ago. We liked also to meet in good restaurants as here at the "Train bleu", with Ann and Muriel.



Also in various hikings as here near Copper Mountain (Co) in 1980





Or here near Seefeld, Tyrol (Austria) in 2000 with Morten and Barbara.



I have been always impressed by his human qualities and his extraordinary wide knowledges in so various fields such as : history, music, archeology, astronomy, photography, nature, environment, and ... chemistry of cooking : here is his favourite recipe of the famous cold cherry soup. All these passions were shared with Ann.

Meggyleves (Cold Cherry Soup)

to Jacquest Muriel:

Ann and Michael Antal Recipe from: Hungary, Born: Michigan

This is a traditional and delicious soup (leves) that is served as a first course in Hungary. Meggyleves is perfect for hot summer days. Other berries or peaches may be substituted for the cherries, but then you would have a different kind of leves. When made with fresh cherries, this soup is heavenly.

Jó étvágyat! Correction: cons of 2 (141/2 02.) cherries

Ingredients:

- 14 1/2 cans of cherries el used one can of tart cherries and one can of Bing cherries, but you could use two cans of tart cherries if desired. Do not drain the cherries. If you have fresh cherries, use two lbs. pitted fresh cherries and 3 1/2 cups of water. Put the cherry pits in a cheesecloth bag with the spices to give the soup more flavor.)
- 4-5 cloves
- 1 stick of cinnamon .
- ²/₃ cup superfine sugar
- Juice of 1 lemon
- 3/4 cup white wine (e.g. Tokay wine) .
- Pinch of salt
- 2 egg yolks
- 3/4 cup half and half
- Whipped cream (optional)

Directions:

- 1) Bring cherries to a boil in their juice with the spices (in a cheesecloth bag), sugar, lemon juice, wine, and salt. Simmer gently for 10-15 min. to blend the flavors.
- Remove half of the cherries from the mixture. Purée the cherries you 2) have removed from the main mixture. Return them to the main mixture.
- 3) Bring the mixture to a boil again and let cool before adding the egg mixture or it will cook the egg.
- Separately mix the egg yolks with the half and half. Add one cupful 4) of the cherry soup to the egg and cream mixture, stirring constantly.
- Now pour all of the egg and half and half mixture into the soup, stirring to mix. Be careful not to let the soup boil when you are mixing in the eggs and half and half, or it will curdle!
- Remove from heat. Remove the bag of spices. Chill the soup thoroughly. Serve the soup chilled, topped with a dollop of whipped cream, if desired.



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I was also impressed by his way of life and his sportive activities as skiing, jogging, dancing and cycling in various places in the world.



Ann and Michael 2014

However, Michael never forgot biomass. And I shall always remember our numerous fruitful and sometimes heated discussions on solar chemistry, pyrolysis reactors, fusion-like phenomenon, Broido Shafizadeh model, active cellulose and much other topics...



energy fuels-

Biomass Pyrolysis in Sealed Vessels. Fixed-Carbon Yields from Avicel Cellulose That Realize the Theoretical Limit

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The time of my presentation is now over. Never forget that, one day before he died, Michael submitted a last paper to Energy and Fuels. In the Acknowledgements, we can read the first sentence written by his co-authors: "The coauthors thank an extraordinary scholar, a mentor, but foremost a friend : "Bon Voyage", Dr ANTAL".

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Thank you,

Michael