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

Fine Arts Museum – Nancy
May 9, 2016

By Dr Jacques Lédé,
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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 was 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.
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.
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.
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.

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

Table 2. High value uses for sirups produced from ligno-cellulosic biomass using a solar fired flash pyrolysis reactor
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".
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.
For example, the spouted bed ...
... 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.

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 misused 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, 1, 1/2, 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,1 and photolysis1 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.2-6 The results of these examinations were recently summarized 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.7-9 Such reactors may be used in research concerning homogeneous catalytic, pyrolytic, photolytic, or solvolytic 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, 1, 1/2, and 2. Methods outlined here can be used to evaluate the magnitude of this systematic error for any other reaction order that may be of interest.

Every one looking at the list of references of his papers is impressed by the number of citations. And 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.
On this example, you can see how Michael analyzed historical papers even written in French (here is a report of Violette of 1851).
See also his brilliant conference at Pyro14.
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 genius 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

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In this review, we summarize the knowledge of the production and properties of charcoal that has been accumulated over the past 38 millennia. 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 pressage 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 38 000 years old, bear witness to Cro-Magnon man's artistic creativity and native chemical engineering talents.2 The antiquity of this breathtaking artwork suggests that charcoal was the first synthetic material produced by man.3 Many millennia thereafter, but still before the dawn of recorded history, man employed shallow pits of charcoal

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2. This review is dedicated to the memory of Dr. John W. Shape, founding Director of the Hawaii Natural Energy Institute of the University of Hawaii at Manoa.

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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)**

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:** 2 (1 4 1/2 oz.) cans of cherries

**Ingredients:**
- 14 1/2 cans of cherries  
- 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 cherries in a cheesecloth bag with the spices to give the soup more flavor.
- 4-5 cloves
- 1 stick of cinnamon
- 3/4 cup superfine sugar
- Juice of 1 lemon
- 1/4 cup white wine (e.g. Tokay wine)
- Pinch of salt
- 2 egg yolks
- 1/4 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.
2. Remove half of the cherries from the mixture. Purée the cherries you 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.
4. Separately mix the egg yolks with the half and half. Add one cupful of the cherry soup to the egg and cream mixture, stirring constantly.
5. 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!
6. 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.
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.
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...
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 co-authors thank an extraordinary scholar, a mentor, but foremost a friend: “Bon voyage”, Dr. Antal.”
Thank you,

Michael