PyNe

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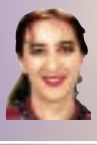

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The Future.

EU + IEA Bioenergy = PyNe

With effect from January 1998, the EC Sponsored Pyrolysis Network amalgamated with the new IEA Bioenergy Pyrolysis Activity and is now to be known as PyNe.

This Newsletter will be maintained as a biannual publication and will report on a wide range of topical and news items. We are pleased to welcome Canada and the USA and are sure that they will make a valuable contribution to the activities of the Network as well as learning about the many European projects.

MARCH 1998 ISSUE 5

Pyrolysis Network.

ASTON UNIVERSITY

Comments and contributions are most welcome on any aspect of the contents.
Please contact your country representative for further details or send material to Claire Humphreys.

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Conference & meeting reports.

Compiled by Filomena Pinto, INETI, Portugal and Cordner Peacocke, Aston University, UK

Workshop–
Residues for Energy Production

This Workshop took place in Coimbra, Portugal, from 24-26 November 1997 with the aim of promoting a dialogue between industrial companies and research institutions for the energetic valorisation of biomass.
This had the objective to not only to show the strategic vectors of energy diversification, but also to clearly identify business opportunities.

The programme was divided into four main areas:

1. Harvesting, processing and conditioning of forest residues
2. Energetic valorisation of forest residues
3. Energetic valorisation of other residues
4. Energy conversion technologies

The following oral presentations were made and discussed with the audience:

- Biomass flux analysis – *CBE, Portugal*
- Finnish technology for wood fuel and integrated wood raw material procurement – *VTT, Finland*
- Present state and perspectives of the utilisation of forest and wood derived industries for heat and power production in Spain – *CIEMAT, Spain*
- Systems for forest fuel handling in Sweden – *Forest Research Institute of Sweden, Sweden*
- Truck hauling in integrated harvesting systems – *Swedish University of Agriculture Sciences, Sweden*
- Fruit tree pruning machine as a potential producer of residues with energy value and in control of bushland – *Evora University, Portugal*
- Energy valorisation of biomass residues in fluidised bed combustion systems – *INETI, Portugal*
- Finnish technology for burning biomass fuels – *VTT, Finland*
- Project implementation of a thermoelectric power plant using forest residues – *EDP Group, Portugal*
- Biomass: source of renewable energy – *Olsson, Portugal*
- BMH Wood Technology – *Oy, Finland*
- Integrated waste management; waste as a resource in the energy and material systems – *NUTEK, Sweden*
- Energy from waste in Austria: development, status and problems – *University of Vienna, Austria*
- Italian situation about Waste for Energy – *ITABIA, Italy*
- Energy production from Lisbon municipal solid waste – *PROET, Portugal*
- The Danish Waste for Energy Plans and the future focus on industrial waste – *DK Teknik, Denmark*
- The future of biomass in Europe: how can we make joint progress and where are the barriers in this new bio-energy sector? – *SUC, Denmark*

It was very useful for Portugal, because it allowed industrial companies to obtain important and useful information from Portuguese and abroad research institutes about the possibilities of getting energy from biomass. This workshop also enabled the establishment of important contacts and participants to share information.

Conference Proceedings

Proceedings can be obtained from:
CBE – Centro da Biomassa para a Energia (Biomass Centre for Energy),

Tel: +351 39 53 436

Fax: +351 39 52 452

Email: cbe@cbe.mailpac.pt

PyNe Kick-off Meeting,
Salzburg, March 1998

The new Pyrolysis Network sponsored by the EC FAIR Programme and IEA Bioenergy had its inaugural meeting in Salzburg, Austria. In addition to welcoming the new representatives from Canada and the USA, the group also welcomed the new EC FAIR Scientific Officer – Ann Segerborg-Fick.

Third Biomass Conference of the Americas, Montreal, Quebec, Canada, 24-29 August 1997

This was the third in a series of conferences, which alternates with the EU Energy from Biomass Conference and is held every two years. The conference was attended by over 500 people representing the wide and diverse interests in biomass utilisation. Pyrolysis was fairly well represented and 12 papers were presented for the proceedings with 3 posters for the interactive cluster session.

Tours

During the course of the conference, there were three scheduled tours of interest to pyrolysis:

- Burlington Gasifier, Vermont
- Pyrovac Institute, Quebec
- Forintek Canada Corporation, Quebec

Vermont Gasifier Tour

The US DoE has funded a 7.5 t/h fluid bed gasifier, located at Burlington, Vermont. This twin fluid bed wood gasifier operates in a similar mode to a high temperature pyrolysis reactor and hence is of interest for technical reasons. The char product is burned in a separate reactor and is used to heat the sand which is returned to the pyrolysis reactor. The aim of the project is to operate a 15 MWe gas turbine on the product gas after cleaning. The facility was still in the construction phase in August, with planned start up in November 1997.

Pyrovac Institute Tour

The Pyrovac technology was featured in the 3rd issue of the PyNE newsletter. The tour of the Pyrovac Institute included the 75 kg/h vacuum pyrolysis plant, which was operating for the visit, giving the tour delegates the opportunity to see the production of vacuum pyrolysis liquids. Professor Christian Roy hosted an excellent and informative tour of their facilities.

Forintek Canada Corporation Tour

Forintek is a leading developer of wood and wood-related products, focusing on sawn limber and composite products. The Forintek offices are in close proximity to the Pyrovac institute and a useful insight into the preparation of wood laminates and composite materials was obtained.

Conference Proceedings

A two-volume set is available:

Title:	Making a business from biomass in Energy, Environment, Chemicals, Fibres and Materials – 3rd Biomass Conference of the Americas.
Editors:	Overend, R.P. and Chornet, E.
Publisher:	Elsevier Science Ltd.
Year:	1997
ISBN:	0080429963

3rd International Management Conference – Waste to Energy

The primary objectives of this conference, which was held in Copenhagen, Denmark, on the 4 & 5 December 1997, were:

- Assessing the future of European thermal waste treatment in a global, environmental and socio-economic context
- Benefiting from an update on political choices and strategic business issues for the waste to energy markets
- Challenging management actions versus new regulations
- Exploring new technological improvements and scientific discoveries that might result in new opportunities for the growing waste to energy markets
- Optimising the efficiency of waste power plant and reducing costs.

Oral presentations were given under the following themes:

- The Regulatory Framework
- Incineration and the Public Opinion on the Environment Impact. What do practical cases from day to day experiences teach us?
- Alternative Energy Production. Thermal Treatment and Waste to Energy
- Economics and Management Strategies.

The conference included an exhibition of products and services.

Mass transfer
may play a role in determining cellulose pyrolysis kinetics

By Eric M. Suuberg, Brown University, USA

part 1

Do cellulose pyrolysis kinetics depend upon heating rate?

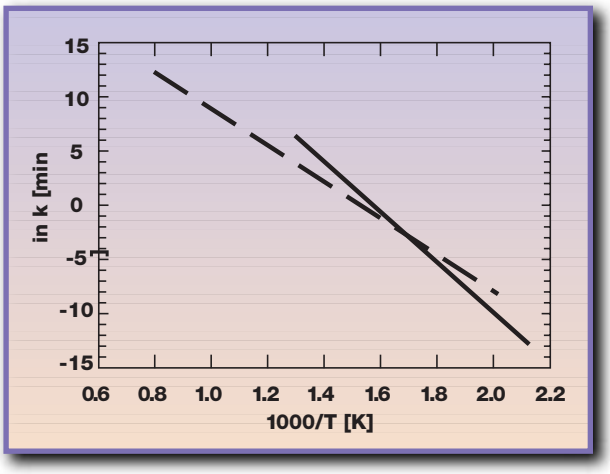

Figure 1: A comparison of published data on mass loss rates for cellulose pyrolysis. The solid line represents a mean from many studies conducted at heating rates less than 10 K/min, and the dashed line represents a mean from many studies at heating rates above this value. The activation energies are around 140 kJ/mol for the higher heating rate studies and 200 kJ/mol for the lower heating rate studies[1].

As worldwide interest in harnessing the energy potential of biomass fuels increases, so too does the interest in improving our understanding of the complicated processes involved in their thermal conversion. Development of advanced process concepts is greatly aided by detailed quantitative models which require such basic understanding. The focus in this article is on the key processing step which is common to all these conversion strategies – pyrolysis.

A Typical Path into the Morass of Cellulose Pyrolysis Kinetics

Upon initial examination of the literature in the field, it appears as though there already exists an almost overwhelming wealth of data; the need to add just a few more experimental results is not at all clear. There have been numerous studies of product composition, pyrolysis kinetics and mechanism and some studies combine several of these aspects. There do, however, tend to be many more of what may be termed "basic" studies on cellulose pyrolysis than on whole biomass pyrolysis. This is easily understood, in terms the difficulty of extracting sound scientific understanding from chemically very complicated systems.

Several years ago, our laboratory was engaged in a study of fire phenomena in bulk cellulosic solids, with a primary focus on the role of transport processes in shaping the slate of products from cellulose pyrolysis. A mathematical model of bulk sample pyrolysis was developed, in which heat transfer control was the central feature, since accompanying experiments clearly indicated this character. The overall model required a kinetic sub-model to describe pyrolysis in some non-heat transfer control regimes.
The selection of the appropriate kinetic model was, however, difficult since different published kinetic models offered widely differing predictions of the extent of pyrolysis in the interior of the sample. This prompted us to more thoroughly review the literature and to conduct our own kinetic experiments on the particular material of interest in our study, Whatman CF-11 cellulose powder (a 99% a-cellulose of very low ash content).

Which Kinetic Constants Are "Correct"?

The review[1] of global mass loss kinetics which we presented in 1995 was immediately somewhat controversial when published. In it, we observed that the literature can be interpreted to suggest that higher heating rate data suggest lower apparent activation energies, and lower heating rate data higher apparent activation energies for the main mass-loss step of pyrolysis. A summary of the reported kinetics is shown as Figure 1.

Is the Discrepancy Due to Heat Transfer Limitations?

It appeared, on the basis of the experiments that we conducted ourselves, that the difference in kinetics was actually more attributable to the temperature at which the decomposition took place, more than the heating rate per se. It was also clear that, as had been observed by many others before us, the modelling of the mass loss process with a single-step reaction was quite a crude approximation. For one thing, a clean determination of order was impossible.

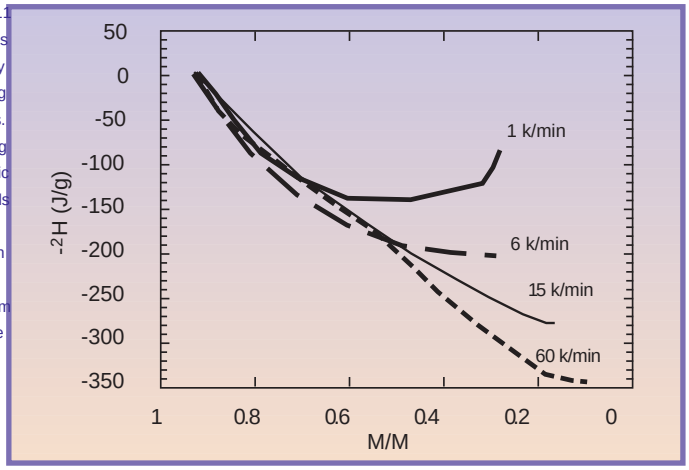

Figure 2: The enthalpy of pyrolysis of Whatman CF-11 cellulose, as a function of mass loss from the sample, and its heating rate. The pyrolysis process is always initially endothermic, and almost linear in mass loss. At high heating rates, this character is maintained throughout the process. At low heating rates, the well-known exothermic char forming processes begin at some point to compete with the basic endothermic nature of the process, and drive it back towards thermoneutrality. There is, however, no evidence of thermodynamically different pathways being followed at high and low heating rates, during the initial stages of pyrolysis. This alone does not assure that a change of mechanism does not occur, but there is also no other evidence to suggest such a change in mechanism with heating rate.

We were aware of the concerns that had been expressed for some time by Antal and coworkers[2] regarding the possibility of heat transfer limitations could cloud the interpretation of kinetics. This seemed unlikely in our own work, in which a thermocouple was placed into direct contact with the samples. Our own heat transfer calculations appeared to rule out a limitation[1]. It is moreover difficult to justify why, in the presence of heat transfer limitations, a relatively constant activation energy of near 140 kJ/mol would emerge, and apply over a very wide range of heating rates, up to 1000 K/s, as seemed to be implied in the literature. Normally, when heat transfer limitations cloud the interpretation of data, it is difficult to find a good constant value of activation energy from the experiments in question.

Evidence in Favor of Transport Limitations

The above review was followed by a second article in which we outlined the results of our examination of pyrolysis kinetics using differential scanning calorimetry[3]. In that work, we could see no evidence of a major shift in the thermal character of the pyrolysis process with heating rate. Some of the evidence is presented in Figure 2, showing the thermal "trajectory" of pyrolysis as a function of mass loss. It would be expected that a major shift in the process would be indicated by a change in thermal trajectory. Such changes are seen, but only indicate the onset of the exothermic retrograde reactions, rather late during pyrolysis. The main tar-evolving part of the process is very similar, consistent with reports suggesting that the tars of high and low heating rate pyrolysis are not much different, provided that they are quickly quenched. This evidence strongly suggested to us that the basic chemical pathway of pyrolysis did not, in fact, change with heating rate, until the exothermic char-formation processes began to occur. This meant that there should be no shift in the activation energy of the processes controlling the main period of mass loss, and yet, such a shift was observed. The inescapable conclusion was that the shift in activation energy was likely to indicate the onset of a transport limitation. Thus we felt that we could not invoke heat transfer limitations for the reasons cited above, and yet had to invoke some transport limitations. The resolution of this apparent paradox came in a hypothesized role of mass transport limitations[4]. These will be discussed in Part 2 of this presentation.

References

1. Ivan Milosavljevic and Eric M. Suuberg, "Cellulose Thermal Decomposition Kinetics: Global Mass Loss Kinetics", Ind. Eng. Chem. Res. 1995, 34, 1081-1091.
2. Michael J. Antal, Jr., H. L. Friedman, and F. E. Rogers, "Kinetics of Cellulose Pyrolysis in Nitrogen and Steam", Combustion Science and Technology 1980, 21, 141-152.
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4. Vahur Oja and Eric M. Suuberg, "Development of a Nonisothermal Knudsen Effusion Method and Application to PAH and Cellulose Tar Vapor Pressure Measurement", Analytical Chemistry 1997, 69, 4619-4626.