



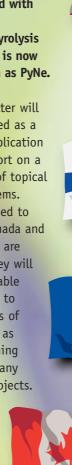


# The Future.



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.





**Pyrolysis** Network.



	ine ruture
2	Conference & Meeting Reports
4	Do Cellulose Pyrolysis Kinetics Depend Upon Heating Rate – Part 1
6	Compact Power
7	Catalytic Upgrading of Biomass – Derived Oils
8	University of Zaragoza
1(	THERMIE
10	JOULE
	INETI
12	Chemicals & Materials from Bio-oil – Part 2
14	Exchange Visits
16	Pyrolysis Modelling
17	Co-Combustion of Biomass on a Fluid Bed Pyrolysis Unit
18	Solar Energy & Biomass Pyrolysis
	News from North America
	Book Reviews
	Diary of Events
	PyNe Membership

**Co-ordinator**Tony Bridgwater

a

da

0

0

Administrator

Bio-Energy Research Group,
Aston University, Birmingham B4 7ET

Tel +44 (0)121 359 3611

Fax +44 (0)121 359 6814

email a.v.bridgwater@aston.ac.uk c.l.humphreys@aston.ac.uk

httn://www.ceac.aston.ac.uk/PvNE/

## 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:

- 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

# Do cellulose pyrolysis kinetics depend upon heating rate?

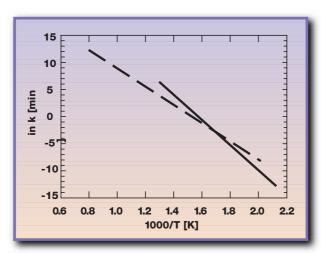


Figure 1: A comparison of published data on mass loss rates for cellulose pyrolysis. The solid line represents a mean from many studies conducted at heating rates less than 10 K/min, and the dashed line represents a mean from many studies at heating rates above this value. The activation energies are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

#### 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"?

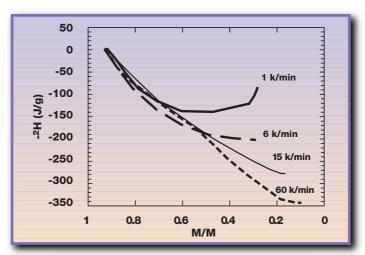
The review¹ of global mass loss kinetics which we presented in 1995 was immediately somewhat controversial when published. In it, we observed that the literature can be interpreted to suggest that higher heating rate data suggest lower apparent activation energies, and lower heating rate data higher 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<sup>3</sup>. 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<sup>2</sup> 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<sup>1</sup>. 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 calorimetry3. 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 limitations4. These will be discussed in Part 2 of this presentation.

#### References

- . Ivan Milosavljevic and Eric M. Suuberg, "Cellulose Thermal Decomposition Kinetics: Global Mass Loss Kinetics", <u>Ind. Eng. Chem. Res.</u>, 1995, <u>34</u>, 1081-1091.
  - Michael J. Antal, Jr., H. L. Friedman, and F. E. Rogers, "Kinetics of Cellulose Pyrolysis in Nitrogen and Steam", <u>Combustion Science and Technology</u>, 1980, <u>21</u>, 141-152.
  - Ivan Milosavljevic, Vahur Oja, and Eric M. Suuberg, "Thermal Effects in Cellulose Pyrolysis: Relationship to Char Formation Processes", <u>Ind. Eng. Chem. Res.</u> 1996, 35, 653-662.
  - Vahur Oja and Eric M. Suuberg, "Development of a Nonisothermal Knudsen Effusion Method and Application to PAH and Cellulose Tar Vapor Pressure Measurement", <u>Analytical Chemistry.</u> 1997, 69, 4619-4626.



## **Compact Power**

By John Acton, Compact Power, UK

**Compact Power**, a UK based company, has developed a combined pyrolysis and gasification process which provides a new and economic solution for the disposal of waste.

Traditionally domestic and commercial wastes have been disposed of by burying in landfill sites but this is becoming an expensive, difficult and, in some instances, unacceptable practice. Incineration has been another option but there is a growing public resistance to such plants due to their size, fears of pollution from their flue gases and the impact they have on local neighbourhoods from lorry traffic, noise and loss of visual amenity.

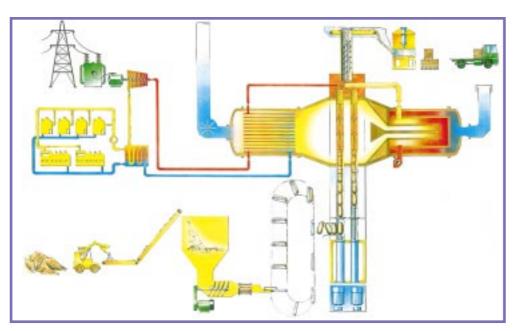


Figure 1: Compact Power - MSW Pyrolyser Plant

The Compact Power process offers modular plant capable of treating a wide variety of wastes including municipal solid waste (MSW), clinical waste, animal and bio-mass wastes, sewage sludge cake, industrial wastes and tyres. The plants are identified by the number of pyrolysis tubes employed ranging from an 'MT2' unit with two tubes capable of treating 6,000 tpa of clinical waste to an 'MT8' with eight tubes capable of treating 30,000 tpa of MSW. Combinations of these units allow the plants to be sized to match the waste available with the advantage that they can be readily up-sized or down-sized as disposal and recycling practices change.

The schematic of the process (Figure 1), shows the various stages of this thermochemical conversion technology. The waste is introduced into the pyrolysis chamber through tubes which form the basic unit of the system. Using the Compact Power process of compacted fuel 'slugs', it is possible to operate the plant on a continuous basis which makes it ideal for CHP and other applications where high grade heat is required without interruption (such as district heating schemes).

The fuel material is pyrolysed at about 700°C to produce hydrocarbon gases which are taken directly into a thermal oxidation reactor operating at 1250°C. This prevents the cooling of the gases and the opportunity for noxious by-products to be formed. The carbon char in the solid residue is then gasified at 1000°C to produce a carbon monoxide and hydrogen off-gas leaving a final ash which is inert and non-leachable and suitable for a number of applications including the production of 'breeze' building blocks.

The high temperature gases are oxidised in the thermal reactor for at least two seconds which at 1250°C is extreme enough to ensure that any pollutant gases and particulates are totally destroyed. The exhaust gases are ducted over the pyrolysis tubes to provide the energy to make the process self-sustaining. From here, the gases are cooled by passing them through a steam boiler designed to reduce the temperature rapidly and thus prevent the reformation of any dioxins or furans.

The exhaust gases are subjected to a final 'polish' by a dry remediation process before being exhausted through a low height chimney sized so as to ensure that the gaseous emission satisfy the highest environmental standards.

Modular design means that the capital cost is low and the multiple tube design provides high availability with low operating and maintenance costs. Compact Power estimate that the plants will cost about 60% of state-of-the-art conventional incineration plant of the same capacity.

Compact Power has successfully completed trials on a 400 kg/hr full sized pilot plant and has now commenced work on the building of a 6,000 tpa MSW and clinical 'Energy from Waste' plant to be sited at Avonmouth, near Bristol, UK.



# Catalytic upgrading of biomass-derived oils

By Narendra Bakhshi, Professor Emeritus, University of Saskatchewan, Canada

An in depth study on the catalytic upgrading of bio-oils is being carried out at the University of Saskatchewan, Saskatoon, Canada. The University of Saskatchewan (UofS) was founded in 1907.

There are nearly 20,000 students in various disciplines at the University, almost 2000 of whom are graduate students. There are about 1,100 faculty members.

The upgrading work is being carried out in the Catalysis and Chemical Reaction Engineering Laboratory in the Department of Chemical Engineering. The major focus of the research in the laboratory is in the following biomassrelated areas. Projects 1 and 2 are funded through Bioenergy Research & Development,



Experimental set up for catalytic conversion of hiomass-derived oils

#### Project 1: Characterization and **Catalytic Conversion of**

The focus of this work is on the physical and chemical characterization of biomass derived oil as well as studies on their stability. Also, various catalysts have been used to study the upgrading characteristics

Catalytic upgrading of biomass-derived oil has been receiving attention as an alternate source of fuels. The major advantages are that these fuels are CO2 neutral and contain very low fractions of bonded sulfur and nitrogen. Thus they contribute little to the greenhouse gases or other regulated

hydrogen to carbon ratio, it needs upgrading

in the presence of hydrogen, also, coking of

The second method uses essentially HZSM-5

Alternative Energy Division, CANMET, Ottawa. Biomass-Derived Oils (BDO)

of biomass derived oils.

air pollutants.

As the biomass derived oil contains a high oxygen content (around 45 wt %) and low before it can be used as regular fuel. Currently, two methods have been used to upgrade these bio-oils. The first method is a typical hydrotreatment process using Co-Mo/A1<sub>2</sub>O<sub>3</sub> or Ni-Mo/A1<sub>2</sub>O<sub>3</sub> catalysts.

The process requires high pressure operation the catalyst is a major problem.

zeolite catalyst for upgrading purposes. The operation is at atmospheric pressure and hydrogen is not required. The product from the first process consists of aliphatic hydrocarbons whereas the product from the second process consists mostly of aromatic hydrocarbons.

Biomass derived oil upgrading has been carried out over a variety of catalysts namely, HZSM-5, HY, mordenite, molecular sieves (SAPOs), silica-alumina, and mixtures of HZSM-5 + silica-alumina. These studies have shown that in some cases, the product slate can be dramatically altered by changing the characteristics (i.e., functionality) of the catalyst. For example, HZSM-5 gave the largest hydrocarbon fraction in the product (mostly aromatics) amongst all the catalysts studied.

On the other hand, HY and mordenite catalysts gave a high selectivity for kerosene range hydrocarbons. Products from SAPOs and pillared clay catalysts consisted of a mixture of aliphatic and aromatic hydrocarbons. On the other hand, with a mixture of 20 wt % HZSM-5 and 80 wt % silica-alumina catalyst, the product composition dramatically changed to almost all aliphatic hydrocarbons (essentially i-octane which has an octane number of 100).

#### Project 2: Steam Gasification of **Biomass Chars**

It has been found that chars formed during the catalytic upgrading of biomass derived oils are highly reactive. When gasified with steam, these chars seem to yield a high calorific gas. Work is being carried out to study the steam gasification of a variety of other chars as well, such as chars produced during the pyrolysis of agricultural materials.

#### Project 3: Production of Fuels and Chemicals from Canola Oil

The thrust of this work is on the conversion of canola oil to a variety of fuels and chemicals, such as C2 - C4 olefins and hydrogen, using a variety of catalysts.



Experimental set up for Steam gasification of biomass chars

Further information on any of these projects can be obtained from:

Narendra Bakhshi. **Professor Emritus CCREL** 

Department of Chemical Engineering University of Saskatchewan Saskatoon, SK S7N 5C9 **CANADA** 

> Tel: +1-306-966-4763 Fax: +1-306-966-4777





# **University of Zaragoza**

By Jesus Arauzo, University of Zaragoza, Spain





The origins of **University of Zaragoza** can be traced back to 1474, when Pope Sixtus IV created a "General Study".

In 1542 this became a university although it was not until 1583 that it actually began to function as such, due mainly to the encouragement and financial backing of Pedro Cerbuna, later to become Bishop of Tarazona.

In its beginnings, the University of Zaragoza offered studies in theology, canon and civil law, medicine and philosophy.

In 1849, theology and canon law were eliminated, heralding a period of decadence.

Although new faculties and schools were created in the second half of the 19th century, it was not until the 1970s that the University of Zaragoza really began to grow with the creation of new centres, the integration of others and its expansion into the nearby towns of Huesca, Teruel and La Almunia de Doña Godina.

Nowadays, the University of Zaragoza is made up from 24 centres and there are 50 departments.

#### The Department of Chemical & Environmental Engineering

The Chemical and Environmental Engineering Department provides a total of 23 subjects in 5 centres. The staff of the Department consists of 31 faculty teachers, 29 post-graduate and post-doctoral students and 5 laboratory and administrative assistants.

The main research lines that are being developed by the different groups in the Department are:

- Use of sepiolite-type materials as adsorbents of pollutants
- Ecotoxicity of industrial cattle farms
- Characterisation of water pollution in industrial effluents
- Investigation of side effects of the use of chlorinated products in water treatment
- Remediation of soils contaminated by volatile organic compounds
- Development of ceramic membranes by the sol-gel method
- Development of new types of reactors for selective oxidation of hydrocarbons
- Development of mixed oxides used as alternative catalysts in selective hydrogenation reactions
- Development of "in situ" redox fluidized-bed processes
- Study of complex deactivation phenomena and of new regeneration strategies for catalysts
- Safety and risk analysis
- Catalytic pyrolysis and gasification of ligno-cellulosic residues and black liquors
- Down-draft air gasification of wastes
- Use of sewage sludge
- Thermal decomposition of ligno-cellulosic materials and behaviour of materials exposed to fire
- Reduction of NO<sub>x</sub> emissions in combustion systems

Data logging unit

Specifically, the biomass group is studying gasification in down-draft moving bed, reduction of emissions of  $NO_{x\nu}$  combustion and pyrolysis.

#### **Pyrolysis of Biomass**

Studies are being carried out on the **thermal decomposition** of the ligno-cellulosic components of cellulose, xylan, lignin; agricultural and forestry residues; black liguor, etc. These studies have been carried in:

- Thermo-gravimetric systems and fixed bed reactors. The most significant publications are in this area (see below)
- Fluidised bed reactors. The research work on this area began seven years ago with preliminary experiments and since 1991 has been related to fast catalytic pyrolysis.



Black liquor pyrolysis

#### **Recent publications**

#### **Fast Pyrolysis**

Arauzo, J., Radlein, D., Piskorz, J., Scott, D.S., A new catalyst for the catalytic gasification of biomass, Energy & Fuels, 8, 1192-1196, (1994)

Arauzo, J., Radlein, D., Piskorz, J., Scott, D.S., Catalytic Pyro-gasification of Biomass. Evaluation of Modified Nickel Catalyst, IEC Research, 36, 1, 67-75, (1997).

#### **Slow Pyrolysis**

Bilbao, R., Salvador, M.L., Garcia, P., Arauzo, J., Solid weight loss in the thermal decomposition of cellulose and pine sawdust, Journal of Analytical and Applied Pyrolysis, 24, 257-271, (1993).

Bilbao, R., Salvador, M.L., Arauzo, J., Influence of the heating rate on the temperature profiles and on the conversion rate of powdery cellulose and pine sawdust, Journal of Analytical and Applied Pyrolysis, 40, 148-159, (1994).

R.Bilbao, J. Arauzo, M.L. Salvador., Kinetics and modelling of gas formation in the thermal decomposition of powdery cellulose and pine sawdust, Ind. Eng. Chem. Res., 34 (3), 786-793, (1995).

#### **Facilities**

Specific facilities on pyrolysis include a fluidised bed reactor based on the Waterloo Fast Pyrolysis Process with a feed rate of 10-300 g/h; and thermo-gravimetric systems and fixed bed reactors with capacities from mg up to 2kg.



# **THERMIE**

By Kyriakos Maniatis, EC, Brussels, Belgium

The objectives of **THERMIE** in demonstrating commercial-scale energy technology projects and promoting and disseminating information through associated measures, still remain as relevant today as they were when the Energy Demonstration Programmes of DG XVII started in the early 1970s.

The activities supported by THERMIE can help contribute to, in the immediate and short term, important policy concerns such as reduction of environmental hazards especially CO<sub>2</sub> emissions - and increasing the competitiveness of important actors in our economies such as Small and Medium-sized Enterprises (SMEs). In addition, technological input as part of a wider implementation of European energy policy is provided by the effective co-ordination between THERMIE and other RTD programmes as well as EU energy programmes like SAVE (policy measures in energy efficiency); ALTENER (policy measures in renewables) and SYNERGY (policy measures towards non-EU countries).

The JOULE-THERMIE programme ran until 1997 and had a total budget of 1,030 MECU of which 566 MECU were allocated to the THERMIE demonstration component of the programme for the support of projects and associated measures. THERMIE focuses on the cost-effective, environmentally-friendly and targeted demonstration technologies and the promotion of clean and efficient energy technologies.

These consist of Renewable Energy
Technologies; Rational Use of Energy in
Industry, Buildings and Transport, and a
clean and more efficient use of Solid Fuels
and Hydrocarbons. Essentially, THERMIE
supports actions which aim to prove both
the technological and economical viability
and validity of energy technologies by
highlighting their benefits and by assuring
a wider replication and market penetration
both in EU and global markets.

THERMIE has participated in all the major technological breakthroughs in energy in the last decade.

In the sector Energy from Biomass and Waste, emphasis has been given in the fields of large-scale biomass gasification and utilisation of biomass and wastes with fossil fuels. However, pending the approval of the 5th Framework programme and the elaboration of its Work-Programme, it is envisaged to open the future calls to the subject of flash pyrolysis depending on the progress achieved in this sector towards industrial applications.

## **JOULE**

By Michail Pappadoyannakis, EC, Brussels, Belgium

JOULE is the R&D component of the Non-Nuclear Energy Programme within the Fourth Framework Programme for the European Union RTD activities. It has a total indicative budget of 450 MECU for the period 1994-1998. The bulk of the funding is absorbed by research projects but there is also the possibility of funding concerted actions (co-ordination of R&TD activities), and SME's in particular are supported by means of exploratory awards and co-operative R&TD projects.

JOULE is divided into five areas, one of which is dedicated to Renewable Energy Sources (RES). Biomass and waste, with particular emphasis on thermochemical conversion of solid biomass, is part of this area. In the successive calls for proposals the initial work programme is supplemented to take into account recent developments, ensure continuity with ongoing projects and focus on the strategic targets.

The presence of industrial partners in the consortia has increased throughout the framework programme to reach approximately 45% in the last call for proposals. Gasification projects have been until now by far the more numerous but the number of projects focusing on combustion has increased considerably.

Another six pyrolysis projects will hopefully be added to the four ongoing projects, thus reaching a total budget in the order of 15 MECU in the present Framework Programme. R&D on flash pyrolysis technologies for optimised bio-oil production and use represent the bulk of the supported work but novel concepts (aqueous pyrolysis) are also promoted. Much emphasis is put on the demonstration of utilisation of the oil in boilers and engines by reliable long testing and this is also reflected in the work programmes of the projects.

Much progress has been achieved but in view of the general orientation of the 5th framework programme towards integrated energy systems, the extent of future support would have to be carefully examined in the light of concrete results and market conditions allowing an introduction of pyrolytic oils and by-products to the fuel markets in the short to medium term.

JOULE involvement in pyrolysis has been active and extensive throughout the last decade and has embraced practically all aspects of pyrolytic oil production, optimisation and use; and has included all technologies and important European players in the field, be they universities, research centres or equipment manufacturers.

Non-European participation in JOULE projects has become more important in the pyrolysis sector. JOULE has been present since the beginning in the construction of all the well known European pilot scale facilities and still remains one of the main supporters of their operation and development.

By Filomena Pinto, INETI, Portugal

**INETI** is a public institution devoted to Research, Development and Demonstration (R, D&D) as well as providing technical, technological and laboratory assistance to industry. **INETI** was created in 1977 under the name of **LNETI** – **National Laboratory of Engineering and Industrial Technology**, to integrate several governmental institutions devoted to research and technical services to industry.

Nowadays, INETI is a corporate entity endowed with academic, administrative and financial autonomy. It belongs to the Ministry of Economy and is integrated in the National Technological System as a Technological Partner for Industry. INETI is currently responsible for a number of R&TD projects, which include contracts with companies, the EU and the Portuguese State.

INETI's present objective is to contribute, mostly in a multi-disciplinary way, to the modernisation of Portuguese industry so that industry can undertake new initiatives and adopt new technologies most suited to its needs. INETI also offers direct technological support and services to companies in areas such as industrial development contracts, information systems development, PEDIP II programme management, quality, design.

INETI's scientific and technological activities are integrated in coherent programmes and projects. The priority areas are integrated into five institutes and three centres:



Equipment for the study of plastic waste Pyrolysis

- IBQTA-Institute of Biotechnology,
   Fine Chemistry and Food Technology
- IMP-Institute of Materials and Production Technologies
- ITA-Institute of Environmental Technology
- ITE-Institute of Energy Technology
- ITI-Institute of Information Technology
- CITI-Centre for Technical Information for Industry
- CEGTI-Centre for Technology and Innovation Management
- CEGEF-Centre for Training Management and Engineering

# **DTC – Department of Combustion and End-Use Technologies**

The Department of Combustion and End-Use Technologies belongs to ITE – Institute of Energy Technology and has developed activities related to:

- Fuel characterisation
- Combustion
- Gasification
- Liquefaction
- Pyrolysis

- Fluidised bed technology
- Emissions control
- Use of alternative fuels and wastes for energy production

#### **Pyrolysis Activities**

Current funding support for the use of biomass for energy is presently given mostly to projects utilising direct combustion in systems that produce both heat and power. Therefore, there are currently only small laboratory scale facilities for the study of pyrolysis of biomass and other wastes. All the pyrolysis work in Portugal is currently done at **INETI – DTC** and the following subjects have been studied:

- biomass flash-pyrolysis
- plastic wastes pyrolysis
- co-pyrolysis of plastic wastes and biomass

The main aims of the work done so far have been optimisation of the overall process by studying the effect of several experimental conditions and catalysts on reactions products, analysis and full characterisation of products obtained,

and review of new pyrolysis technologies to report them to national authorities and industry.

Future aims include a better understanding of the process mechanism and reaction kinetics and the construction of pilot-scale units that would allow a better understanding of the process which would subsequently help scale-up to industrial plant.



Some members of the Pyrolysis team

# Chemicals and Materials from Bio-oil

By Desmond Radlein, Resource Transforms International Ltd., Canada

Part 1 of this feature in PyNE newsletter 4 described the opportunities for individual chemicals. This second and concluding part focuses onthe whole oil.

#### Utilization of whole bio-oil

The alternative approach to the isolation of individual compounds consists of exploitation of the chemical character of bio-oil to find applications for the whole oil or fractions thereof. Pyrolysis liquids contain high concentrations of carbonyl, carboxyl, and phenolic functional groups (see figure 1) which suggests various applications as a reactive feedstock. This concept is illustrated by the following examples.

	Moles Functional Groups/kg Organic Liquid					
Feedstock	Carbonyl	Carbonyl	Hydroxyl	Phenolic	Methoxyl	
Maple	2.1	5.7	0.92	2.8	2.1	
Wheat Straw	1.4	<b>5.</b> 3	1.40	3.0	1.1	
Poplar-Aspen	2.1	6.2	0.77	2.8	1.6	
Peat Moss	1.2	3.0	1.30	1.8	0.7	

Fiaure 1.

#### **Fertilizers and Soil Conditioners**

Reaction of the bio-oil with ammonia, urea and other amino compounds produces stable amides, imines and Mannich reaction products, etc., which are non-toxic to plants and therefore can function as slow release organic fertilizers. (Patents pending).

Typical nitrogen controlled release fertilizers vary in price from US\$250/ton for sulfur coated urea to \$1250/ton for polymer coated fertilizers so a product such as this is likely to be far more valuable than simple fuel applications.

There are also additional benefits. The cracked (pyrolytic) lignin and its reaction products with amino compounds are not only good sources of humic material for soil conditioning but also excellent chelants or complexing agents for micronutrient trace metals like Mo, Fe, B, Zn, Mn and Cu. Functional groups also exist for binding other nutrients like Ca, K, and P.

Besides functioning as simple organic soil conditioners, the merits of humic substances for control of soil acidity, amelioration of the effects of excess Al and Fe, increasing availability of phosphate, and as crop stimulants, among other benefits, is well documented.

Within the context of current concerns with the reduction of greenhouse gases this technology may be thought of as a method for storing carbon in the soil thereby mitigating the effects of CO<sub>2</sub> emissions and providing a basis for sustainable agriculture and silviculture. At the same time the binding of nitrogen solves problems of nitrate and ammonium pollution of lakes and rivers and represents a potential solution to the broader problem of the disposal of manures.



#### **Acetalization and Esterification**

**The reactivity of carbonyl and carboxyl groups** can also be exploited by reaction with alcohols to generate acetals, ketals and esters (Patents pending). The alcohol undergoes esterification and trans-esterification with carboxylate functionalities and (hemi) acetalization with carbonyls. Being renewable, ethanol is the alcohol of choice.

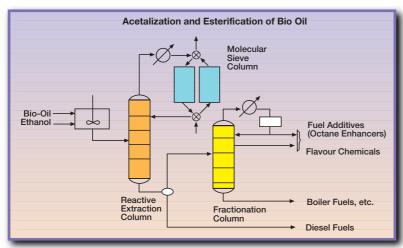


Figure 2: Acetalisation and esterification of bio-oi

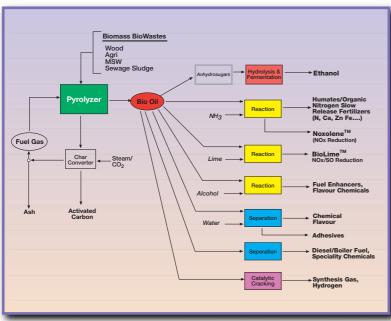


Figure 3: Concept of a bio-refinery for chemicals and fuels by fast pyrolysis of biomas

#### For fuel applications these conversions:

- reduce acidity
- increase heating value by up to 30%
- decrease the flash point
- reduce aging rate
- decrease viscosity (when excess alcohol is retained in the product).

Since the reaction products have increased hydrophobicity and volatility there is a large increase in the distillable fraction as well. Hence other useful products may be more readily recovered by conventional fractionation methods, (Figure 2). Such additional applications include:

- flavour chemicals
- octane enhancers
- solvents, resins, varnishes
- conversion to ethers

#### BioLime™

A final example of this approach is the production of BioLime™ being developed by Dynamotive Corp. of Vancouver, B.C., as an agent for control of SO<sub>x</sub> and NO<sub>x</sub> emissions in coal combustors, [8]. Whole bio-oil is reacted with lime to generate various organo-calcium salts. Compared to lime, this enables very high utilization rates of calcium for SO<sub>x</sub> capture. Furthermore some of the various classes of organic compounds are effective catalysts for the destruction of nitrogen oxides. The calcium capacity can be further enhanced by pre-oxidation of the bio-oil.

#### Conclusions

Figure 3 summarizes the concept of a bio-refinery based on bio-oil presented here. Efforts to proceed with the commercialization of these technologies is on-going.

We believe that these efforts will bear fruit in the near future. The authors welcome partners and collaborators in this endeavour.

#### References

McAllister, R., PyNE Newsletter, Issue 3, March, 1997.



# **CNRS Nancy**

By Olivier Boutin, CNRS Nancy, France

Olivier Boutin is from the Laboratoire des Sciences du Genie Chimique (LSGC-CNRS-ENSIC) in Nancy, France, working under the direction of Dr Jacques Lédé. The aim of the visit was to perform the chemical analysis of a number of samples from products obtained from the thermal decomposition of cellulose and lignin exposed to a concentrated radiation.

 $\begin{array}{cccc} & & & & & CH_3 \\ R-OH+X-Si-CH_3 & \longrightarrow & R-O-Si-CH_3 + X-H \\ & & & & CH_3 \end{array}$ 

Figure 1.

The following two exchange visits took place at the Institute of Wood Chemistry (IWC) n Hamburg, Germany nder the supervision f Dr Dietrich Meier. The IWC has become the most popular place for young researchers who are sponsored by the PyNe Network to visit because of their xpertise in analysis and characterisation and the variety of equipment available.

The 5kWth image furnace at Nancy gives a very concentrated heat flux, higher than 10° W m-², under very clean conditions (See page 18). These are very favourable conditions for flash pyrolysis. Samples of pure cellulose (Whatman CC31 microgranular) and pure lignin (Organicell from Dr Meier at IWC) are placed at the small (about 1cm diameter) focus of the furnace and then undergo rapid thermal decomposition. Several experiments have been made and the corresponding products obtained after quenching were taken to Hamburg in order to determine their chemical composition.

The analysis confirmed that the cellulose used for the experiments in Nancy was pure and did not contain any trace of hemicellulose or lignin, as also measured by complete acid hydrolysis followed by sugar analysis with liquid chromatography. The analysis of the initial thermal degradation products of fast pyrolysis were analysed by gas chromatography coupled to a mass spectrometer (GC-MS analysis). However, some of the products were found to be too polar and did not vaporise in the injector of the GC. Therefore, a special silylation method was applied to form the trimethylsilylethers.

Figure 1 shows the equation representing this reaction where the -OH group are replaced by -Osi(CH<sub>3</sub>) in order to yield more volatile compounds.

Several tests were made to determine the right silylating reagent and the best conditions. The procedure followed for each sample of pyrolysis product was as follows:

- extract the products from the pure cellulose with water
- eliminate any trace of water
- add silylating reagent and solvent
- wait enough time for the complete sylilation reaction
- carry out the first analysis in a simple GC
- carry out the complete analysis in a GC-MS

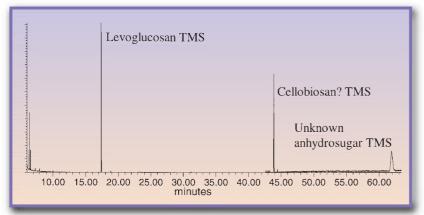


Figure 2: Typical chromatogram obtained in gas chromatography

Figure 2 shows a typical chromatogram. It shows that relatively few peaks were obtained. In particular, two main peaks were very interesting: the peak at 17.36 min was from levoglucosan and the peak at 43.88 min was from cellobiose.

The corresponding mass spectra are given in Figure 3.

The particular value of the visit was to learn about chemical analysis, especially on sylilated products analysed in a GC-MS. It was also interesting to develop and test a method for the analysis of the Nancy products.

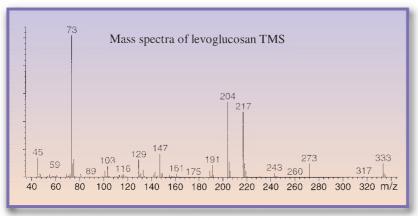


Figure 3: Just levoglucosan the other compound is not yet verified

# **VTT** energy

By Johanna Levander - VTT Energy, Finland

Johanna Levander of the Technical Research Centre of Finland (VTT) visited the Institute of Wood Chemistry (IWC) in Hamburg, Germany in January 1997. VTT has a small fluid bed pyrolyser for catalytic upgrading of pyrolysis vapours similar to that of IWC, and the objective of the visit was to improve familiarity with the equipment. Dr Dietrich Meier at IWC has a long experience in catalytic upgrading of various feedstocks and Peter Wulzinger, who has been operating the pyrolyser and coupled catalytic reactor, was available to help with the operation.

At VTT the study is focused on physical upgrading of pyrolysis liquids. Catalytic treatment of pyrolysis vapours has been studied since 1996 by using a micro-scale modified Pyroprobe catalytic system. The study will be continued with this larger (150g/h pyrolyser) equipment.

During the visit four experiments were carried out, two without the catalytic reactor and two with it.

The value of the visit was to see the details in preparing and conducting the run and the product recovery system. After the visit, some small modifications were made in VTT's equipment. The first experimental run with birch powder was successful. The trials and the installation of the catalytic reactor at VTT will be carried out during the summer 1997.



References

1. Di Blasi, Multi-phase moisture transfer in the

Engineering Science, in press, 1997.

high-temperature drying of wood particles, Chemical

2. Di Blasi, Heat, momentum and mass transfer through a

shrinking biomass particle exposed to thermal radiation,

3. Di Blasi, Kinetic and heat transfer control in the slow

Chemical Engineering Science, 51: 1121-1132, 1996.

4. Di Blasi, Heat transfer mechanisms and multi-step

kinetics in the ablative pyrolysis of cellulose. Chemical

5. Lanzetta, C. Di Blasi and F. Buonanno, An experimental

and flash pyrolysis of solids, Ind. Eng. Chem.

Engineering Science, 51: 2211-2220, 1996.

investigation of heat transfer limitations in the

flash pyrolysis of cellulose, Ind. Eng. Chem.

Res., 35:37-47, 1996.

Res., 36:542-552, 1997.

# **Pyrolysis modelling**

By Colomba Di Blasi, University of Napoli "Federico II", Italy

The development of mathematical models for biomass pyrolysis is an important part of the research activity on thermochemical conversion of solid fuels currently underway at the Department of Chemical Engineering of the University of Napoli "Federico II".

The main purposes of the modelling activity are:

- 1) to identify system characteristics useful to experiment programming,
- 2) to analyse the effects of process parameters in order to provide useful data for the design and optimisation of chemical reactors and other process equipment.

Detailed mathematical models have been developed for the dynamics of single-particle drying [1] and pyrolysis taking place through indirect external heating (convection and radiation) [2, 3] and direct external heating (hot-plate contact) [4]. Transport models for flash pyrolysis units (fluidised-bed and ablative reactors) are under development. Also, laboratory scale experiments are carried out to get "input data" for process simulation, such as the kinetic constants for flash pyrolysis [5] and process variable measurements such as conversion time, temperature dynamics, product yields, gas and liquid composition, for model validation.

The mathematical description of particle drying includes the phenomena of water vapour convection and diffusion and capillary water convection in the pores of the particle, and bound water diffusion in the solid wood. Momentum transfer for the liquid and the gas phase, is described according to the multiphase Darcy law.

Local thermodynamic equilibrium is assumed, with a sorption isotherm that couples the moisture contents in the solid and the gas phase. Predictions which exhibit good quantitative agreement with experimental data, have been used to determine the conditions for fast and slow drying and the controlling mechanisms.

In the pyrolysis models, primary and secondary chemical kinetics are described by means of lumped-parameter mechanisms, where the products are grouped into char, gas and tar. For the case of indirect heating, the transport model describes the main physical processes occurring across the porous particle, that is:

- property (porosity, permeability, thermal conductivity, thermal capacity, mass diffusivity) variation with the conversion level
- accumulation of volatile species mass and enthalpy within the pores
- heat transfer by convection, conduction and radiation
- convective and diffusive transport of volatile species
- gas pressure and velocity variations
- particle shrink age and/or swelling

Furthermore, a two-dimensional unsteady version of the model equations has allowed the role played by medium anisotropy on the pyrolysis characteristics to be investigated.

Extensive numerical simulations of the problem of a biomass particle have been used to analyse time and space evolution of the main variables and product distribution as the heating conditions and the particle properties are varied.

For the case of hot plate contact, a cylindrical particle pressed against a hot, spinning disk has been modelled. For main lines, all the physical processes listed above have been taken into consideration with the further description of the formation of a molten phase and the subsequent vaporisation process.

Simulations have confirmed some important experimental findings.

#### Field, % by weight of cellulose 90 $\Delta_{\Delta}$ 80 Δ 70 Δ 60 8 **TAR** 50 40 GAS $\triangle$ 30 0 Δ 20 4 0 Δ 10 450 600 750 900 1050 1200 **T**, [K]

Figure 1: Final tar, gas and char yields as functions of Tr for two particle half-thicknesses (values x 100 [m] reported in figure) as simulated for Trea = Tr.

Experimental data by Scott et al. (1988) (empty symbols) and by Shafizadeh et al. (1979) (filled symbols) are included for comparison purposes ( ○ gas, △ tar, ◇ char).



# Co-combustion of biomass based on a fluid bed Pyrolysis Unit

By Søren Houmøller, dk-TEKNIK Energy and Environment, Denmark

# Use a lot of biomass to produce electricity - and do it fast!

This was essentially the message from the Danish authorities when, in 1993, they directed the utilities to increase the use of straw and wood by 1.4 million tonnes per year by 2000. But how can this be accomplished in such a short period of time?

#### The Idea

One solution is to co-combust straw with coal in existing boilers by using a fluid bed pyrolysis unit to first convert the biomass into a gas. Traditionally, co-combustion of

with expendable boilers as the alkali (potassium and sodium) and chlorine content in the straw accelerate corrosion. But by pre-treating the straw in a fluid bed pyrolysis unit, most of the potassium, sodium, and out of the volatile phase and retained

Such a pyrolysis development since

1994 by dk-TEKNIK Energy and Environment and the Department of Energy Engineering (DEE) at the Technical University of Denmark and is shown in Figure 1. DEE is leading the field in two-stage gasification and dk-TEKNIK is an independent consultancy participating in several R&D projects on biomass utilisation.

#### **Operation**

The straw is pyrolysed in the fluid bed pyrolysis reactor and the char is separated from the gases in a cyclone. By keeping the pyrolysis temperature below a certain level, the bulk of the sodium, potassium and chlorine in the input straw remains in the char. The gas, with only limited amounts of these harmful components, is partly used for fluidisation of the pyrolyser by recirculation with a blower and partly sent to a conventional power plant boiler.

The majority of the energy originally in the straw is transferred to this gas while the char retains most of the alkali metals along with other residues. These residues can be utilised as the biomass ash is not contaminated with fossil fuel ash.

00000 00000

Fossil residue

Gas

straw and coal is a task for daring utilities

chlorine can be kept in the char.

unit has been under

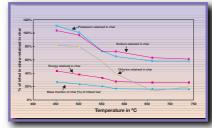
The bench scale fluid bed pyrolysis unit with part of the instrumentation, ready for experiments

#### Results

Experiments with a bench-scale reactor have shown that the energy content of the gas increases with increasing temperature, so to supply as much energy as possible to the boiler, the pyrolysis temperature should be as high as possible. To retain the alkali and chlorine in the char, however, the pyrolysis temperature needs to be low.

Below 500°C about 45 per cent of energy in the straw is contained in the char fraction along with all of the potassium and sodium and about 80 per cent of the chlorine. At 550°C the sodium, potassium and chlorine levels start to decrease and continue to reduce as the pyrolysis temperature increases. The results are shown in Figure 2. The fluid bed experiments generally show a lower retention of harmful components and less energy than batch testing in an oven.

These results show that straw can be converted into a usable gas as expected and that the unit can help the utilities to solve their problems with electricity production from straw.



Results from straw expe



# Solar energy and biomass pyrolysis

By Jacques Lédé, CNRS-ENSIC, France

a a e d d a t t d d it t t A

Nancy's SKW image furnace

Solar energy is responsible for the formation of biomass by the process of photosynthesis. Solar energy can also be used with two different objectives: as a heat source in thermochemical conversion processes of biomass and/or for studying its fast elementary reactions of thermal decomposition. As the maximum available heat flux delivered by the sun on the earth's surface does not exceed 1000 W/m², it is necessary to concentrate the solar radiation.

#### Available concentrating technologies

There are three main systems used for solar concentration:

#### 1. Parabolic troughs

The reflective surface of a parabolic trough concentrates sunlight onto a receiver tube located along the trough's focal line. However concentration ratios of only a few tens are reached and temperatures are not high enough to perform pyrolysis.

#### 2. Power towers

Several hundreds of mirrors (heliostats) track the sun and reflect the solar energy onto a receiver mounted at the top of a central tower. Such big plants are currently under development in several countries, where powers of several MW are obtained. These plants are usually designed for the conversion of solar energy to electricity. It is anticipated that they could be also considered in the future for high temperature chemistry. These power towers usually achieve concentration ratios of 300 to 1500 and can operate at temperatures up to about 1500°C.

#### 3. Dish concentrators, solar furnaces

The solar parallel radiation is concentrated inside a receiver located at the focal zone of a parabolic mirror. Powers as high as 1 MW can be reached as well as concentration ratios of several thousands and temperatures above 3000°C. The heat flux densities in the focal zone can reach 10°W/m².

Flash pyrolysis of small samples of biomass at th focus
of a solar simulator (LSGC-CNRS, Nancy-France).
The reaction occurs inside a receiver located at the first
focus of an elliptical mirror (right part of the photo)
reflecting the light delivered by a high power Xenon lamp
associated to another elliptical mirror (on the left side
of the set up, not seen on the photo).

### Biomass solar thermal conversion processes

The high heat fluxes and temperatures that can be achieved after sunlight concentration can be favourably used for the gasification and/or pyrolysis of biomass. The concentrated radiation can be absorbed either directly by the biomass particles that react in conditions of high purity, or through a wall (or inert or catalyst particles) indirectly heating the biomass. There are several main advantages of such clean processes. Solar energy provides the necessary heat of the reaction (sensible heat and enthalpy of the endothermic steps) with several advantages: economy of external fuel; transformation of the whole biomass into valuable compounds; products less diluted with N2, and CO2; no pollution from by combustion gases. The energy recovered in the products is the sum of the energy stored during photosynthesis and under the form of enthalpy of reaction. The products are liberated into a cool environment with the possibility of thermal quenching.

Several countries have reported laboratory scale experiments and pilot scale projects in the field of solar gasification and pyrolysis such as France, USA, Israel, Germany and Switzerland. In addition, these activities bring the opportunity to design new types of reactors with optimal combination of solar energy absorption efficiency with biomass feeding and conversion and development new quenching devices.

There are potential markets in the southern zones of Europe mainly around the Mediterranean, but also in other countries such as Brazil, India and Australia. Solar biomass conversion can be particularly attractive in very sunny areas where large quantities of agricultural wastes are produced for example from greenhouses.



#### Concentrated radiation for studying the fundamental aspect of biomass pyrolysis

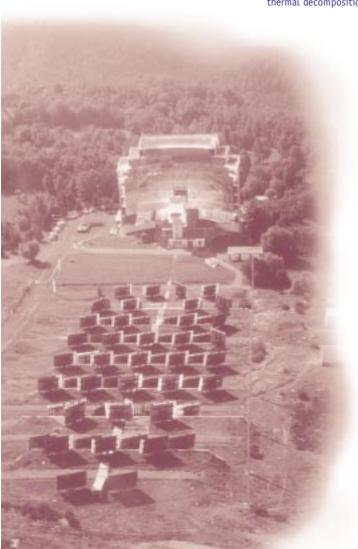
The heat flux densities that can be obtained inside a concentrated radiation zone can be easily modified by changing the level of concentration and/or the level of occultation of the incident radiation. So, it is possible to control and also to measure the available heat flux densities inside relatively large domains. If samples of biomass are put at the focus of a concentrator, it is hence easy to precisely know in which conditions the pyrolysis occurs.

The heat fluxes densities that can be achieved in these conditions can be similar to those existing in ablative pyrolysis. However the mass transfer efficiencies are quite different. The comparison of the experimental results obtained in both cases, and the use of a mathematical model, provide valuable information on the kinetics of some of the competitive and consecutive primary reactions occurring during biomass thermal decomposition.

Such work is being carried out in the CNRS Laboratoire des Sciences du Génie Chimique of Nancy (France) in the framework of an AGRICE (ADEME) contract. At the present time, small scale experiments are being performed in a solar simulator (image furnace) operating with a high power xenon lamp associated with two elliptical mirrors as shown in the photographs opposite. The achievable heat flux densities can be higher than 5\*10<sup>6</sup> W/m² inside a circle of approximately 0.5 cm². The work is made in collaboration with the CNRS-IMP Laboratory of Odeillo (France) where experiments are planned in a 2.5 kW solar furnace.

#### Conclusion

These unusual aspects of biomass pyrolysis open new and fascinating fields of research and applications. They also give the opportunity for fruitful collaboration between two different scientific communities involved in the fields of "Solar Chemistry" (this is the subject of the Task II of the IEA SolarPACES programme) and of biomass thermochemical conversion.





# **Biomass pyrolysis** activities at NREL in 1997/1998

By Stefan Czernik, NREL, USA

The **NREL** activities related to biomass pyrolysis are supported by three Department of Energy programs; Biomass Power, Industrial Technologies, and Hydrogen.

The facilities used to carry out the projects have been previously described (No. 3 issue of the PyNE newsletter).

The Biomass Power Program sponsors research on development of integrated biomass gasification/fuel cell system (IGFC). The Thermochemical Process Development Unit (modified vortex ablative pyrolysis reactor system – see Figure 1, is operated in pyrolysis/gasification mode to generate gas suitable (after conditioning) for use in a molten carbonate fuel cell. The vortex reactor operating conditions are similar to those used for the oil generation; biomass feed rate is 15-20 kg/h, reactor wall is maintained at the temperature of 650°C.

However, steam is used as a carrier gas and pyrolysis vapors are thermally cracked in the secondary reactor at 800-850°C. Conversion of biomass to gas is of the order of 80%. The gas composition is very similar to that generated in Battelle dual fluidised bed system.



Figure 1: The Thermochemical Process Development Unit

This summer a molten carbonate fuel cell will be coupled to the PDU to determine its operability using gas generated from biomass thermo-processing. Though currently dedicated to generate gas, the PDU can be any time used to produce bio-oils just by bypassing the vapor cracker.

The Office of Industrial Technologies supports the NREL work on producing chemicals for brightness stabilization of paper. The focus of this project is the isolation of specific pyrolysis oil fraction that effectively slows down yellowing of paper prepared from bleached thermo-mechanical pulp. NREL is developing the product in collaboration with Mineral Technologies, Inc. A four-inch diameter fluidised bed reactor is used to generate bio-oils for this study and is shown in Figure 2.



Figure 3: Tubular fixed bed reactor







Figure 4: Two-inch diameter fluidised bed reactor

The Hydrogen Program sponsors NREL Biomass to Hydrogen project. The studied approach to generate hydrogen from biomass proposes combined two-stage processing; fast pyrolysis to produce bio-oil and catalytic steam reforming of the bio-oil to hydrogen and carbon dioxide. The efforts have been focused on the second stage, steam reforming bio-oil and its fractions. The research performed using a tubular fixed-bed reactor system proved technical feasibility of the concept as shown in Figure 3. Future experiments will be mostly carried out using a two-inch diameter fluidized bed reactor with a commercial nickel-based catalyst shown in Figure 4.

In addition to the DOE sponsored research NREL also carries out three biomass pyrolysis projects funded by private companies.



# R&D news from canada

By Ed Hogan, Natural Resources Canada, Canada

#### **Bio-Oil Utilisation Gas Turbines**

Orenda is finalising a project that demonstrated the "Proof of Principle" of the concept of utilising biomass pyrolysis oil in a gas turbine. Orenda was able to achieve stable operation of their GT2500 2.5 MWe engine using 100% bio-oil over its operational entire range. The turbine has been operated using various ratios of bio-oil and diesel with a total of 13,000 litres of bio-oil combusted.

Orenda is preparing to start a follow-on commercialisation programme which will examine:

- upgrading fuel quality by post production processing; redesign of sections of the GT2500 to deal with the viscosity, ash, acidity and particulate content of the bio-oil
- performance and emission tests over longer term engine operation with upgraded hot section components (up to 150 hours)
- development of specifications for the engine, auxiliary, and fuel handling systems for commercial application.

The successful completion of this commercialisation phase will allow Orenda to provide warranties for the use of the turbine with biomass pyrolysis oils.

#### **Microemulsions**

The CANMET Energy Technology Centre has developed a pyrolysis liquid in diesel oil micro-emulsion fuel. Tests to date indicate that stable emulsions of bio-oil in diesel ranging from 5% - 40% can be produced. Bio-oil produced from hardwood, softwood and agricultural feedstocks have been successfully processed and various qualities of diesel fuel can be used. The next phase of the work will examine additional bio-oil feedstocks, further optimise the process and examine fuel quality and combustion characteristics of the various emulsion mixtures.

#### **Biodegradability**

In other recently completed work, RTI Ltd. has performed preliminary studies on the biodegradability of bio-oil using respirometry methods. It was determined that bio-oil is highly degradable, much more than hydrocarbon fuels. This was especially true if the bio-oil is brought to a neutral pH. These results are important assurances concerning the safety of pyrolysis oils in commercial applications. A final report outlining the test procedures and results is available from RTI Ltd.

# Book reviews

#### Biomass gastification & pyrolysis state of the art and future prospects

Edited by M. Kaltschmitt and A.V. Bridgwater 1997, 550 pp, ECU 150 CPL Scientific Limited, 43 Kingfisher Court, Newbury, Berkshire RG14 5SJ, U.K ISBN: 1 872691 714

Gasification and Pyrolysis are very promising options for further use of biomass in Europe especially for electricity production. Both technologies have made significant progress over the last three years and although neither is truly economic in the absence of fiscal incentives, the scientific and technical knowledge base has grown considerably and is thereby aiding the improvement of the technology and reducing costs.

This book includes all the papers offered at the final meeting of the EC sponsored Gasification Network which was combined with a meeting of the Pyrolysis Network - PyNE. This conference was held in Stuttgart from 9-11 April 1997.

Several overviews are included in which the status and prospects of biomass for energy, the development of gasification and pyrolysis, the characteristics of biomass and of its conversion products are discussed. Two sections follow dedicated to the presentations of gasification and pyrolysis. Conclusions and recommendations complete the work.

In the gasification section, research and applications in fixed bed and in fluidized bed reactors are reported. Experiences with demonstration plants are also explained. A large part of the proceedings is dedicated to gas cleaning; tar removal and environmental aspects of gasification.

The pyrolysis section contains a state of the art review of pyrolysis processes and includes some experiences on pilot and demonstration plants. Subsequently several papers are dedicated to the upgrading and characterisation of the bio-oils. The bio-oil as source of chemicals and the utilization as fuel for engines or boilers are also embraced. A description of PyNE, the pyrolysis network for Europe, ends the section.

Biomass Gasification & Pyrolysis contains more than 50 papers and represents a very useful update for everyone to know about the latest developments and successes in both areas.

# Making a business from biomass in energy, environment, chemicals, fibres and materials

Edited by R.P. Overend and E. Chornet 1998 New York, 2 Vol. US \$ 400 Elsevier Science Inc., 660 White Plains Road, Tarrytown, New York 10591-5153, U.S.A. ISBN: 0080429963

The work, published in two volumes, reports the proceedings of the 3rd Biomass Conference of the Americas, Montréal, Québec, Canada, 24-29 August 1997.

The papers reflect the theme that a novel biomass industry is progressively emerging, with diversified technologies and applications, complementing and expanding upon traditional biomass sectors.

Technology transfer, scale-up demonstrations, commercial applications and new business development ventures are presented in depth. Emphasis is placed on how to make a profitable business from biomass within a vision on sustainability, flexible chemical processing and energy efficiency.

The proceedings comprise the following key areas:

- Resource Base cost effective development and expansion of biomass production.
- Environmental Impact and Sustainability

   issues surrounding increased biomass
   production and usage.
- Heat and Power conversion of biomass to bioenergy in order to produce heat and power and combined heat and power (CHP).
- Pyrolysis and Bio-oils an emerging area at the intersection of energy and chemicals.
- Chemicals and Materials product development based upon the conversion of biomass to chemicals and materials.
- Biofuels major technological advances in this area.
- Anaerobic digestion complementary viewpoints, scientific and commercial applications.
- Systems Integration biomass-driven industries as unique opportunities for future generations.
- Economics and Business case studies of specific biomass projects.

This publication is an invaluable reference tool for those engaged in research and the commercial applications of the above emerging biomass and bioenergy technologies.

# Physical characterisation of biomass-based pyrolysis liquids

Anja Oasmaa, Ero Leppamaki, Paivi Koponen, Johanna Levander, Eija Tapola 1997, 76 pp. VTT Technical Research Centre of Finland, Vuorimiehentie 5, P.O. Box 2000, FIN-02044 VTT Finland ISBN: 951-38-5051

Biomass pyrolysis liquids differ a great deal from petroleum-based fuels in both physical properties and chemical composition. Pyrolysis liquids contain more water and usually more solids, are acidic, have a low heating value and are unstable when heated, especially in air. Due to these differences the standard fuel oil methods developed for mineral oils may not be suitable as such for pyrolysis liquids.

The book reports a study performed by VTT, focuses on testing and modifying the standard fuel oil analyses routinely used.

The book is divided in two parts. In the first one the main characteristics of bio-oils and the problems linked with their determinations are discussed. The second part consists of 13 appendices in which some analytical methods and results are briefly described.

This book represents a useful reference point for researches engaged in the study of the biomass pyrolysis process and in the development of bio-oils applications.

#### **Contents:**

- 1. Introduction
- 2. Production and Homogeneity of Pyrolysis Liquids
- 3. Sampling
- 4. Water, Ash and Elemental
- 5. Fuel-oil Properties
- 6. Acidity and Material corrosion
- 7. Miscibility
- 8. Lubricity
- 9. Stability
- 10. Recommendations
- 11. References
- 12. Appendices 1-13

# **Diary of Events**

#### International Workshop CUBASOLAR '98 Science Development and Solidarity

Venue: Habana, Cuba 13-17 April 1998 Date: SOCIE, Calle Luz No. 375, Contact: e/ Picota y Compostcla,

Havana Vieja C Havana, Cuba

Tel: +537 612846

+537 331732 and 332699 Fax:

#### **Energetic and Material Utilisation** of Renewable Resources

Germany Venue:

20-22 April 1998 Date: Contact:

DGMK, Frau Christa Jenke, P.B. 60 05 49, D-22205, Hamburg

#### MAVA '98

#### International Business Convention on Thermal Treatment and Energy Recovery from Waste and Biomass

Venue: Switzerland Date: 4-5 May 1998

Contact: Hubert Klun or Christophe

Estermann, Case Postalel 293, CH-1000 Lausanne 22, Switzerland

Tel: +41 24 426 11 11 +41 24 426 77 77 Fax: E-mail: mava@fastnet.ch

#### 14th International Symposium on **Analytical and Applied Pyrolysis**

Munich, Germany Venue: 18-20 May 1998 Date: Contact: c/o Ulla Schrodel, GSF -

Forschungszentrum, Congress Service, Postfach 11 29, D-85758

Neuherberg, Germany Tel: +49 89 3187 3030/2669 +49 89 3187 3362 Fax:

#### AGROENVIRON '98 - Towards 21st Century **International Symposium**

Venue: Pakistan 25-30 May 1998 Date:

Faculty of Agricultural Engineering Contact: & Technology, University of

Agriculture, Faisalabad, Pakistan Tel: +92 41 3028189 Fxt 434 +92 41 647846/30769 Fax:

#### **Biomass for Energy and Industry** 10th European Conference and Technology Exhibition

Congress Centre Wurzburg, Germany Venue:

Date: 8-11 June 1998

Contact: WIP, Sylvensteinstrasse 2,

D-81369 Munchen, Germany +49 89 720 1232

Tel: +49 89 720 1291 Fax: Website: http://www.wip.tnet.de

#### The 9th Global Warming International Conference

Venue: Hong Kong 8-11 June 1998 Date:

GW9 Conference Secretariat, Contact:

PO Box 5275, Woodridge, IL 60517. USA.

+1 630 910 1551 Tel: Fax: +1 630 910 1561

#### 2nd Asia Pacific Conference on Sustainable Energy and Energy and Environmental Technology

Venue: ANA Hotel, Gold Coast, Australia

Date: 14-17 June 1998 APCSEET '98 Secretariat Contact: Tel: +61 7336 90477 Fax: +61 7336 91512 Email: apc@cheque.uq.edu.au

#### **Power Production from Biomass III**

Hanasaari Cultural Centre, Finland Venue: 14-15 September 1998 Date:

Mrs Maija Korhonen, VTT Energy, Contact: Seminar Power Production

from Biomass III, PO Box 1601, FIN-02044 VTT, Espoo, Finland +358 9 460 493

Fax: Email: Maija.Korhonen@vtt.fi

#### **World Renewable Energy Congress**

Venue: Florence, Italy 20-25 September 1998 Date: Professor A A M Sayigh, Contact:

World Renewable Energy Network, 147 Hilmanton, Lower Earley, Reading, RG6 4HN, UK

+44 (0) 118 961 1364 Tel: +44 (0) 118 961 1365 Fax.

#### Gasification - The Gateway to a Cleaner Future

Venue: Dresden Hilton, Dresden, Germany Date: 23-24 September 1998 Tracy Lepkowska, (Gasif 3), Contact:

IChemE Conference Department, 165-189 Railway Terrace, Rugby, Warwickshire, CV21 3HQ, UK.

Tel: +44 (0)1788 578214 +44 (0)1788 577182 Fax: tlepkowska@icheme.org.uk Email:

#### 8th Biennial Conference

Madison, Wisconsin Venue: 4-8 October 1998 Date: Fred Kuzel or Naureen Rana. Contact: Great Lakes Regional Biomass Energy Program, 35 East Wacker Drive, Suite 1850, Chicago, IL 60601, USA +1 312 407 0177 +1 312 407 0038 Tel·

Fax: Email: fkuzel@cglg.org OR nrana@cglg.org

http://www.cglg.org/bioenergy98 Website:

#### Materials and Energy from Refuse

Oostende, Belgium Venue: Date: 12-14 October 1998

Ms Rita Peys, c/o Technologisch Contact: Instituut vzw, Desguinlei 214,

B-2018 Antwerpen, Belgium. Tel: +32 3 216 09 96 +32 3 216 06 89 Fax: Email: mer@ti.kviv.be

http://www.kviv.be/ti/mer.htm Website:

#### 2nd International Conference LCA in Agriculture, Agro-Industry and Forestry

Brussels, Belgium Venue: 3-4 December 1998 Date: Mrs Mieke Engelen, Product Contact: and Process Assessment, VITO,

Boeretang 200, B-2400 Mol, Belgium.

+32 14 33 58 53 Tel: +32 14 32 11 85 Fax: Email: engelenm@vito.be

#### SUSTAIN '99

#### The World Sustainable Energy Trade Fair

Amsterdam RAI, The Netherlands Venue:

Date: 25-27 May 1999 +44 181 289 8989 Tel: +44 181 289 8484 Fax: Website: http://www.emml.com

## Please contact your country representative for further information.



#### Tony Bridgwater

Aston University Birmingham **B4 7ET** UNITED KINGDOM

Tel: +44 121 359 3611 Fax: +44 121 359 6814/4094 Email: a.v.bridgwater@aston.ac.uk



#### **Maximilian Lauer**

Institute for Energy Research Joanneum Research Elisabethstrasse 11 A-8010 Graz **AUSTRIA** 

+43 316 876 332 Tel: +43 316 876 320 Email: max.lauer@joanneum.ac.at



#### **Belgium**

#### Rosanna Maggi

Université Catholique de Louvain Unite de Catalyse et Chimie des Matériaux

Place Croix du Sud 2/17 Louvain-la-Neuve 1348 **BELGIUM** 

Tel: +32 10 473 652 Fax: +32 10 473 649 Email: maggi@cata.ucl.ac.be



#### Jan Piskorz

RTI - Resource Transforms International Ltd 110 Baffin Place, Unit 5

Waterloo **Ontario** N2V 1Z7 **CANADA** 

Tel: +1 519 884 4910 Fax: +1 519 884 7681 Email: jpiskorz@rtiltd.com



#### Karsten Pedersen

Danish Technological Institute Technology Park

Aarhus C, DK-8000 **DENMARK** 

Tel: +45 89 43 8617 +45 89 43 8673 Fax: Email: karsten.pedersen@dti.dk



#### Anja Oasmaa

VTT Energy **Fuel Processing Laboratory** PO Box 1601 Espoo

FIN-02044 VTT **FINLAND** 

+358 9 456 5517 +358 9 460 493 Fax: Email: Anja.Oasmaa@vtt.fi



#### **Philippe Girard**

Cirad Forêt Maison de la Technologie

73 rue J.F. Breton

BP5035

Montpellier Cedex 34032 FRANCE

Tel: +33 467 61 44 90 Fax: +33 467 61 65 15 Email: girard.p@cirad.fr



#### **Dietrich Meier**

BFH-Institute for Wood Chemistry Leuschnerstrasse 91

D-21031 Hamburg **GFRMANY** 

Tel: +49 40 739 62 517 +49 40 739 62 296/480

Email: dmeier@aixh0501.holz.uni-hamburg.de



#### **Yannis Boukis**

C.R.E.S. - Biomass Department 19th km Athinon Marathona Ave

Pikermi – Attikis GR - 190 09 GREECE

+30 1 60 39 900 Tel: +30 1 60 39 904/905 Fax:

Email: ibookis@cresdb.cress.ariadne-t.gr



#### **Pearse Buckley**

University of Dublin

Dept of Civil, Structural & Environmental Engineering

Museum Building, Trinity College Dublin 2

**IRELAND** 

Tel: +353 1 608 2343 +353 1 677 3072 Email: pbuckley@tcd.ie



#### **Leonetto Conti**

University of Sassari Dipartimento di Chimica

Via Vienna 2 Sassari I-07100

**ITALY** Tel:

+39 79 229533 +39 79 229559/212069 Fax: Email: conti@ssmain.uniss.it



#### **Wolter Prins**

Twente University of Technology BTG **Chemical Engineering Laboratory** PO Box 217

7500 AE Enschede **NETHERLANDS** 

Tel: +31 53 489 2891 Fax: +31 53 489 4774 Email: w.prins@ct.utwente.nl



#### **Norway**

#### Morten Gronli

Department of Thermal Energy and Hydropower

7034 Trondheim NORWAY

Tel: +47 73 59 37 25 Fax: +47 73 59 37 25 Email: Morten.Gronli@energy.sintef.no



#### **Portugal**

Filomena Pinto INETI-ITE-DTC Azinhaga dos Lameiro Estrada do Paço do Lumiar 1699 Lisboa Codex PORTUGAL

Tel: +351 1 716 52 99 +351 1 716 46 35

Email: Filomena.Pinto@ite.ineti.pt



#### 🕵 Spain

Universidad de Zaragoza Chemical and Environmental Engineering

Maria de Luna 3 SPAIN

Tel: +34 97 676 1878/60 Fax: +34 97 676 1861



#### Sweden

TPS Termiska Processer AB Studsvik

S-611 82 Nykoping **SWEDEN** 

Tel: +46 155 221385 +46 155 263052 Email: erik.rensfelt@tps.se



#### Stefan Czernik

NRFI 1617 Cole Boulevard Golden Colorado 80401-3393

**IISA** +1 303 275 3821 Tel: Fax: +1 303 275 3896

Email: czerniks@tcplink.nrel.gov



