Biorefining and Carbon Cycling Program at the University of Georgia

By Dr K C Das, University of Georgia, USA

In 2004, the University of Georgia (UGA) began a coordinated effort in biorefining and carbon cycling research, outreach, and education. The vision of the program is to combine biomass production and conversion with carbon cycling (Figure 1), thereby creating a sustainable process. Biomass is obtained from agriculture, forestry, and municipal sources and processed to multiple products in a biorefinery. Some products, e.g. carbon based products from a pyrolysis biorefinery, are transformed to fertiliser products that are returned to the soil for nutrient value and long-term carbon sequestration. The UGA program includes different colleges and departments on the university campus, departments from other partner universities and national laboratories. The focus of the effort covers biorefining through both thermochemical (pyrolysis) and biological routes and integration within these two pathways.

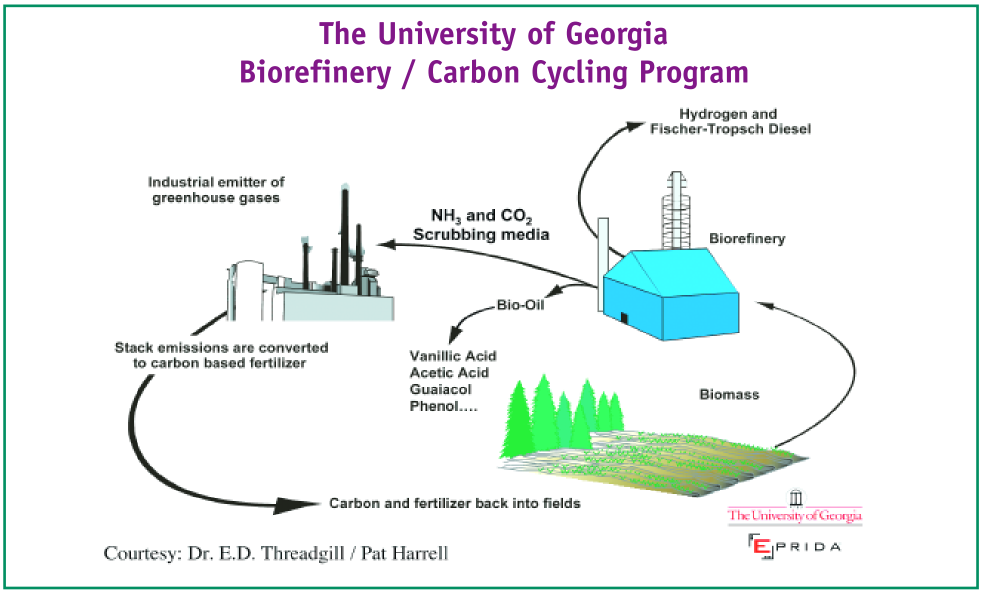

Figure 1: Biomass production and conversion with carbon cycling.

The key strengths of the UGA program include:

1. A world class school of forest resources.
2. A well integrated cooperative extension service that works closely within the agricultural and forestry sectors.
3. A wide range of scientists and educators in the basic sciences and engineering, who understand plant biology, chemistry, processing, etc.
4. Close links to private companies in Georgia that are commercialising biomass conversion technologies.
5. Research collaboration with national laboratories who are leaders in the field of technology development and dissemination.

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Comments and contributions are most welcome on any aspect of the contents.
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Activities within the program include development of new technology, accelerating technology transfer, and offering educational programming that facilitates the transition to a future biobased economy. The UGA is assisting a key local partner to commercialise biomass pyrolysis technology (see *www.eprida.com* for additional details). The present focus is on completing a 1000-hour demonstration of pyrolysis and steam reforming to produce hydrogen from biomass.

The UGA Faculty of Engineering Outreach Service (see *http://www.engr.uga.edu/service/outreach* for additional details) is conducting bioenergy based technology transfer to industries in the southeastern USA. Activities include emission testing from commercial biomass gasification operations, collection and upgrading of pyrolysis oil from pilot and commercial operations, development of ethanol and biodiesel pilot plants, and offering training courses in biodiesel production.

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Research efforts at the UGA are highly interdisciplinary and multidirectional. They can be broadly classified into seven areas:

1. Biomass development including breeding and genetic engineering in forestry and agriculture.
2. Harvesting technologies, time motion studies, and pretreatment of biomass.
3. Fermentation technology – including ethanol from lignocellulosics.
4. Thermochemical conversion technology.
5. Products from pyrolysis oil.
6. Applications of char including catalyst applications and soil applications.
7. Carbon dioxide used as a carbon source for fermentation.

Other fundamental research efforts include development of the atomic layer epitaxy process applied to fuel cell manufacturing [Chemistry department]. Biotechnology researchers are working on metabolic engineering of biochemical pathways to enhance the ability of organisms to use gaseous CO_2 as a co-substrate and produce value added chemicals. Engineering faculty members are working on upgrading pyrolysis oil for use in diesel engines. Other partners are looking at extracting products out of pyrolysis oil using a fractionation process within a condensation train. Products include developing nutrient enriched manufactured soils, binding agents for pellet production, and odour suppressants for the poultry industry. In addition, char is being used as a catalyst for air pollution control.

The UGA program has a strong interdisciplinary focus that targets educational programming to provide unique, pertinent, and comprehensive training and educational experiences to prospective students. Degree programs are available in varied disciplines including Engineering, Forestry, Ecology, Economics, Biology, Microbiology, Biochemistry, Physics, Chemistry, etc. Students pursuing masters and doctoral degree objectives can work with researchers in more than one field of work, thereby developing a truly interdisciplinary program of study.

Biomass Fast Pyrolysis in a Fluidised Bed: Results of Modeling and Laboratory Scale Experiments

By Dr Wolter Prins, The University of Twente, The Netherlands

University of Twente
Enschede - The Netherlands

A recently completed project at the University of Twente has investigated biomass fast pyrolysis both theoretically and experimentally in a laboratory-scale fluidised bed. The work was carried out by Xiaoquan Wang. The objectives were to both assess the value of fundamental (single-particle) modeling for reaction engineering purposes and develop a new concept of in-situ filtering of the fast pyrolysis vapors by filter elements submerged in the fluidised bed.

Reaction modeling

Unfortunately it is quite difficult to extract reliable quantitative information on conversion rates and product yields from the literature on biomass pyrolysis. There is an extensive scatter in the reported biomass kinetics and selectivity data, even for a single biomass type. Intrinsic reaction rates published for different biomass types vary by up to a factor of 10, and even trends are not always uniform. For kinetic studies, pyrolysis products have usually been lumped into three classes: gas, liquid and char. However the quality/composition of these product classes (e.g. the water content of the liquid) remains unspecified, which is a serious shortcoming in practical application.

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Figure 1: 1kg/h fluid bed pyrolysis unit.

Figure 2: Close up of the reactor section.

The pyrolysis time of biomass particles in the size range of 1 to 5mm, usually applied in full-scale reactors at 500°C, is influenced by the following three mechanisms:

1. The heat transfer from the bulk of the reactor to the particle.
2. The intra-particle heat conduction.
3. The pyrolysis kinetics.

Model calculations further show that the external heat transfer coefficient (related to the reactor type) has hardly any influence on the product yields at typical fast pyrolysis conditions (t = 500°C; dp > 1mm). Single particle models also predict (for all available kinetics) that the influence of the particle size on the liquid yield is small.

Millimetre sized wood particles (pine, beech, bamboo, demolition wood) have been pyrolysed batch-wise in a fluid bed laboratory set-up. The results of the various experiments were compared with model predictions. The main observations are listed below:

- Wood particles stay intact during fluid bed pyrolysis but shrink in volume by approximately 40%.
- Product yields of pine and beech wood obtained are quite similar. Between 450 and 550°C, the bio-oil yield is maximised, and the water content of the bio-oil is minimised. A relatively high yield of char is produced from bamboo particles and demolition wood pellets.
- In the fluid bed setup used, (with a low char hold-up), the residence time of the pyrolysis vapors was not very critical: μ < 5 seconds appeared to be acceptable at 500°C.
- In agreement with the model predictions, experiments showed that the particle size only has a minor effect on the total liquid yield up to a diameter of 20mm. But when measured for 3mm pine wood particles, the water content of the bio-oil produced increases substantially.
- Existing single particle models have a limited predictive power with respect to the product distribution and the conversion time of small particles (< 3 mm), due to a wide variation in reported decomposition kinetics.
- Variations in bio-oil quality (e.g. water content of the liquid) cannot be predicted by existing single particle models.

In-bed filtration

The concept of in-situ extraction and cleaning of pyrolysis vapors through a filter immersed in a fluidised bed reactor has been tested in various arrangements. Oil samples have been produced that were free of solid particles, magnesium and sodium. These samples still contained some potassium that may have entered the oil via the vapor phase.

With respect to the filtering, no severe problems have been encountered while operating a continuous bench-scale setup (1 kg/hr feed rate). The filtered oil contained half the particles but five times less ash than the non-filtered oil: the difference is caused by solids formation behind the filter. The bio-oil was shown to be much more stable than the non-filtered oil. From visual inspection, there is evidence that char fines and bed material passed through the 10 to 15 μm filter during the 13 hours of operation.

A full-scale filter-assisted fluid bed reactor (10 tons of biomass per hour) in which 80% of the vapors and gases are extracted through immersed filters, would be significantly smaller in volume than a fluid bed pyrolysis reactor without filters, but only when the biomass feed particles are below 3mm diameter. For larger biomass particles, hold-up considerations determine the reactor volume.

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Acknowledgements

The work was carried out in the research group of Prof. Van Swaaij at the University of Twente by PhD student Xiaoquan Wang, supervised by Dr. Sascha Kersten. The research was enabled by financial contributions from the EC, the Dutch government through NWO and Senter, and Shell.

Upgrading of Flash Pyrolysis Liquid using Mild Oxidation with Ozone

By F. Mahfud, H. Heeres and H.J. Heeres, University of Groningen, Netherlands

RuG

Flash pyrolysis liquid (also called bio-oil or bio-crude-oil, BCO) is a biomass derived liquid product. It is produced using a fast pyrolysis process in yields up to 70wt% [1-4]. BCO may be used for energy and heat generation (boiler fuel, co-firing in power stations) and also has potential to be used as a liquid transportation fuel for internal combustion engines. For the latter applications, upgrading will be required for example to improve the caloric value and to reduce colour and odour.

We have performed exploratory experimental studies on the upgrading of BCO using ozone with the primary aim to produce a colourless, odourless and transparent liquid bio-oil. Ozone is a known oxidant for wastewater treatment and bleaching processes [5].

Treatment of BCO (obtained from beech wood by fast pyrolysis using the Rotating Cone technology) in methanol with ozone under mild conditions of atmospheric pressure and 1°C for less than 15 minutes, resulted in the formation of a slightly yellow, transparent BCO with a mild odour. Extended ozonation did not result in significant colour changes as shown in Figure 1.

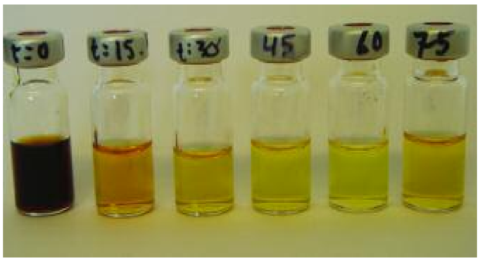

Figure 1: Visual appearance of BCO during ozonation (time in minutes).

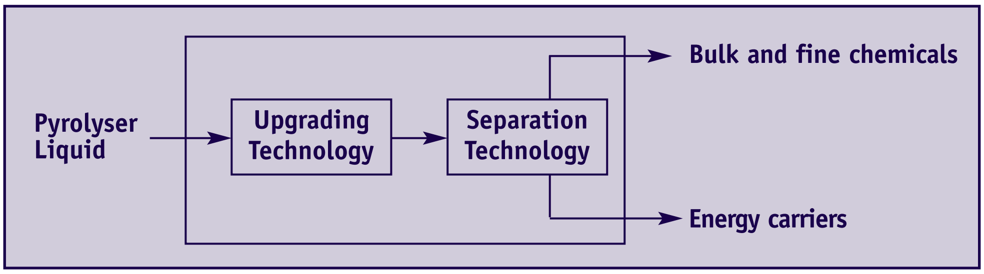

Figure 2. Integrated concept for BCO upgrading.

Storage of the treated BCO at room temperature for at least a month preserved the yellow colour and did not cause the colour to darken.

To gain insights in the molecular processes taking place during ozone treatment, the samples were analysed with several analytical techniques including 2D-GC, GC/MS and NMR. BCO is a complex mixture with hundreds of oxygenated organic molecules present [1]. Analysis reveals that the phenolic compounds that arise from the lignin fraction of wood, are converted to form ring-opened oxygenated compounds. Large amounts of oxalic acid and the methylester of oxalic acid (due to esterification with methanol) were produced. These findings are in line with the results obtained by Rubio et al. [6] for ozonation of raw almond shell.

A number of the oxygenates formed by ozonation (such as oxalic acid) are interesting chemicals for bulk and fine-chemical applications. As such, ozonation could be a useful technology to be incorporated in an integrated energy-chemical concept for BCO upgrading as indicated in Figure 2.

In conclusion, we have shown that mild oxidation of BCO with ozone is an interesting methodology to upgrade the properties of BCO. In addition, a variety of interesting oxygenated products are produced with high added value. Further studies to identify and quantify the amounts of the various oxygenates and the development of efficient separation technology are in progress.

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We would like to thank BTG, Enschede for providing the pyrolysis oil and for stimulating discussions.

Pyrolysis of Perennial Grasses from Southern Europe

By Mark Coulson, Aston University, UK

Introduction

Aston University has recently completed work on the EC funded Framework 5 "Bio-Energy Chains" project. The three-year project focussed on four promising energy crops previously identified as producing high biomass yields in southern Mediterranean climatic conditions. These were:

- Giant reed (Arundo donax)
- Elephant Grass (Miscanthus giganteus)
- Switchgrass (Panicum virgatum)
- Cardoon (Cynara cardunculus)

The objective of the overall project was to examine the full energy chain from the planting of the crops to the delivery of a final energy product. The project involved ten partners from eight countries and included conversion of biomass by pyrolysis, gasification and combustion.

Pyrolysis of grasses

The main focus of the pyrolysis investigation was to determine the yields, composition and quality of the pyrolysis products from each crop. Experiments were performed at a range of temperatures in order to determine the best reactor temperature to maximise the yield of organic liquids, and hence the overall energy conversion efficiency of the process.

Figure 1: 1kg/hr fluidised bed pyrolysis rig with two cyclones, quench and electrostatic precipitator.

Crop samples were provided from the agricultural partners in the project, which had been grown and harvested in a number of different ways and it was immediately apparent that the ash content and composition of each crop could vary significantly. This was expected to have an impact on pyrolysis yields since it is known that high ash biomass tends to produce low liquid yields. In particular, the presence of alkali metals is known to catalyse secondary reactions in the vapour phase that reduce liquid yield and increase gas and water yields.

In particular, crops that matured late in the year and were then left to over-winter in the field had lower ash and alkali metals content due to rain leaching. Conversely, crops harvested in dry dusty conditions and with poorly developed harvesting methods had extremely high ash contents due to soil contamination, even up to 18wt% on a dry basis. The lowest ash content samples from each type of crop were selected for pyrolysis experiments, and ranged from 1.9 to 5% d.b. The alkali metal content varied from ~0.1 to ~0.7wt % on biomass d.b.

Pyrolysis experiments were performed in the laboratory fluid beds at Aston. The smaller rig of 100g/hr was used for determining optimum yield conditions by testing at a range of temperatures, and the larger rig of 1kg/hr was used to obtain larger oil samples for quality assessment and for performing more detailed energy balances. See Figures 1 & 2.

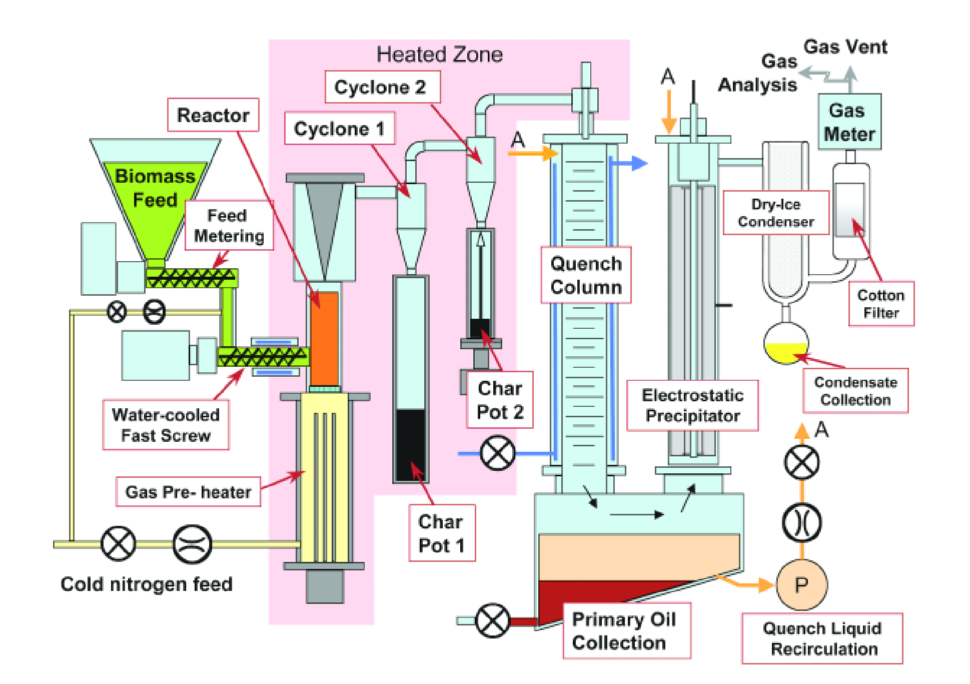

Figure 2: Schematic of 1kg/hr fast pyrolysis unit.

Results

A total of 21 tests with detailed mass balances were performed and it became apparent that the liquid yields were not strongly dependent upon the particular crop but upon its inorganic (ash) content and composition. The composition of each crop was measured, and the yields were correlated with ash content, and a range of individual metal contents.

The results of the analysis showed that the temperature at which the maximum organic liquid yield occurred increased as the alkali metal content reduced. Similarly, as the alkali metals reduced, the organic liquid yield increased as shown in Figure 3.

When crops had alkali metals of <0.1 wt% then their optimum pyrolysis temperature was around 500°C and at this temperature their organic liquid yields were over 60wt% on a dry ash free feedstock basis (d.a.f.). These results are similar to those presented in the literature for clean wood feedstocks.

Conversely as alkali metals increased (to >0.5wt % d.b.) the optimum temperature reduced towards ~450°C and the maximum organic liquid yield obtained at this temperature decreased to as little as 44wt% d.a.f.

While the lignin content of the samples was not measured, literature data suggested relatively small variation between the crops tested and it would seem that alkali metals are the dominant influence on yields.

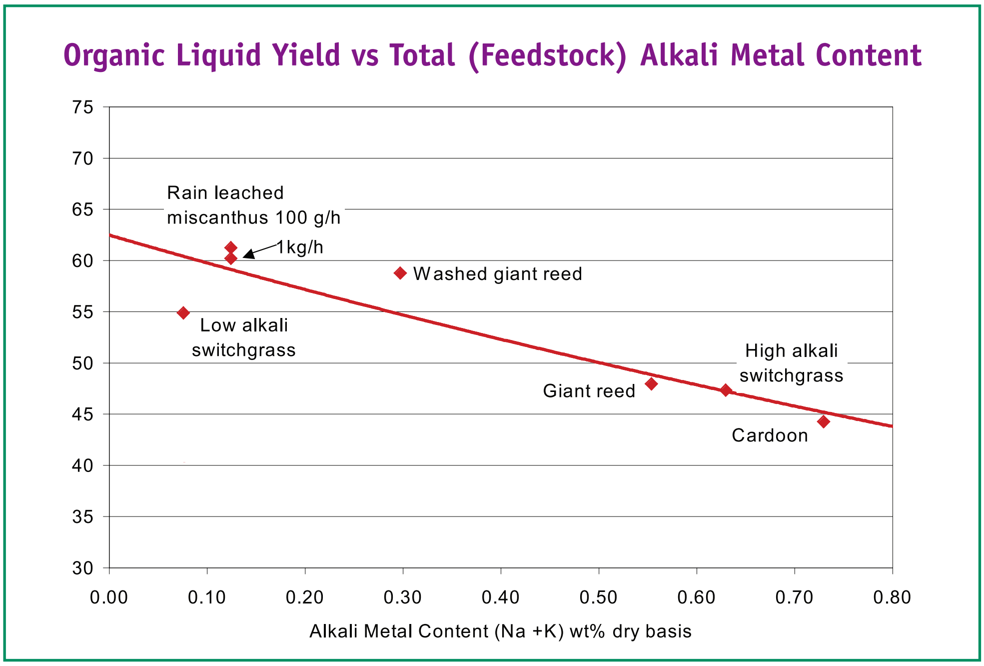

Figure 3: Liquid yield vs feedstock alkali metal content.

Similarly, the low alkali metal content crops produced oils of the highest quality, with the lowest water content. These oils were single phase and comparable with oils produced from wood feedstocks. The best oil produced, from rain leached miscanthus at a temperature of 500°C had a water content of 23% and a lower heating value of 17 MJ/kg, and represented an energy conversion of 70%.

Problems were experienced with the conversion of cardoon. In particular, bed agglomeration was observed, and it proved impossible to pyrolyse this crop at temperatures above about 470°C. Reasons for this are unclear but sticky low melting point eutectics in the ash fraction of the char are suspected.

Washing

The work detailed above led to the conclusion that these crops will only be suitable for fast pyrolysis if their alkali metals and in particular potassium content can be minimised. Since rain leaching is not a reliable means of achieving this, a number of simple washing methods were investigated to evaluate their effectiveness in reducing such metals.

These experiments showed that (when the biomass is ground to a small particle size suitable for pyrolysis) alkali metals reductions of >80% should be easily achievable with a short (<1hr) wash/rinse cycle using cold water. However, the amount of water required to do this is relatively large (perhaps >15 times the mass of the biomass) and economics would probably dictate that such a process is not feasible. More work needs to be done to consider the economics and process integration aspects of washing, for example combining washing with a densification process to reduce biomass transportation costs.

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Preconditioning of Biomass Through Fast Pyrolysis for Different Biofuels Applications (PRECOND')

By François Broust and Philippe Girard, CIRAD-Forestry Department, Montpellier, France

A new French project funded by the Research National Agency (ANR) and coordinated by CIRAD aims at defining a decentralised route of biomass preconditioning through fast pyrolysis for the production of bio-oils as intermediate bio-fuels dedicated to centralised bio-energy production.

Scope of project

The PRECOND project covers thermochemical conversion of biomass for production of the following bio-energy products:

- transport bio-fuels through gasification and FT-synthesis
- transport bio-fuels through petroleum co-refining
- heat and/or electricity through combustion in boilers.

Biomass is a resource with variable composition, wide geographical dispersion and low energy density. These are important drawbacks when large-scale bio-energy production units are considered: for instance, throughputs of about 3 million t/year of dry biomass are necessary to make a FT unit competitive. In order to minimise the impact of transport, an alternative to the direct upgrading of biomass consists of preconditioning it on decentralised sites before transportation to a centralised bio-energy production unit.

The route considered in this project is fast pyrolysis for the preparation of a liquid biofuel (in this case bio-oil), which has a promising potential either for overcoming the problem of biomass variability and/or for improving bioenergy system efficiency in both mass and energy terms.

Objectives of the project

The main purpose consists of validating the concept of a fast pyrolysis reactor for:

- producing bio-oils which meet the specifications required for transport and further upgrading for each projected method of utilisation
- high bio-oils yields (>75%) and high thermal efficiency (80%)
- able to accept a wide range of biomass resources from various origins, in particular those that are identified as the most promising at the national scale.

Outcomes

The outcomes will be to:

- define the final technical requirements of a demonstration-scale pilot unit (0.5-1 t/h feed rate) that will be dedicated to large scale tests
- assess the viability of the whole route from the resource to the transformation unit in technical, economical and environmental terms (Figure 1).

The main scientific stakes are:

- to define these specification limits regarding each end-application: gasifier (to syngas), petroleum refinery unit or boilers
- to evaluate the optimisation parameters of the reactor with regards to mass and energy efficiencies and the specifications of bio-oils produced.

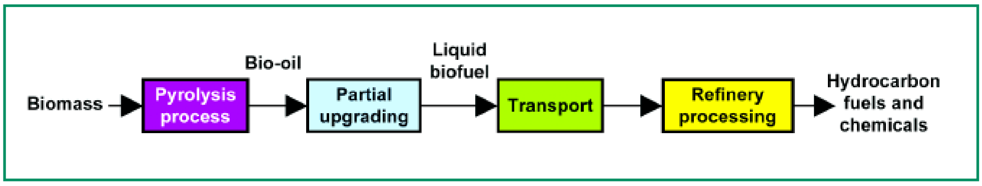

Figure 1: Bioenergy system to be evaluated.

Work programme

The project is divided into 5 main work packages:

1) Definition of bio-oil specifications required for the final utilisation in transformation units by evaluation of the existing processes with regards to these specifications.
2) Design and construction of a laboratory scale pilot reactor (3-5 kg/h) at CIRAD. Experiments will be carried out on different kinds of biomass, with the aim of evaluating the optimisation parameters with regards to mass and energy efficiencies and the specifications of the bio-oils produced.
3) Modelling of the reactor for its further optimisation and scale-up.
4) Development of new methods for characterisation of bio-oils and their formulation into pre-conditioned feedstocks suitable for transport and feeding into the transformation units.
5) Finally, a techno-economic and environmental assessment of the whole pre-conditioning route will be performed from the data collected, and compared to other routes such as torrefaction.

Project information

Partners

Research centres: CIRAD (coordinator); IFP; CEA
University laboratories: CNRS-LSGC; GRADIENT-UTC
Industrial partners: TOTAL; EDF R&D
University overseas partner: Aston University

Funding

The project is funded by the French National Research Agency (ANR) / Programme National de Recherche sur les Bioénergies. Starting date: January 2006. Duration: 3 years.

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The All-Russian Scientific Research Institute for Electrification of Agriculture (VIESH)

By Prof. Dr. Dmitry S. Strebkov, VIESH, Russia

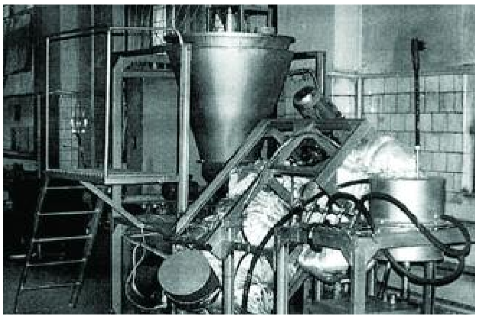

Figure 1: Pyrolysis module: 3 kg of plant biomass (wood dust, peat, etc) per hour.

VIESH is a State scientific institution, founded in 1930, which is a federal research centre on power supply, electrification and automation in agriculture, technological development and utilisation of renewable and non-conventional energy sources. There are 220 skilled experts, including 20 doctors of sciences and 70 researchers. The institute offers postgraduate studies and the specialised Council on doctor's and master's theses in four areas of speciality:

- Electricity technologies and electrical equipment in agriculture.
- Energy installations based on renewable energy sources.
- Automation and control of technological processes in agricultural production.
- Agriculture technologies and mechanisation.

VIESH issues reports on power, electrification and automation in agriculture and organises scientific and technical conferences on rural energy and electrification.

Basic activities of VIESH

1. Scientific forecasts and strategies for power supply, electrification and energy saving in agriculture, environmentally safe technologies, and systems for electrification of agricultural processes.
2. Effective electricity generation technologies, thermal and electrical equipment and automation systems for animal industries, plant cultivation, primary processing and storage, electric tractors and electric transportation systems in agriculture.
3. Development of methods and systems for reliable rural power generation and transmission systems, electrical installations, operation and safety of electrical equipment, including stand alone power systems.
4. Systems and methods for electrification and mechanisation in cattle breeding.
5. Prospective technologies and development of new applications of renewable energy sources in agriculture.
6. Scientific education and improvement of professional skills.
7. Commercial activities and international scientific and technical cooperation in the field of rural and renewable energy.
8. Information, consulting and implementation services.

In the field of biomass, we focus on micro- and mini-thermo-electric systems with plant biomass pyrolysis modules based on the principal of direct contact heating. Our main objectives are the minimisation of plant weight and dimensions; and the cost of pyrolysis equipment.

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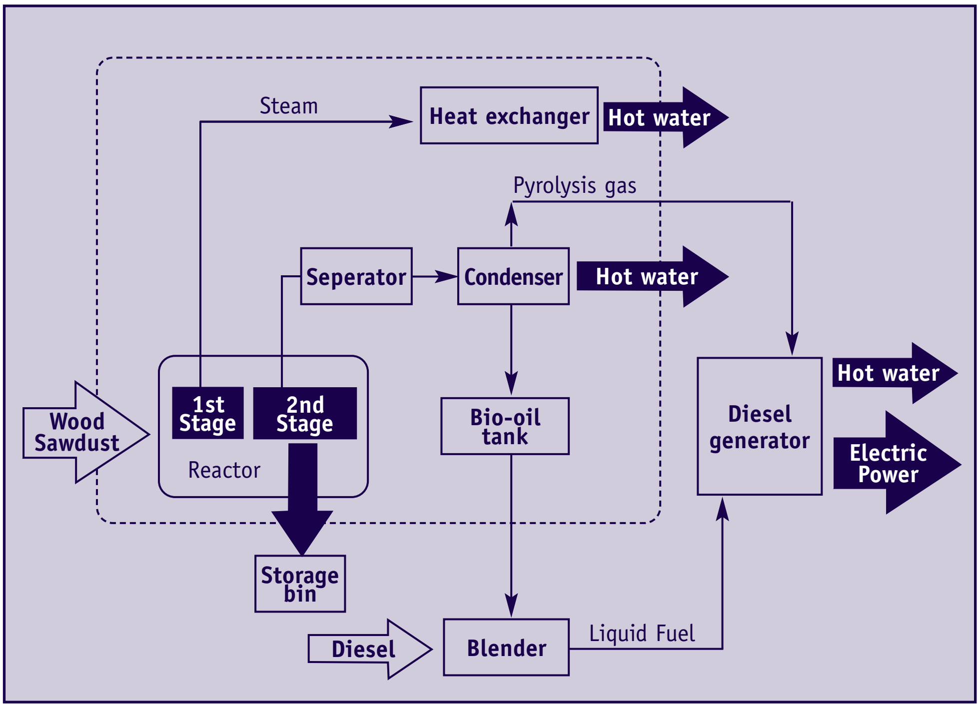

Figure 2: Block diagram of pyrolysis process.

Pilot pyrolysis unit

A pilot plant for production of fluid fuels from sawdust and other plant wastes has been developed in the frame of a contract from the RF Ministry of Power. The plant is designed to produce more than 500 kg/day of liquid and gaseous fuels. A block diagram of the process is shown in Figure 2, followed by a short description. Figure 1 (previous page) and Figure 3 show two of the pilot installations.

Wood sawdust or other crushed organic material is processed to separate possible extraneous objects. The prepared feed is then fed into a two stage thermal conversion reactor where drying is carried out in the first stage. The second stage comprises pyrolysis that produces mainly vaporised products. The byproduct char is removed from the reactor and is collected in a storage bin.

In the separator, the vaporised products are separated from the suspended solids and are then cooled to give liquid bio-oil, which is collected in a tank. The non-condensable fraction, pyrolysis gas, is fed to a diesel engine operating in gas-and-diesel mode to generate electric power.

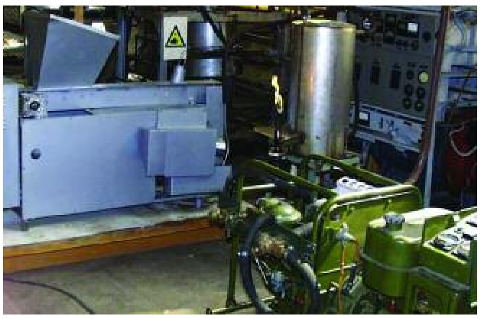

Figure 3: 50 kg/h plant biomass pyrolysis module.

Bio-oil can be used as boiler fuel or blended into conventional diesel fuel fed to the diesel engine. This fuel blend normally comprises about 5% of bio-oil but the proportion can be increased up to 15%, if necessary. Heat produced from the thermochemical process is recovered in heat exchangers for local heating and hot water supply.

The pilot plant has been tested with different feedstocks such as wood chips, wood sawdust, peat, lignite, rice husks, wastes from coffee extraction, etc. The typical product distribution from wood sawdust pyrolysis at temperatures of 450°C to 550°C is shown in Table 1.

Table 1 – Product distribution from fast pyrolysis plant at VIESH.

Product fraction	Yield (mass %)
Char	15 to 20
Bio-oil	40 to 60
Pyrolysis gas	15 to 40

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PyNe Biorefinery Task Activity Report Lignin Pyrolysis Round Robin

By Doug Elliott, PNNL, USA

Table 1 – PyNe member laboratories and relevant facilities.

Laboratory	Process
Institut Francais de Petrol	Analytical, TGA
Aston University	Fluid bed, TGA, Py-GCMS
Forschungszentrum Karlsruhe	Fluid bed, screw feed
ECN	Fluid bed
University Napoli	Batch
University Twente	Fluid bed
USDA-ERRC	Fluid bed, TGA
CIRAD	Analytical
BFHamburg	Fluid bed, EF
VTT	Py-GC-AED
PNNL	Analytical, TGA
NREL	Entrained flow

Table 2 – Potential sources of lignin for testing.

Lignin without sulfur
ENEA, steam explosion
Baltic hydrolysis
ILI
Abengoa hydrolysis lignin
Genencor enzyme hydrolysis lignin
Mondi
Lignol
Iogen
Sulfur containing lignin
Kraft lignin

Round Robin

At the PyNe meeting in Innsbruck in September 2005, a Round Robin on lignin pyrolysis was ranked as a high interest item to include in the Biorefinery Task. After some discussion it was decided to proceed with both process scale testing and fundamental testing, e.g. Thermal Gravimetric Analysis (TGA), as available at individual laboratories. Potential laboratory participants and test types are listed in Table 1 (left).

The amount of feedstock needed by each laboratory was also estimated. For each lignin feedstock to be tested in all laboratories, we will need about 130 kilograms. The types of available lignin were also discussed. It appears that only Kraft lignin is available easily and cheaply in the large quantities required for this round robin. Other potential sources were identified. Commercial sources of a wide variety of lignin types are advertised but are priced at dollars per gram or at best a few grams per dollar, such that the costs for the process scale tests would be very expensive. Potential lignin sources are listed in Table 2 (left).

Pyrolysis Biorefinery Techno-Economic Assessment

Development of a techno-economic assessment of pyrolysis biorefineries was also identified as a topic of high interest at Innsbruck. Additional input was received on biorefineries concepts and was discussed. Some other activities on biorefinery were identified, however it was noted that most projects mentioned are in very early stages or have not yet started. It is therefore unlikely that they will provide results which can be used by the PyNe group. There is a US industrial activity on this area that will soon be available and the USDOE will also try to involve pyrolysis in their work on biorefineries.

Biorefinery Concepts to be evaluated

The following institutions agreed to provide the relevant information for the concepts listed below, and these would form the basis of an evaluation exercise. It was agreed to keep to processes where pyrolysis is involved.

- USDA - compare pyrolysis to combustion in ethanol plants.
- IWC – pre-separation concept and pyrolyse products (lignin), maximise by-products and chemicals from the process, particularly phenols.
- FZK – bio-slurry gasification + synthesis.
- PNNL – distributed pyrolysis to central refinery for upgrading and integration.
- BTG – direct gasification of bio-oil in existing gasifier + synthesis.
- Aston – speciality chemicals and fuels.
- Rodim – chemicals and animal pharmaceuticals and fertiliser.
- JR – pyrolysis + CHP stand-alone.
- ECN – comparison with biomass gasification routes.

Figure 1: Biorefinery workshop in Lille, April 2006.

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Characterisation and Analysis of Pyrolysis Liquids – Progress in PyNe

By Anja Oasmaa, VTT, Finland and Dietrich Meier, BFH-IWC, Germany

Scope

The main scope of this activity within PyNe and ThermalNet is to:

- provide data on factors affecting fuel oil quality of pyrolysis liquids (PL)
- suggest methods to characterise the critical properties
- find solutions for possible problems in liquid fuel oil use.

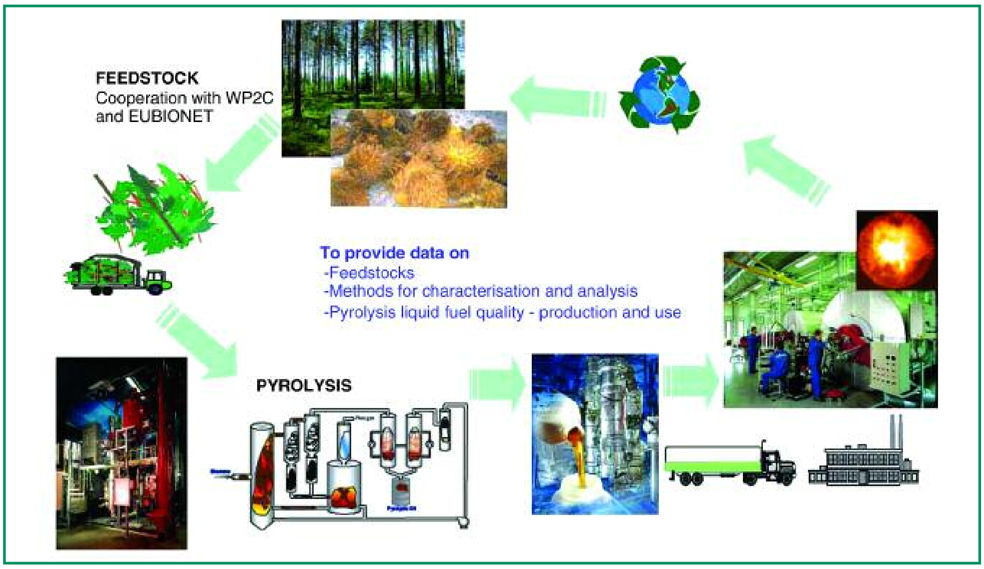

Figure 1: Scope of activity on analysis and characterisation.

Feedstocks

In feedstock issues, co-operation with the feedstock activity in ThermalNet and EUBIONET is agreed. Correlations between feedstocks and liquid quality will be studied by initiating a database containing data on feedstocks, pyrolysis process and conditions, yields, and the properties of feedstocks and products. A questionnaire on these subjects has been circulated within the ThermalNet network.

Fuel oil quality

Pyrolysis liquid fuel quality is a critical issue for most end users.[1] Quality control should cover the whole chain from feedstock processing through pyrolysis to the customer. Feedback from liquid end-users will provide information on the critical properties to be specified and standardised. Methods for quality control and characterisation and analysis will be provided. Fuel oil analyses suitable for pyrolysis liquids have been reviewed in earlier studies.[2-4]

Methods for characterisation of pyrolysis liquid

Pyrolysis liquid is a complex mixture of various compounds often present in small quantities. About 40 wt% of the components of pyrolysis liquid can be characterised by GC-MS methods.

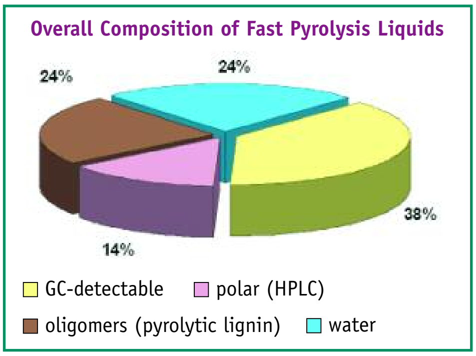

Figure 2: Overall composition of fast pyrolysis liquid.

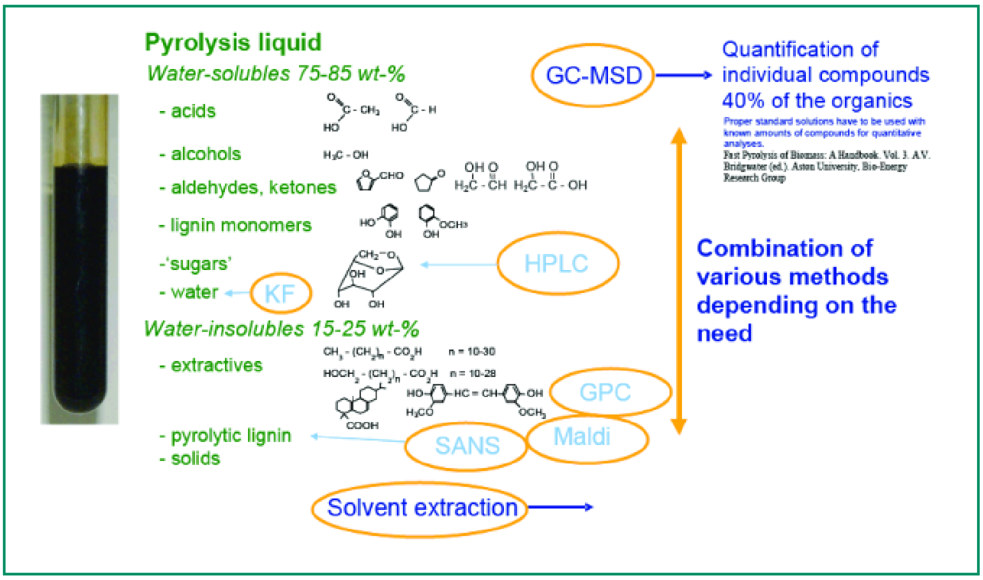

Figure 3: Product groups in pyrolysis liquid and methods of analysis.

In the latest Round Robin[5], uniform methods for GC-MS characterisation as well as a standard samples for calibration were suggested. The whole pyrolysis liquid can be fractionated into compound groups using solvent fractionation methods.[6] These two approaches can also be combined[7] to get more information on the fractions.

IFP (Institute Français du Pétrole) have carried out pyrolysis liquid analyses using IR, 2D-GC, 1H and 13C NMR, TG-MS, and Maldi/TOF/MS, including hyphenated techniques. On-line hyphenation with two different types of columns through a cryogenic modulator gives highly structured chromatograms in three dimensions showing “boiling point” versus “polarity” versus “concentration”. In the future IFP will compare various pyrolysis liquids and their fractions and also gather quantified information using sophisticated methods.

Methods for characterisation of lignin and pyrolytic lignin

Recent work in PyNe has mainly focused on lignin characterisation of pyrolysis liquid. A recent paper[8] presents the results from using SANS (Small Angle Neutron Scattering) on studying the shape and size of high-molecular-mass lignin during ageing of pyrolysis liquid.

Meier has characterised[9] pyrolytic lignin by SEC, Py-FI/MS MALDI-TOF/MS, and LDI-TOF/MS. The amount of pyrolytic lignin in the liquid can be determined by water extraction. The amount of pyrolytic lignin for softwood liquids is 15-21 wt%, and for hardwood liquids 12-19 wt%.

By SEC (Size Exclusion Chromatography), the mean Mw (molecular weight) of PL’s between 700 and 1000 Da (Dalton) was measured. Using Py-FIMS (Pyrolysis-Field Ionisation Mass Spectroscopy) it was shown that PL gives more dimers compared to MWL (milled wood lignin). Maldi-TOF/MS (Matrix Assisted Laser Desorption Ionisation – Time of Flight/Mass Spectrometry) was suitable for molecules below 200 000 Da, and measurements of fractions with low dispersity was possible. By LDI-TOF/MS good separation in the lower mass range (below 400 Da) was obtained and there were no disturbance by matrix effects. The conclusions for the analyses were:

- The average Mw of the examined PL is between 560 and 840 Da, with a maximum deviation of 20%, depending on the age (storage time below one week) of the liquid.
- The size of PL-dimers was between 270 and 400 Da.
- The numerous detected masses indicate, in contrast to native lignin, a big variety of different types of side chains or linkages.

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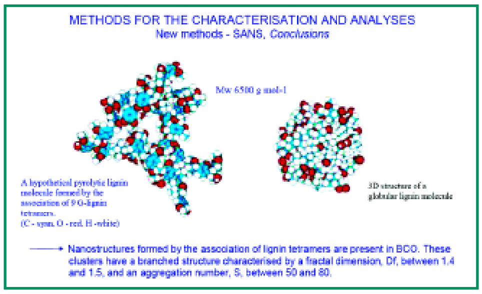

Figure 4: Methods for the characterisation and analysis of lignin.

Figure 5: Isolation of pyrolytic lignin.

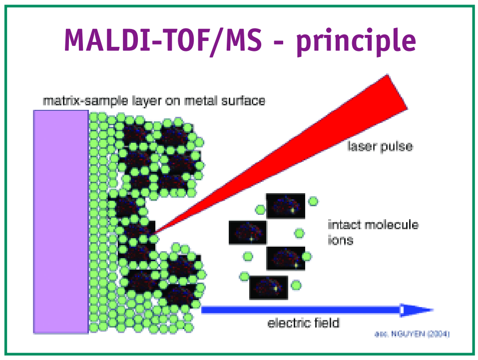

Figure 6: Principle of Maldi TOF analysis.

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