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Task 34 Pyrolysis

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Welcome to Task 34

By Doug Elliott, Task 34 Leader

The IEA Bioenergy Task 34 for Pyrolysis is hard at work in the new triennium, from 2010 to 2012. Current participants in the Task are Canada, Finland, Germany, the UK with leadership provided by the US. This newsletter is produced by the Task to stimulate the interaction of researchers with commercial entities in the field of biomass pyrolysis.

Aims & Objectives
The overall objective of Task 34 is to improve the rate of implementation and success of fast pyrolysis for fuels and chemicals by contributing to the resolution of critical technical areas and disseminating relevant information particularly to industry and policy makers.

The scope of the Task will be to monitor, review, and contribute to the resolution of issues that will permit more successful and more rapid implementation of pyrolysis technology, including identification of opportunities to provide a substantial contribution to bioenergy. This will be achieved by the following activities:

Priority Topics for Task 34
- Norms and standards
- Analysis – methods comparison and developments
- Country reports updates/ review of state of the art
- Fuels and chemicals from pyrolysis

In this issue of the newsletter, you will find short introductory articles from the national team leaders from each of the participating countries summarizing the particular biomass pyrolysis efforts in their countries and an overview of the latest Task meeting including information on the Round Robin on bio-oil viscosity and aging. Also, there are several articles from the participants describing the

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Welcome...continued

latest developments in fast pyrolysis including work in Finland on standards for solid biomass, in Germany on the catalytic conversion of bio-oil in sub-critical water, and in the UK at several of the universities including, Leeds, Southampton and Edinburgh.

From Canada we have a report of the work on pyrolysis research at the University of Toronto and from the US we have input from the USDA-ERRC on their catalytic pyrolysis work, a contribution from the University of Massachusetts Amherst on aerosol production in fast pyrolysis, discussions of collaborative projects with Canada and Finland, and an update of progress within the National Advanced Biofuels Consortium. There is also a report from the tcbiomass 2011 conference recently held in Chicago, and an updated calendar of events of interest to the biomass pyrolysis community.

This newsletter is published twice a year. Comments and suggestions for future input are invited: please contact the editor, Irene Watkinson at i.i.watkinson@aston.ac.uk.

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Catalytic pyrolysis research at the United States Department of Agriculture (USDA)

Update from Charles Mullen (above) and Akwasi Boateng (below)

The Agricultural Research Service (ARS), the principal intramural research arm of the United States Department of Agriculture (USDA) has been researching the production of partially deoxygenated pyrolysis liquids through incorporation of heterogeneous catalysts in the pyrolysis process. ARS researchers at the Eastern Regional Research Center (ERRC, Wyndmoor PA USA), including Drs. Akwasi (Kwesi) Boateng and Charles Mullen have been conducting this research under the ARS Bioenergy National Program 213.

This is in partnership with two US-DOE contracts led by UOP, a Honeywell Company, under projects (i) Pyrolysis Oil Stabilization program (ARS Agreement No. 58-3K95-9-1354, and DOE award No. DE-FG36-08GO18213) and (ii) National Advanced Biofuels Consortium (NABC).

> *"Research at ARS demonstrates the production of partially deoxygenated pyrolysis liquids is more suitable as refinable feedstocks for 'drop-in' fuels."*

The ARS research is part of the project entitled 'Distributed scale pyrolysis of agricultural biomass for production of refinable crude bio-oil and valuable co-products,' for which Kwesi is the lead scientist. So far, the research has focused on zeolite catalysts for catalytic cracking type reactions, but

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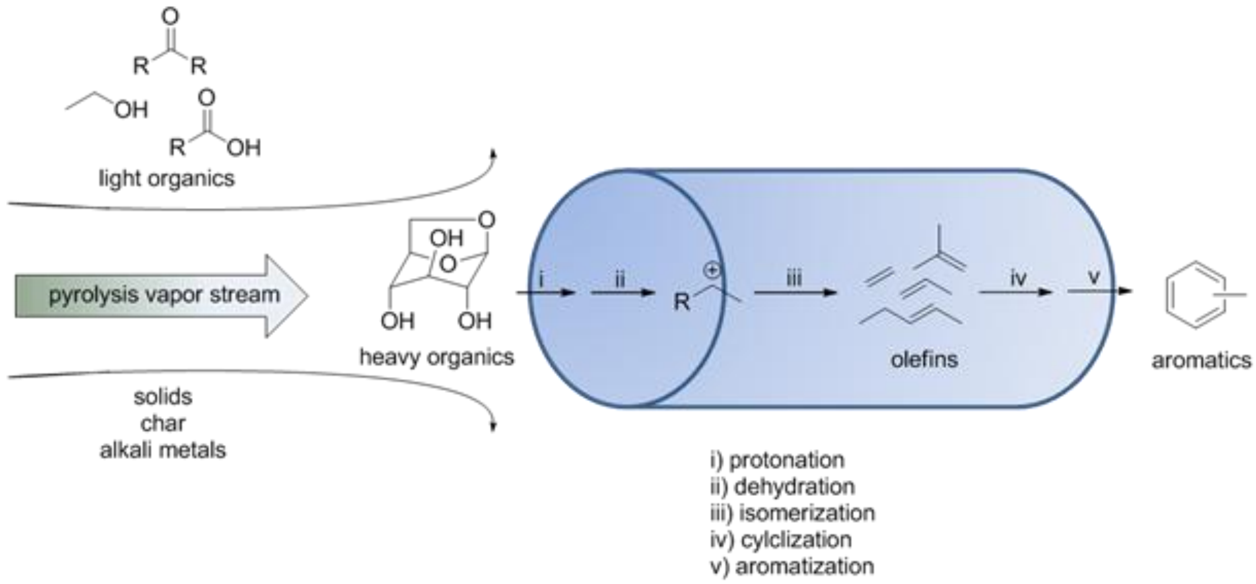

Figure 1: Progressive removal of water vapor, light organics, and solids from the pyrolytic vapor stream allow for a higher concentration higher-order carbon containing pyrolysis components, to undergo a two-step deoxygenation which leads to isomerization, cyclization, and aromatization to produce hydrocarbons.

Catalytic pyrolysis research at USDA...continued

Table 1: Analysis of catalytic and non-catalytic oak wood pyrolysis oils.

	No Catalyst	**Catalyst, 350g oak per cycle**	**Catalyst, 175g oak per cycle**
Carbon (wt%, db)	54.59	65.8	76.5
Hydrogen (wt%,db)	5.78	5.78	5.63
Nitrogen (wt%, db)	0.16	0.22	0.38
Oxygen (wt%, db)	39.48	28.22	17.4
C:O (mol)	1.8:1	3.1:1	5.9:1
H:C (mol)	1.3:1	1.1:1	0.9:1
HHV (MJ/kg, db)	22.5	25.0	32.3
TAN (mg KOH/g)	130	112	68
pH	2.5	2.5	2.8

future studies include catalysts for varying types of beneficial reactions that can produce more stable and upgradable pyrolysis oils.

The researchers have utilized a 5 kg/h bubbling fluidized bed pyrolysis system developed by Kwesi at ERRC (the "Kwesinator") to study *in situ* catalytic upgrading at different points in the process from pyrolytic decomposition of the biomass to condensation of pyrolysis liquids. The research has included not only direct catalytic pyrolysis where biomass contacts hot catalysts in the fluidized bed, but also upgrading of pyrolysis vapors where the vapors are cracked in a second stage fixed catalyst bed downstream of the cyclone collector which removes biochar from the vapor stream.

In the in-bed catalytic process, where the standard fluidized bed material, silica sand, is replaced with catalytic materials experiments have resulted in improvements in the resultant pyrolysis liquids' composition and properties including decreases in acidity, and increases in energy content. In the best case, the C/O molar ratio of pyrolysis oil derived from oak wood was improved from 1.8/1 with silica sand medium to 5.9/1 when a catalyst was incorporated. There are still research barriers to overcome for this process including that the deoxygenation was done with a penalty to the overall liquid yield due to coke formation.

Coke formation is a result of the catalysts promoting reactions that remove hydrogen from already hydrogen deficient biomass. As expected, this coke also deposits on the catalyst, causing deactivation. However, the catalyst can be regenerated in the bubbling fluidized bed by successive pyrolysis/combustion cycles. The shorter the pyrolysis cycle, the less biomass the catalyst is exposed to before regeneration, and the more effective the catalyst is because less coke can form (Table 1). Details of this work were published in *Energy and Fuels* (C.A. Mullen, A.A. Boateng, M.J Mihalcik and N.M. Goldberg, Catalytic Fast Pyrolysis of White Oak Wood in a Bubbling Fluidized Bed, DOI: 10.1021/ef201286z).

In the second process, a portion of the pyrolysis vapors produced over silica sand in the fluidized bed reactor were catalytically processed in a packed bed reactor. Potential advantages of this "vapor upgrading" process compared with direct contact between biomass and catalysts include the ability to remove biochar from the stream and the ability to tune the composition of the stream via fractional condensation prior to upgrading.

The ERRC pyrolysis system performs five-point fractionation of the vapors (four impingement condensers and an electrostatic precipitator). By locating the upgrading step at different locations along this train, the composition of the vapor stream changes by removing various components including water and small highly oxygenated water-soluble components. As moisture and small water-soluble molecules are removed from the stream contacting the catalyst, trends were observed in catalyst robustness, coke formation and product selectivity (Figure 1).

The products were found to be rich in aromatic hydrocarbons which formed a separate layer from water produced via oxygen rejecting dehydration reactions. The selectivity for single aromatic ring compounds (benzenes) versus two aromatic ring compounds (naphthalenes) also increased as the vapor stream became drier. This is because in the streams containing more

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Catalytic pyrolysis research at USDA...continued

water, the small active sites in the pores of the catalysts become occupied by water molecules forcing the reactivity of the organics to the surface of the catalyst where the larger two ring molecules are able to form. When the vapor stream contains less water these small pores are available to accept organic molecules, resulting in the formation of smaller single ring benzene products.

This work was also published in *Industrial and Engineering Chemistry Research* (D.J. Mihalcik, A.A. Boateng, C.A. Mullen, N.M. Goldberg, Packed-Bed Catalytic Upgrading of Oak-Derived Pyrolytic Vapors, DOI: 10.1021/ie201831e).

The next steps for this work include scaling up to perform vapor upgrading of the full stream of vapors from the 5 kg/h system.

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USDA United States Department of Agriculture

Other news from USDA

USDA and DOE fund ten research projects to accelerate bioenergy crop production

In August 2011, the United States Department of Agriculture (USDA) and Department of Energy (DoE) announced that they have awarded ten grants totalling $12.2 million to spur research into improving the efficiency and cost-effectiveness of growing biofuel and bioenergy crops.

Overall these projects are designed to improve crops grown for biofuels, including selected trees and grasses—by increasing their yield, quality and ability to adapt to extreme environments. Researchers will rely on the most advanced techniques of modern genomics to develop breeding and other strategies to improve the crops. The research will be conducted on switchgrass, poplar, Miscanthus and Brachypodium, among other plants.

Figure 1: Miscanthus grasses.

The ten projects are located in California, Colorado, Illinois, Florida, Kansas, Missouri, Oklahoma, South Carolina and Virginia.

The grant provides funding to the University of Florida in Gainesville to improve energy production from cane biomass.

This project will produce a range of foundational genetic resources and genetic makers for energy cane breeders to efficiently develop energy cane cultivators with increased biomass production and reduced input requirement.

www.usda.gov

Pyrolysis oil conversion research at University of Toronto

Murray Thomson outlines the fast pyrolysis liquid combustion research activities at the University of Toronto in Canada

Since 2006, the Combustion Research Laboratory at the University of Toronto has been actively involved in fast pyrolysis liquid research. The goal of the research program, directed by Professor Murray J. Thomson in the department of Mechanical and Industrial Engineering, is to demonstrate bio-oil's potential as a renewable 2nd generation biofuel by producing heat and electricity in a Stirling engine. This project represents an important step towards displacing fossil fuels with biofuels in stationary heat and power applications.

Firstly, to understand the combustion properties of pyrolysis liquid relative to conventional hydrocarbon fuels, a 10 kW spray based swirl burner with air-blast atomization, pilot flame ignition and air preheat was constructed. The burner was tested with a hardwood derived bio-oil/ethanol blend (80/20 by % volume) under a wide range of operating conditions and compared to No. 2 (diesel) and No. 4 (heavy) fuel oil using gaseous and particulate matter (PM) emissions diagnostics, as well as flame imaging techniques.

Results indicate that stable combustion and thorough burnout (up to 99.5% fuel carbon conversion efficiency) are achievable with pyrolysis liquid by adjusting available burner parameters, such as the degree of swirl or air preheat. With a larger burner (>200 kW), and thus longer hot residence times, the unburned hydrocarbon (UHC), CO and solid carbonaceous residue (CR) emissions could be reduced to very low levels. The NO_x emissions behave in a similar way to other nitrogen containing fuels.

Compared to No. 2 fuel oil, bio-oil is more sensitive to changes in flame stability and blow-off brought upon by varying burner parameters outside of their optimal range. This results in a narrow regime over which bio-oil exhibits relatively low gaseous and PM emissions. The greater susceptibility to combustion

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> *"This project represents an important step towards displacing fossil fuels with biofuels in stationary heat and power applications."*

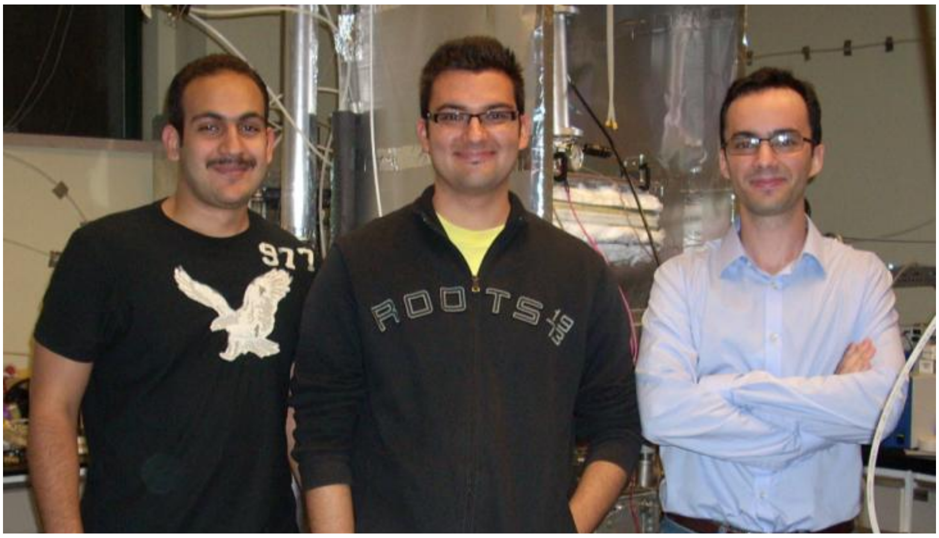

Figure 1: Bio-oil team members (from left to right) Milad Zarghami, Tom Tzanetakis, and Sina Moloodi in the bio-oil combustion laboratory at the University of Toronto.

Pyrolysis oil conversion research at University of Toronto...continued

instability is caused by the water and low energy content compounds that initially evaporate from the fuel. These compounds do not contribute significantly to early flame heat release and stabilization as much as pure, volatile hydrocarbons. Compared to No. 4 fuel oil, which also contains a non-distillable fraction, the gaseous emissions are still higher, but the solid CR is lower under similar conditions.

The second phase of research was devoted to understanding the effect of solids, ash, water content, and ethanol addition on bio-oil combustion. These properties are controllable, to a certain extent, during fast pyrolysis, and their optimization could help mitigate some of bio-oil's detrimental fuel characteristics, such as poor ignitability. Furthermore, these properties should be specified in an eventual bio-oil fuel standard. Several bio-oil samples with varying solids, ash, water, and ethanol blend contents were thus tested in the burner under similar conditions. Results indicate that high solids and ash content fuels produce higher UHC, CO and CR emissions. Removing water from bio-oil does not improve combustion quality because of subsequent increases in viscosity and non-distillable residue concentration within the fuel.

The amount of CR emissions is a strong function of the measured, thermogravimetric (TGA) residue and solids content in the fuel. Based on this, the non-distillable TGA residue can be used to estimate the CR generation potential of different bio-oils. Finally, ethanol addition to bio-oil (at least 10% by volume) increases flame stability while decreasing UHC and CO emissions.

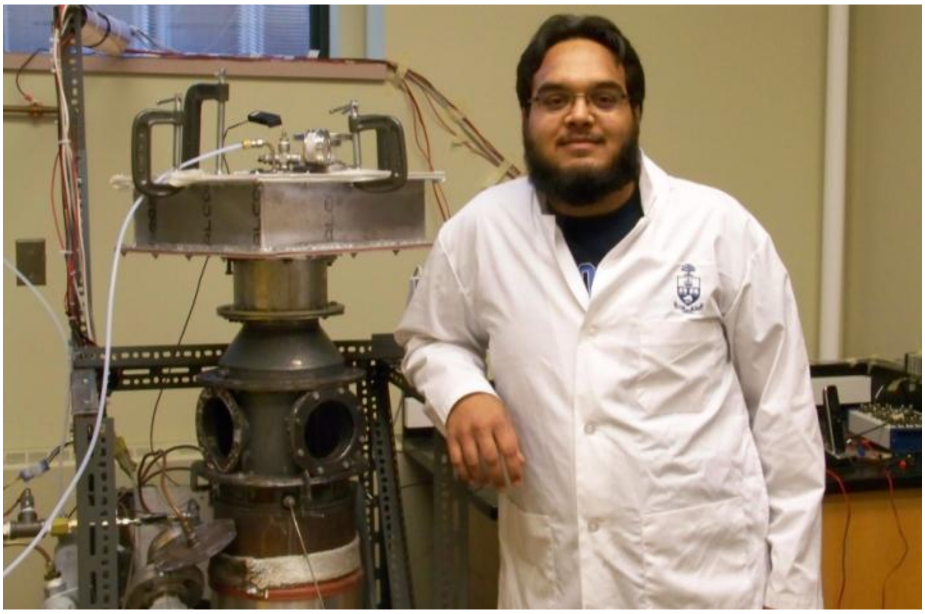

Figure 2: Bio-oil team member Umer Khan beside the Whispergen Stirling engine adapted to work with pyrolysis liquid using a spray based swirl burner.

Another important aspect of bio-oil is its tendency to undergo a decrease in volatility and increase in viscosity, or age, over time. One current project underway is to investigate the effect of aging on bio-oil combustion. Burner results operated with aged bio-oil samples will be compared to fresh control batches. The ability of ethanol addition to counteract the detrimental effects of aging will also be investigated.

Concurrent with the above research, Professor Thomson's team has been working with a Whispergen^{TM} combined heat and power (CHP) Stirling engine (5.5 kW_{th}, 0.8 kW_e). The system was originally designed as a CHP unit for boats and works with an evaporative diesel burner. The engine has been modified to run successfully with bio-diesel, ethanol and most recently, 80/20 volume % bio-oil/ethanol blends. A spray burner was adapted to the unit and run using a zero-ash, low solids (0.03 wt%) bio-oil in order to produce 7.5 kW_{th} and 0.3 kW_e.

Emissions measurements and more detailed efficiency analyses are currently underway. Further details can be found in articles published in *Energy and Fuels*.

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New European standards for solid biofuels

A synopsis from Eija Alakangas of VTT (Technical Research Centre of Finland)

> *"This article describes the main principles of fuel specification and classes standards, and especially classification of pellets."*

Introduction to standards, certification and fuel specification

In 2000, the European Commission gave a mandate to the European Committee for Standardization, CEN under committee TC335 to prepare standards for solid biofuels. In the first phase 27 pre-standards (technical specifications) were published during 2003–2006. These pre-standards have been updated to full European EN-standards during 2007–2011. In total 36 standards will be published.

The standards will be included in the following topics:

- terminology, EN 14588 fuel specification and classes, EN 14961 series
- quality assurance, EN 15234 series
- sampling and sample preparation, EN 14778 and EN 14780
- analysis physical, mechanical and chemical properties (21 different standards)

26 EN-standards have been published and the rest will be published during 2012. When EN-standards are published the conflicting national standards shall be withdrawn.

This article describes the main principles of fuel specification and classes standards (EN 14961-series), and especially classification of pellets. Because of CEN copyright reasons no tables of standards are provided.

The European Pellet Council, which is working under AEBIOM is launching the certification scheme (ENplus and EN) for wood pellets for non-industrial use (www.pelletcouncil.eu). Also German DINplus has updated their certification system to EN standards. Certification is third-party attestation (i.e. issue of a statement) that specified requirements related to wood pellets have been fulfilled. ENplus and DINplus certification systems are based on European standards EN 14961-2 and EN 15234-2 with some modifications.

EUBIONET III (www.eubionet.net) has carried out a survey of the product standard for industrial use. Results of this survey will be used for prISO standard: Graded pellets ISO 17225-2, which is under preparation.

Fuel specification and classes and quality assurance – multipart standard

The two most important standards being developed deal with classification and specification (EN 14961) and quality assurance for solid biofuels (EN 15234). Both these standards will be published as multipart standards.

Working Group 2 of CEN/TC 335 has developed the following pellet standards:

- EN 14961-1:2010 General requirements
- EN14961-2:2011 Wood pellets for non-industrial use
- EN 14961-3:2011 Wood briquettes for non-industrial use
- EN 14961-4:2011 Wood chips for non-industrial use
- EN 14961-5:2011 Firewood for non-industrial use
- FprEN14961-6 for non-woody pellets for non-

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New European standards for solid biofuels ...continued

industrial use (approved).

EN 14961-2 to 6 are so-called product standards for non-industrial use, which means fuel intended to be used in smaller appliances, in households, small commercial and public sector buildings. In the product standards all properties are normative and they bind together to form a class. For wood pellets and briquettes A1, A2 and B classes are specified.

Classification of raw material according to EN 14961-1

EN 14961-1 includes specification of 14 different biomass fuels (traded forms): pellets, briquettes, wood chips, hog fuel, straw, miscanthus and reed canary grass bales, olive residues, shaving, bark etc. EN 14961-1 also includes the raw material classification, which is based on their origin and source. The fuel production chain of fuels shall be unambiguously traceable back over the whole chain.

The solid biofuels are divided into the following sub-categories for classification in EN 14961-1:
1) Woody biomass;
2) Herbaceous biomass;
3) Fruit biomass;
4) Blends and mixtures.

Woody biomass is biomass from trees, bushes and shrubs. Wood biomass is divided into three classes: forest, plantation and other virgin wood (1.1), by-products and residues from wood processing industry (1.2) and used wood (1.3).

Herbaceous biomass is from plants that have a non-woody stem and which die back at the end of the growing season. It includes grains and their agro-industrial by-products such as cereals. Fruit biomass is the biomass from the parts of a plant which are from or hold seeds.

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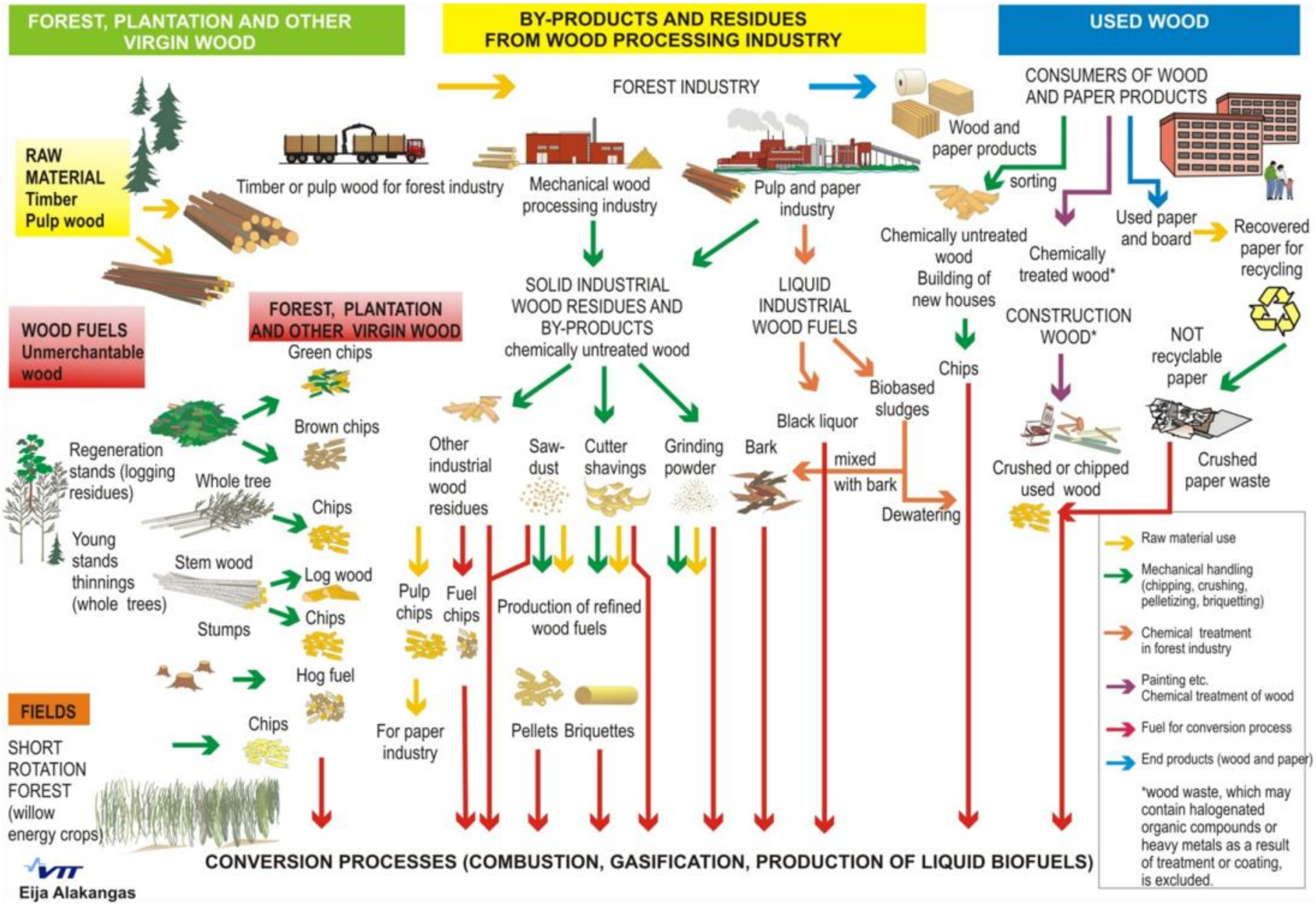

Figure 1: Classification of woody biomass. Drawing Eija Alakangas, VTT.

New European standards for solid biofuels ...continued

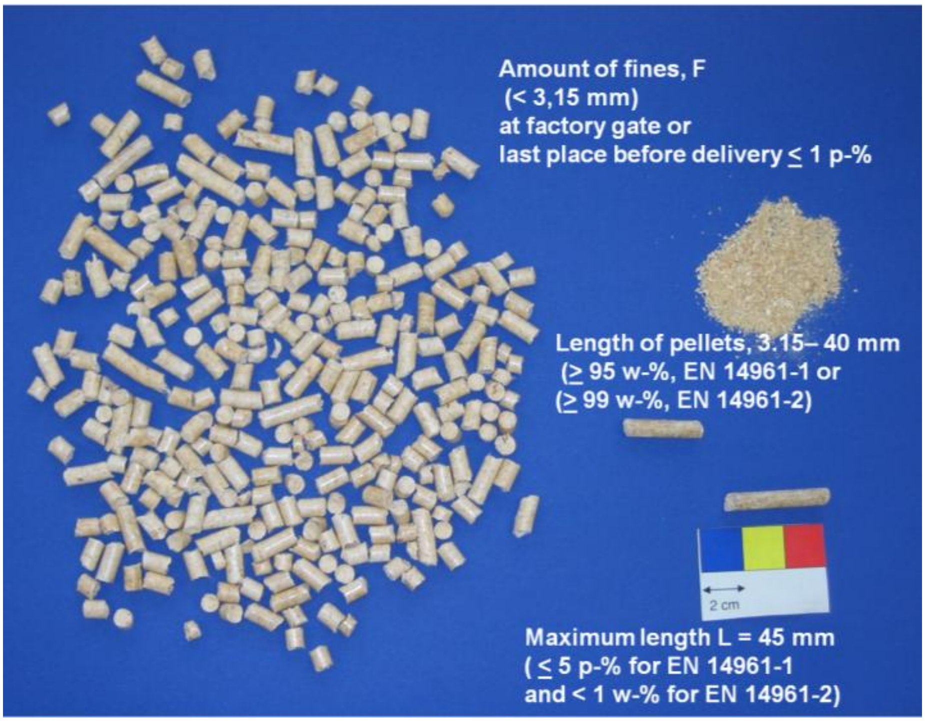

Figure 2: Dimensions of 8mm wood pellets according to EN 14961-1 and EN 14961-2.

The term "Blends and mixtures" in EN14961-1 refers to material of various origins within the given box in the classification table and appears on four levels. Blends are intentionally mixed biofuels, whereas mixtures are unintentionally mixed biofuels. The difference for blend and mixture is the composition of blend is known. The origin of the blend and mixture shall be described using Table 1 in EN 14961-1.

The purpose of classification is to allow the possibility to differentiate and specify raw material based on origin with as much detail as needed (4 – digit code system).

Examples:

- Sawdust from pine (1.2.1.2)
- Blend of sawdust from spruce (95w-%) and glued wood (5 w-%), (95w-% 1.2.1.2 and 5w-% 1.2.2.1 and content of glue < 0.2 w -% of total amount of wood
- Reed canary grass, straw part (2.1.2.2)
- Pallet (1.3.1)

Glued, painted, lacquered wood is classified as chemically treated by-product or residue from wood processing industry (1.2.2). Demolition wood is not included in the EN 14961-1. Also contaminated wood, which includes heavy metals and halogenated organic compounds is not allowed as a raw material. Also note that virgin wood includes small amounts of heavy metals, and in EN 14961-2 standard there is also threshold values for certain chemical compounds. In class B in EN 14961-2 chemically treated wood and used wood is also allowed, but threshold values for heavy metals are the same as in classes A1 and A2. If either solid biofuel blend or mixture contains chemically treated material, it has to be informed e.g. by describing it in more detail.

The most significant characteristics are mandatory, normative, and shall be given in the fuel specification. These characteristics vary for different traded form, while the most significant characteristics for all solid biofuels are moisture content (M), particle size/dimensions (P or D/L) and ash content (A). For example, the average moisture content of fuels is given as a value after the symbol (e.g. M10), which means that the average moisture content of the fuel shall be £ 10 w-%. Some characteristics, e.g., bulk density (BD), are voluntary, informative.

For pellets the most important properties are: dimensions (L, D), moisture content (M), mechanical durability (DU), ash content (A), amount of fines (F), additives, and net calorific value. If, for example, glued wood is used then nitrogen (N), sulphur (S) and chlorine (Cl) content is also mandatory for biomass pellets in EN 14961-1.

EN 14961-2 Wood pellets for non-industrial use

Wood pellets for non-industrial use are specified according to EN 14961-2. Torrefied pellets are excluded from the scope of this standard. In ISO 17225-1 there will be a special quality table for thermally treated biomass (e.g. torrefied biomass).

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New European standards for solid biofuels ...continued

Property class A1 for wood pellets represents virgin woods and chemically untreated wood residues low in ash and nitrogen content. Fuels with slightly higher ash and nitrogen content fall within grade A2. Property class B also allows chemically treated industrial wood by-products and residues and used wood, but there are same strict threshold values for heavy metals as for classes A1 and A2.

EN 14961-6 Non-woody pellets for non-industrial use
This standard determines the fuel quality classes and specifications of non-woody pellets. It covers only those pellets produced from the following raw materials (Table 1 in EN 14961-1):

- Herbaceous biomass
- Fruit biomass
- Biomass blends and mixtures

EN 14961-6 standard will include specifications for straw, miscanthus and reed canary grass pellets and non-woody pellets from blends and mixtures. Blends and mixtures include blends and mixtures from woody, herbaceous biomass and fruit biomass. This standard has been approved and will be published in the beginning of next year.

Eija Alakangas of VTT is convenor of WG2 of CEN/TC 335 and ISO/ TC 238

SolidStandards project

The SolidStandards project (www.solidstandards.eu) supports implementing solid biofuel standards in practice, and addresses ongoing and recent developments related to solid biofuel quality and sustainability issues, in particular the development of related standards and certification systems. The core of the action is the organisation of 35 training events for producers, traders and end-users of solid biofuels and actors involved in standardization and certification. Training aims at increasing the target group’s ability to implement quality and sustainability standardization and certification.

The consortium will work with seven selected solid biofuel companies and support them in implementing European quality standards. The process will be documented and shall serve as a guideline for standard implementation. The SolidStandards project is funded by the Intelligent Energy Programme and coordinated by WIP.

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USA – Canada collaboration on pyrolysis and upgrading of wood and forest residue

Alan Zacher reviews research activities conducted in converting Mountain Pine Beetle Killed (MPBK) trees to biofuels using pyrolysis processes

> *"This effort is a part of the USA/Canada Clean Energy Dialogue."*

This effort is a part of the USA/Canada Clean Energy Dialogue, specifically meeting national commitments in the agreement listed as Priority Action 5, to "undertake analysis of the economic feasibility of converting Mountain Pine Beetle Killed (MPBK) trees to biofuels using pyrolysis processes."

Both USA and Canadian governments are conducting R&D on utilization of biomass as a source of fuels, particularly in biomass pyrolysis to crude bio-oil and subsequent upgrading for specific uses. In the USA, the focus is often production of hydrocarbon gasoline, diesel, and jet fuels to directly replace petroleum. In Canada, there is also interest in fuels for electricity generation that require less upgrading. In any case, the crude bio-oil will require upgrading to meet certain specifications depending on application.

The USA and Canada agreed to leverage existing research teams to conduct collaborative R&D in this area, funding their own researchers to address key technical barriers. The team in Canada was led by Fernando Preto at Canmet Energy, and in the US the NREL team was led by Kristiina Iisa, and the PNNL team was led by Alan Zacher.

The feeds provided by Canadian mills included Mountain Pine Beetle Killed wood (MPBK); Pine from Thunder Bay, ON; Birch from Northern Ontario; reference hog fuel (RHF); coastal hog fuel; and salt-laden hog fuel from BC. Hog fuel is a mix of waste wood chips, bark, sawdust, and planer shavings from a sawmill operation, usually burned for heat value. Salt and contaminants in hog fuel can impact their use as fuels, particularly coastal and salt-laden fuels from growing near or transported in salt water.

At PNNL, the focus was examining bench-scale pyrolysis and upgrading of the oil to liquid transportation fuels. The six feeds were pyrolyzed in a bench-scale, continuous bubbling fluid bed reactor, described in PyNe 26. Each wood was fed for 4 to 6.5h at ~1kg/hr, 480°C, and 0.8s vapor residence time, with some variations. Liquid mass yields for the pine and MPBK were 60% to 65%, while the hog fuel liquid mass yields were 55% to 39%, trending lower with assumed feed salt content. Both coastal and salt-laden hog fuel feeds were over 10% ash, which lowered mass yield by dilution and by reaction with the biomass, resulting in higher yields to gas and char/solids, even calculating yields on an ash-free basis.

The MPBK and reference hog fuel bio-oils were then upgraded in a bench-scale, dual zone, fixed-bed catalytic hydrotreater/ hydrocracker to produce liquid transportation fuels in the diesel, gasoline, and Jet A range. Oils were processed at 40ml/hr over a hydrotreating and then a hydrocracking catalyst at 170°C and 405°C respectively at 2000psi while feeding hydrogen. The MPBK oil was fed continuously for 40 hours before a plug in the catalyst

Continued on page 13

USA – Canada collaboration...continued

bed ended the run. The RHF test ended after running out of feed at 59 hours, but product oxygen content and density suggested that a plug was imminent.

The upgraded fuels were analyzed by Simdis to determine the relative concentrations of fuels.

For both feeds, there is significant amount of product in the gasoline, diesel, and Jet A ranges. Trending with hours on stream, both the oxygen content and the population of higher boiling compounds increase as catalyst activity is lost.

Overall this is positive, particularly that the upgrading catalysts maintained activity for a similar period. Except for the pyrolysis yield losses due to ash, forest reside upgrading to liquid transportation fuels is comparable to results obtained using clean wood feeds in other, similar research. We look forward to additional results from the other partners.

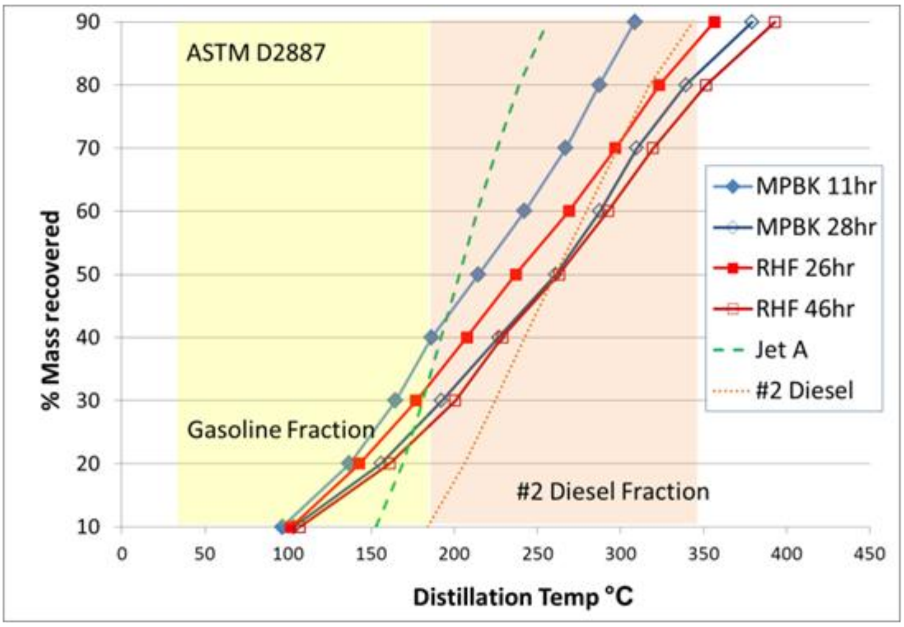

Figure 1 and Table 1: Simdis of upgraded fuel from MPBK and reference hog fuel wood by hours on stream compared to reference fuels.

Fraction (BP range)	MPBK 11hr	MPBK 28hr	RHF 26hr	RHF 46hr
Gasoline IBP-184°C	39%	27%	33%	26%
Diesel 184-344°C	57%	55%	54%	52%
Heavies >344°C	4%	18%	13%	22%
Jet A (overlap) 153-256°C	40%	29%	33%	30%
Oxygen%	0.3%	1.73%	0.68%	2.6%

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Discussion on the analyses used in IEA Round Robin 2011

A joint review by Anja Oasmaa (above) of VTT (Technical Research Centre of Finland) and Douglas Elliott (below) of PNNL (Pacific Northwest National Laboratory) in USA

An important part of the scope of work in the current triennium for Task 34 is the Round Robin on bio-oil viscosity and aging. For this Round Robin, two bio-oil samples were distributed to 15 laboratories in the participating countries. The primary focus for the Round Robin assessment was the measurement of viscosity and the stability (thermal aging) test, which is based on viscosity measurement. Analytical results from selected optional analyses, such as moisture, solids, CHN, and molecular weight were also collected. Full results of this Round Robin will be reported in a later issue of this newsletter.

Fast pyrolysis bio-oils (pyrolysis liquids) are totally different from mineral oils and hence the standard fuel oil analyses cannot always be used as written. The standard analyses have been systematically tested for pyrolysis liquids, modifications have been suggested, and some new methods have been developed. A first set of burner fuel specifications has been accepted for fast pyrolysis bio-oil as ASTM D7544.

There have been four earlier Round Robins[1-4] on fast pyrolysis bio-oils with different targets. The main conclusions from those were:

- Clear instructions for

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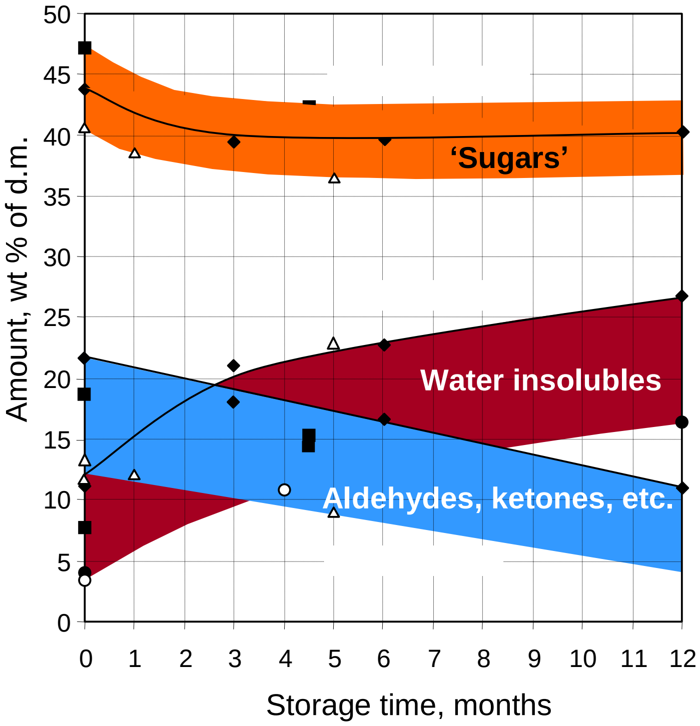

Figure 1: Main changes in forestry residue pyrolysis bio-oils during storage. Presented on dry basis. Data has been produced by following changes of several softwood and hardwood pyrolysis bio-oils at room temperature using solvent fractionation scheme (from Oasmaa, Anja. 2003. Fuel oil quality properties of wood-based pyrolysis liquids. Academic dissertation. Jyväskylä, Department of Chemistry, University of Jyväskylä. 32 p. + app. 251 p. Research Report Series, Report; 99. ISBN 951-39-1572-7).

Discussion on the analyses used in IEA Round Robin 2011...continued

analyses are needed.

- Good background knowledge of the analysis sample, and good laboratory practice, such as proper calibration of equipment, and use of similar reference sample, prevents systematic errors.
- Poor oil quality leads typically to poor accuracy.
- Karl-Fischer titration is recommended as a suitable method for determination of water content of fast pyrolysis bio-oils. Xylene distillation EN 95 cannot be used because it measures the water-soluble compounds with water.
- The precision of carbon, hydrogen, and density has been good.
- High variations have been obtained for nitrogen, special attention should be paid to nitrogen standards, which should have a similar range of nitrogen as the sample.

> *"In fast pyrolysis, about 12 wt% char is typically produced as a by-product from clean, bark-free wood."*

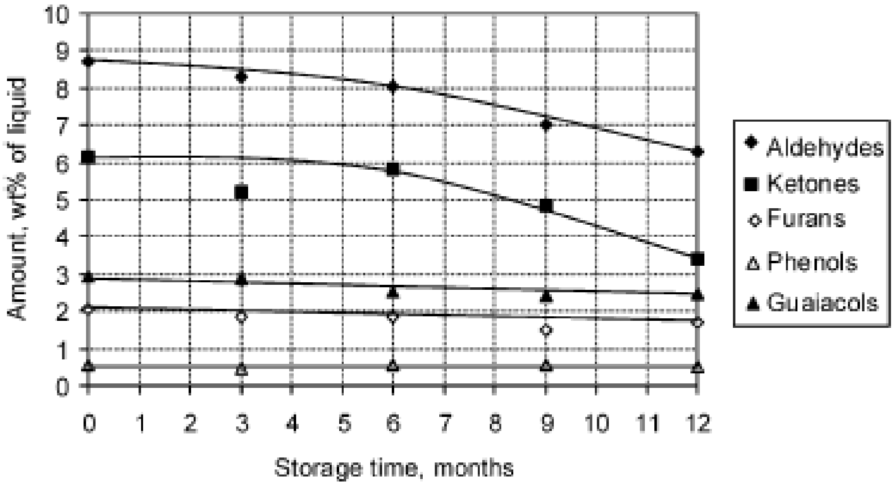

Figure 2: Changes in carbonyl compounds at room temperature measured by GC. (from Oasmaa, A.; Kuoppala, E. 2003. Fast Pyrolysis of Forestry Residue. 3. Storage Stability of Liquid Fuel. Energy & Fuels, 17, 4, 1075 – 1084).

- pH measurement is prone to errors, and frequent calibration is recommended.
- Kinematic viscosity at 40°C is accurate for viscosity measurement of homogeneous bio-oils.
- The reproducibility of the stability test based on viscosity has not been good. Special attention should be paid on accurate control of temperature of the heating oven, and reproducibility of viscosity measurements. A standard pyrolysis bio-oil reference sample having known stability was suggested.

Fast pyrolysis bio-oils contain low-boiling (below 100°C) and water-soluble compounds, and hence conventional drying methods or xylene distillation cannot be used without a significant loss of low molecular weight chemicals and secondary reaction within the liquids. The recommended analysis for water content in bio-oil is by Karl Fischer (KF) titration according to ASTM E 203-96: Standard Test Method to Water Using Volumetric KF Titration. With a proper choice of sample size, KF reagent concentration and apparatus, volumetric titration is suitable for the measurement of water over a wide concentration range.

Bio-oil typically contains less than 0.5 wt% solids having an average particle size of approximately 5 µm when cyclone(s) are used to remove the char from the hot products during pyrolysis. In fast pyrolysis, about 12 wt% char is typically produced as a by-product from clean, bark-free wood. Some char comes directly from the solid biomass and there is also evidence that secondary cracking gives coke or soot, which may be associated with the primary char.

A standard method, ASTM D7579, has been accepted for the solids content in bio-oil. In the method a pyrolysis bio-oil sample is dissolved in a methanol and dichloromethane solution (1:1), which is then

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Discussion on the analyses used in IEA Round Robin 2011...continued

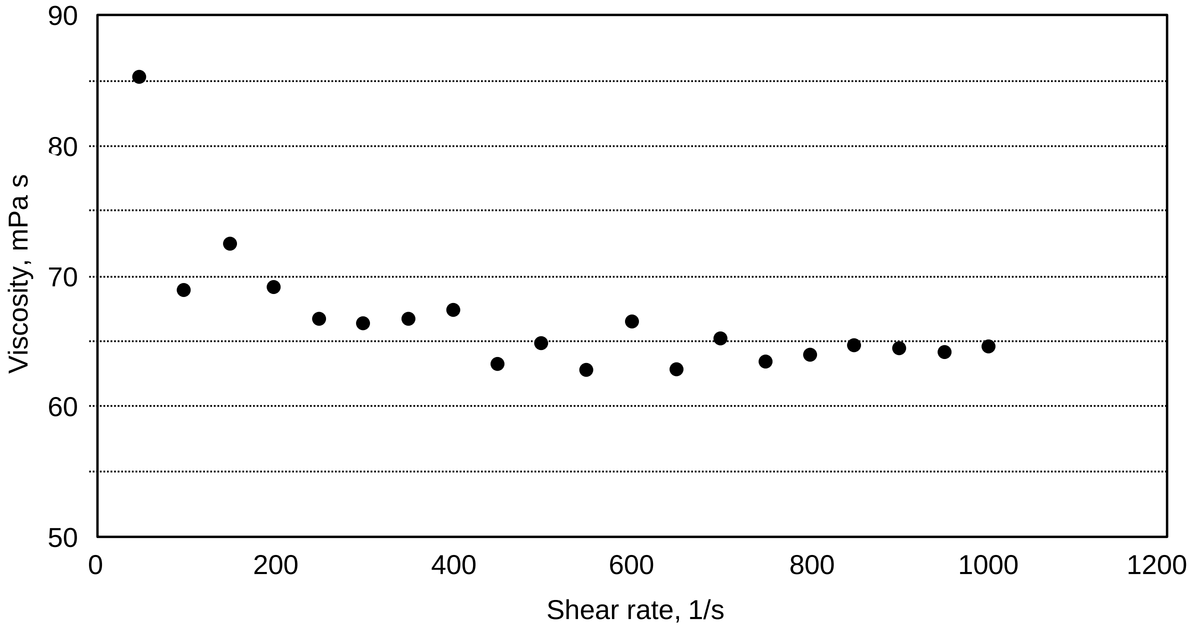

Figure 3: Measurement of dynamic viscosity for a bio-oil sample. Round Robin sample 2 measured at 40°C by Haake VT 550 using NV cup (sample amount 9.0 ml).

filtered through a vacuum filter system using a specified filter membrane. After filtering, the filtrand is washed with the solvent until the filtrate is clear.

The filter is removed, dried and weighed. The pyrolysis solids content is calculated based on the original pyrolysis liquid sample. The required analysis was carried out by two laboratories using three pyrolysis bio-oil samples. The difference in results obtained by the same operator using the same apparatus under constant operating conditions on identical test material in a short amount of time, would in the long run, in the normal and correct operation of this test method, exceed 0.1303X wt% only in one case in twenty.

Fast pyrolysis bio-oils are not chemically and thermally as stable as conventional petroleum fuels due to their high content of reactive oxygen-containing compounds and low-boiling volatiles. A number of methods have been investigated in order to stabilize these oils. The instability of fast pyrolysis bio-oils can be observed as increased viscosity over time, i.e. ”aging”, particularly when heated.

The most significant reactions of pyrolysis bio-oils take place immediately after quenching of the bio-oil and cease during the first months of storage. The volatile acids content remains unchanged. The principal changes during aging (Figure 1) include a reduction in carbonyl compounds (aldehydes and ketones), and an increase in the heavy water-insoluble fraction. Aldehydes can react with each other to form polyacetal oligomers and polymers.

The poly(oxymethylene) polymer has limited solubility in water. In addition, the water content increases and the volatility of the bio-oil decreases. Finally, a phase separation, separation of heavier lignin-rich fraction out from the aqueous phase takes place.

Since the major changes in ageing happens in carbonyl and water insoluble fractions, the changes in these product groups can be used as stability indicators. The changes in carbonyls (Figure 2) can be measured by GC analyzing aldehydes and ketones, by carbonyl titration, or by FTIR. The changes in water-insolubles can be determined as changes in viscosity or in molecular weight.

The change in water-insoluble content correlates with increased molecular weight distribution and viscosity. Both molecular weight

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Discussion on the analyses used in IEA Round Robin 2011...continued

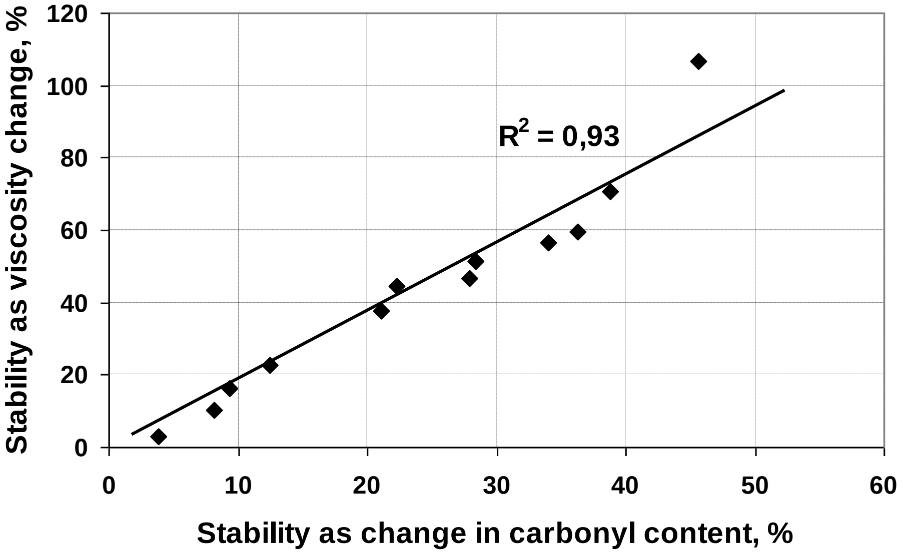

Figure 4: Correlation between change in carbonyl content and change in viscosity for pine pyrolysis bio-oil samples kept at 80°C for up to 60 hours.

distribution and viscosity can be used for following the stability of bio-oils. However, the viscosity increase-based stability test (80°C for 24 h) is more common. The IEA Bioenergy Round Robin in 2011 was focused on validating this stability test based on viscosity change.

The viscosity is measured most accurately as kinematic viscosity according to ASTM D445. If rotational viscometers are used the kinematic viscosity is obtained by dividing the dynamic viscosity by density at the measurement temperature.

The following items have to be included in the method:

- Careful mixing of the sample;
- No air bubbles allowed;
- Exact sample volume specified for the cup used;
- Use of lid to avoid sample evaporation;
- Checking the shear rate area where the sample behaves like Newtonian (shear rate does not affect to viscosity) liquid and area which is specified for the sample cup used;
- The shear rate to be chosen to be 5 – 95 % of the maximal shear rate, viscosity measurement (Figure 3) with a fresh sample.

The change in carbonyl content of pyrolysis bio-oil correlates with the change in viscosity. Due to the clear correlation (Figure 4) between the methods, comparison of results from different laboratories should be straightforward.

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Biofuels Research Infrastructure for Sharing Knowledge - BRISK

Tony Bridgwater outlines a new European research initiative which is available to all in Europe

BRISK, a new four year initiative from the European Commission Seventh Framework Programme (FP7), is co-ordinated by KTH Royal Institute of Technology in Sweden, and includes partners from Austria, Denmark, Finland, Germany, Greece, Italy, Netherlands, Norway, Poland, Spain, Sweden, Switzerland, Turkey and the United Kingdom.

This project aims to develop a European research infrastructure for thermochemical biomass conversion – an innovative process whereby fast growing wood, energy crops, agricultural wastes and other biogenic materials can be thermally converted into liquids, gases and solids for production of electricity, heat, transport fuels and a wide variety of chemicals.

Enhancing biomass utilization without risking its sustainability is a European energy priority, and can be linked to targets for curbing greenhouse gas emissions by 20% by 2020 and 50% by 2050: enhanced energy security and integration with other industrial sectors, such as agriculture, also play a role. Improved use of biofuels and products in advanced biomass conversion units and biorefineries is seen as a key element in achieving this goal.

In recent years industrial nations have established facilities in which their researchers have addressed the challenges associated with the production of biofuels and the establishment of biorefineries. At present, there remains some fragmentation in terms of access to high-level experimental equipment necessary for achieving significant advances in this field. The BRISK project aims

Continued on page 19

Figure 1: Country locations of BRISK partners shown in dark green on map. See Table 1 for more details.

BRISK...continued

to overcome this hurdle by integrating networking activities in the EU scientific community in order to foster a culture of co-operation not only between the project's 26 partners, but also the whole of the European Union.

Infrastructure available to all in Europe
The BRISK international network will encourage and facilitate cooperative research in the project partners' laboratories. Anyone based in Europe, including those outside of the project, can apply to go to any of the project partners located outside of their home country to utilize the thermochemical biomass conversion installations.

The project will cover the cost of travel and subsistence and will pay for the costs of accessing the facilities. Table 1 summarizes the partners involved in the BRISK initiative and their geographical location.

Applications for access
If you are interested in making an application, or require further information please contact Tony Bridgwater at Aston University in the UK.

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Table 1: BRISK partners, including details of their location.

BRISK Partner	Location
Royal Institute of Technology (KTH) - Project Coordinator	Stockholm, Sweden
Åbo Akademi University	Åbo, Finland
Aston University Bioenergy Research Group	Birmingham, UK
BIOENERGY 2020+ in co-operation with Graz University of Technology	Graz, Austria
Cardiff University	Cardiff, UK
Centre for Research and Technology (CERTH)	Thessaloniki, Greece
CIUDEN	Ponferrada, Spain
Delft University of Technology	Delft, Netherlands
ECN	Petten, Netherlands
ENEA	Rome, Italy
ETC	Piteå, Sweden
Graz University of Technology	Graz, Austria
INERCO	Seville, Spain
Institute for Energy (JRC-IE Petten)	Petten, Netherlands
International Flame Research Foundation (IFRF)	Pisa, Italy
Norwegian University of Science and Technology	Trondheim, Norway
PALL Filtersystems	Bad Kreuznach, Germany
Paul Scherrer Institute	Villigen, Switzerland
SINTEF	Trondheim, Norway
Technical University of Denmark	Kongens Lyngby, Denmark
Technical University of Munich	Garching, Germany
TUBITAK, Marmara Research Centre	Gebze, Turkey
University of Naples Federico II	Naples, Italy
University of Zaragoza	Zaragoza, Spain
Vienna University of Technology	Vienna, Austria
Wroclaw University of Technology	Wroclaw, Poland

Aerosol generation from pyrolysis of biomass by reactive boiling ejection

Paul Dauenhauer of University of Massachusetts Amherst, USA outlines the discovery of a new mechanism—'reactive boiling ejection'

The pyrolysis of cellulose generates a small amount of solid char residue as well as gases and condensable vapors which can be collected and upgraded to biofuels and chemicals. In addition to these products, exhaustive experimental analysis has revealed a fraction of the pyrolysis products to be non-volatile carbohydrate oligomers [1]. The mysterious origin of these non-volatile products within condensed vapors has led to the postulation of an unidentified mechanism for directly expelling solid biomass during pyrolysis [2].

We reveal in the recent issue of *Energy & Environmental Science* the discovery of a new mechanism, referred to here as 'reactive boiling ejection,' whereby non-volatile polymeric material is spontaneously ejected from cellulose during pyrolysis [3]. As shown in high-speed photography in Figure 1, a particle of Avicel Cellulose thermally decomposes to an intermediate liquid droplet in about 100 milliseconds. In the course of one millisecond, a visible streak resulting from the trace of a high-velocity aerosol is observed to extend from the liquid droplet (108 ms). One millisecond later, the ejected aerosol is observed to slow (109 ms).

The ejected aerosols were shown to transport non-volatile organic material into the gas phase. Chemical characterization of collected aerosols indicates that they contain levoglucosan, cellobiosan, cellotriosan, and higher anhydro-oligomers. Additionally, particle size analysis reveals that most ejected particles are smaller than one micron, and the observed ejections such as those in Figure 1 represent the maximum size of ejected aerosols.

The ejection of an aerosol results from the unstable characteristics of the intermediate cellulose liquid. As observed in Figure 1, the droplet is rapidly evaporating to produce the volatile products frequently associated with cellulose pyrolysis such as levoglucosan, glycolaldehyde, and several different furans. Simultaneously, vapor bubbles are nucleating and growing within the intermediate cellulose liquid such that the droplet violently boils.

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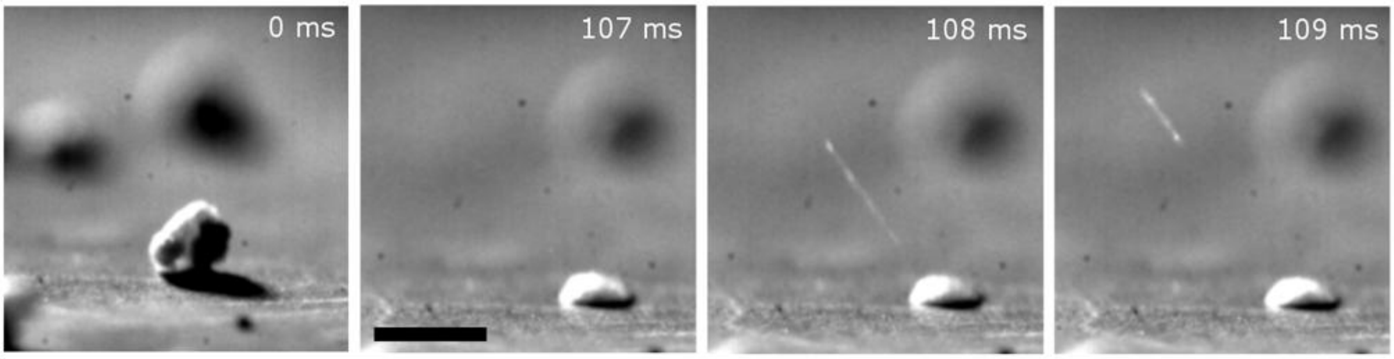

Figure 1: Photography of reactive boiling ejection of molten cellulose. A particle of cellulose (Avicel) thermally decomposes on 700°C alumina to an intermediate liquid which spontaneously ejects an aerosol (108 ms). Scale Bar = 300 μm.

Aerosol generation...continued

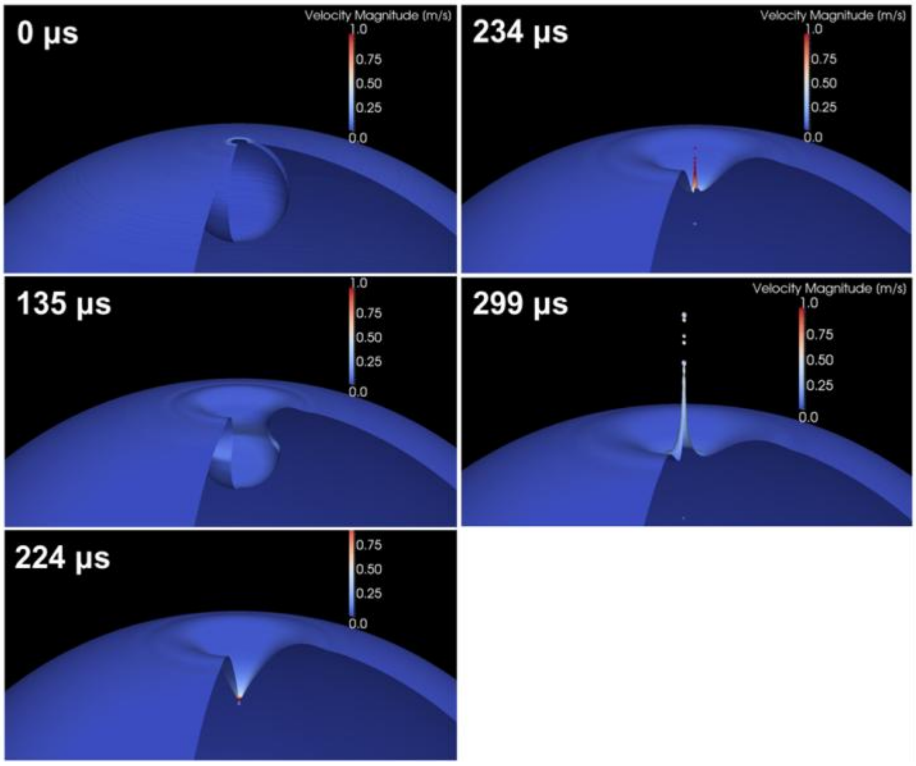

Figure 2: Mechanism of reactive boiling ejection of molten cellulose. A vapor bubble (0 μs) within the liquid droplet collapses (135 μs) eventually coalescing (224 μs) and forming a liquid jet (234 μs) which fragments to ejected aerosols travelling at about 0.5 m/s (299 μs).

Through measurement of a set of ejection speeds, we were able to determine the surface tension of the intermediate liquid cellulose to be in the range of 10^{-6} to 10^{-5} N/m.

Through first principles fluid modeling shown in Figure 2, we were able to determine the mechanism of reactive boiling ejection. A bubble of pyrolysis vapor rises to the vapor/liquid interface thus rupturing the liquid film between the vapor bubble and the external environment (0 μs). The resulting vapor cavity begins to collapse (135 μs) due to surface tension such that the entire cavity is eventually filled with intermediate liquid (220-230 μs). The resulting momentum of the collapsing liquid produces a liquid jet which extends into the gas phase (234 μs) and eventually fragments to ejected aerosols (299 μs).

The discovery of the reactive boiling ejection mechanism, recently highlighted in *Science* [4], for direct generation of aerosols is part of a larger effort at the University of Massachusetts Amherst to gain deeper insight into the chemistry of biomass pyrolysis. In particular, the UMass research team is focusing on developing molecular level understanding of the composition of the intermediate liquid, the reactions which produce the distribution of pyrolysis products, and the role of inorganic impurities in altering pyrolysis chemistry.

Support
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Hot off the press

Paul Dauenhauer is part of a research team from the Catalysis Center for Energy Innovation (DOE EFRC), who have just had a major pyrolysis discovery published. See below link.

http://pubs.rsc.org/en/Content/ArticleLanding/2012/EE/C1EE02743C

Fast pyrolysis research at University of Southampton

Update from Sai Gu in the UK regarding research he is leading focusing on the modelling of biomass thermal conversions

Computational models offer an indispensable tool in the quantification and visualization of thermophysical phenomena. Dr Sai Gu is leading a research team at the University of Southampton to make some major breakthrough in modelling of biomass thermal conversions.

Computational modelling of fluidised bed fast pyrolysis systems

Among the number of reactors being developed for fast pyrolysis, the fluidised bed reactor technology is one of the most promising technologies with the advantages of no moving part, easy operation and straightforward scale-up. However it represents some great challenges to model with many different phases including biomass, sand, fluidising gas, pyrolysis products, such as vapour, gases and char. The research team has developed two approaches to simulate the multiphase flow within the fluidised bed reactors.

Eulerian model

In this model, the sand is treated as a continuous phase. This will greatly reduce the computational cost. Biomass is included as individual particleswith momentum and heat transfer between the continuous sand and fluidising gas phases [1, 2]. The results show the development of fluidised bed and interaction with biomass particle. The model allows a comprehensive study of biomass particles including shape, size, shrinkage and product yield. The major benefit for this Eulerian model is its suitability for large scale simulation. This code has been developed using UDF (user defined function) in commercial software Fluent, so industrial users can apply it for design validation and optimisation.

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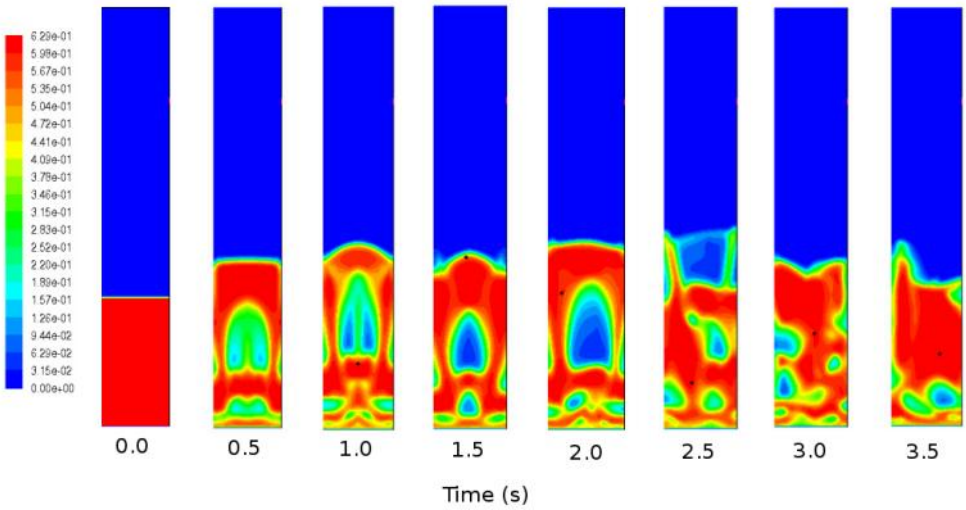
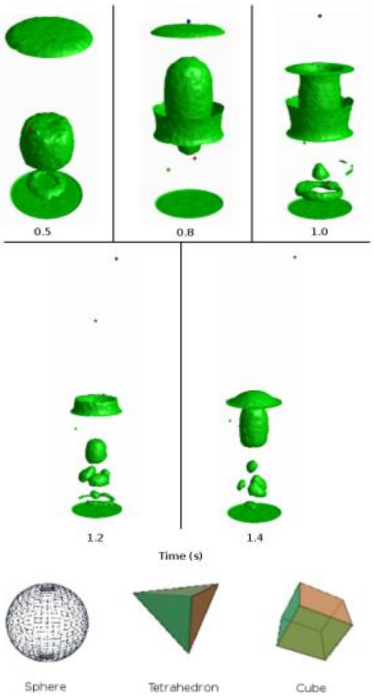
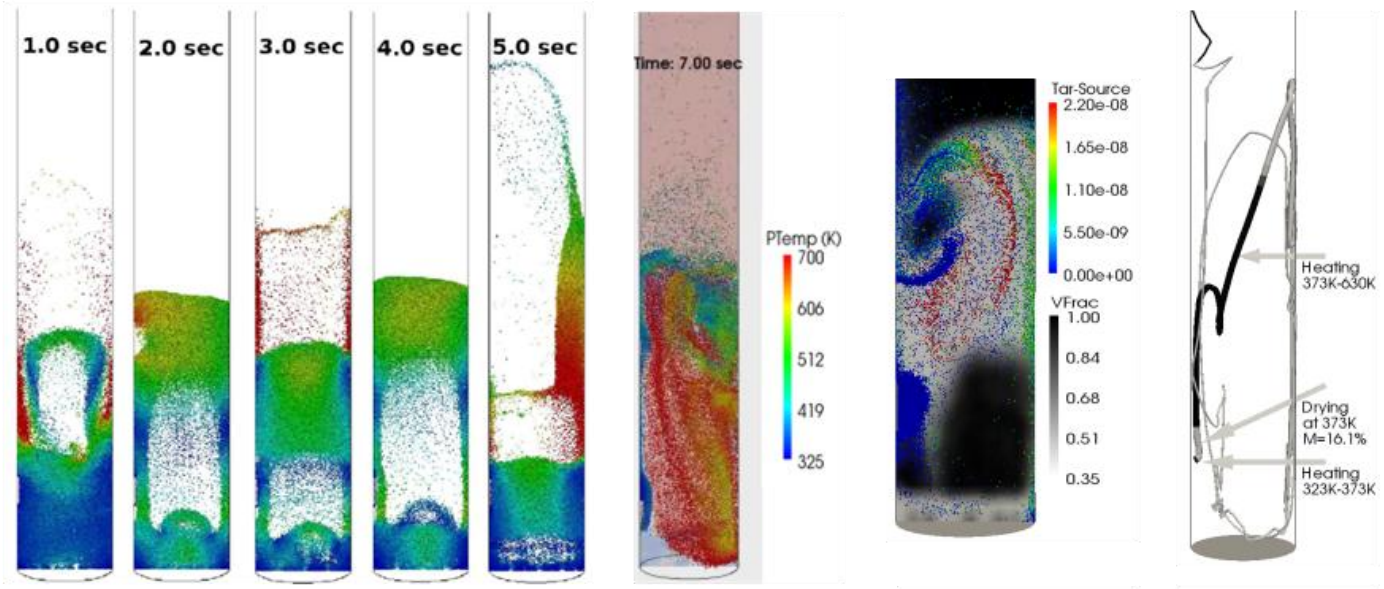


Figure 1: Biomass particle interaction with fluidised bed.



Fast pyrolysis research at University of Southampton...continued



Fluidisation of Sand

Biomass Mixing

Bio-oil Distribution

Biomass evolution

Figure 2: Discrete Element Model (DEM).

Discrete Element Model (DEM)
The team has also developed a DEM code to physically represent the interaction of millions of particles within fluidised bed reactor with heat transfer and chemical reaction. The results show a simulation which has about a million sand particles set as bed materials with a continuous feeding of biomass particles. The simulation was carried out using the UK national super computing facility, HEACTOR, with over 1000 processors used. The results show the fluidisation of sand particles before biomass injected, the mixing of biomass, the distribution of bio-oils within the reactor and the dynamic evolution of biomass to char during fast pyrolysis.

Quenching Model
In addition to the reactors, the quenching process is also a critical part for collection of bio-oils. The team has developed a quenching model to include the major components of bio-oils [3]. The results show the vapour to liquid process in a double surface water condenser.

International Collaborations
The research team has actively engaged in international collaboration with Dr Sai Gu coordinating a number of international projects as follows:

1) EPSRC Collaborative Research in Energy with South Africa: Scale-up modelling to answer "Pyrolysis Challenge"
This is a collaboration with University of Stellenbosch. Researchers from both teams work together to validate the computational models and make them more adaptive to the various processes. The advanced models developed in Southampton will be used by the South African partner to optimize their pilot plants and support process scale-up.

2) ECOFUEL
This is an EU-China network to look at the full product cycle from biomass to biofuel including fundamental kinetics, process modelling and scale-up, bio-oil upgrading to transportation fuels and engine test. The core partners are University of Southampton, Aston University, Aalto University, Shanghai Jiaotong University and Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences.

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Fast pyrolysis research at University of Southampton...continued

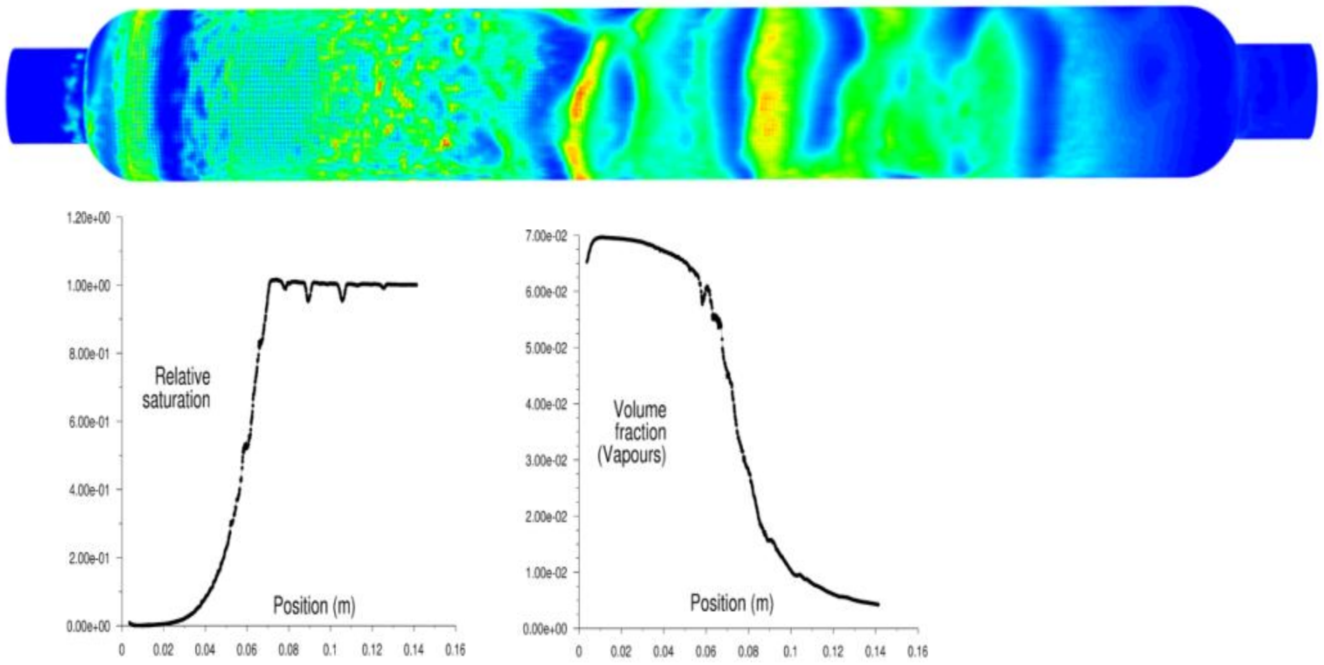

Figure 3: Bio-oil formation inside condenser.

3) Royal Society Africa Award in Development of the second generation of biofuel technologies in Ghana
This is a collaboration with the Institute of Industrial Research, Council for Scientific and Industrial Research (CSIR) Ghana. The project is to help the Ghanaian partner to develop research capacity for the pyrolysis based second generation biofuel technologies and promote research, awareness and implementation of second generation biofuel technologies in Ghana. A comprehensive assessment of biofuel potential in Ghana is published in *Renewable & Sustainable Energy Reviews* [4, 5].

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Task 34 Pyrolysis meeting

Richland, Washington, USA
October 2011

Doug Elliott, Task 34 Leader gives an update on the recent Pyrolysis meeting

Figure 1: Left to right: Dietrich Meier, Daniel Nowaskowski, Anja Oasmaa, Doug Elliott and Christian Lindfors.

> *"Dynamic viscosity measurements were less consistent compared to kinematic viscosity."*

Task 34 members convened in Richland, Washington, USA, on October 3-4, 2011. At the meeting the agenda included Country Reports, status of the bio-oil viscosity and aging Round Robin results, discussion of advances and needs for Norms and Standards.

Agenda of the TASK 34 Meeting

1. Introductions
Participating countries were represented by their team leads (Douglas Elliott, US; Anja Oasmaa, Finland; Dietrich Meier, Germany) with additional participants in supporting roles (Alan Zacher, Mariefel Olarte, Iva Tews, Daniel Santosa, Rick Orth, Dan Anderson PNNL US; Christian Lindfors, VTT Finland) and country observers from UK (Daniel Nowakowski) and Canada (Stefan Mueller, Ensyn and Wenli Duo FPInnovations).

2. Country Reports
Presented by representatives from US, Finland, Germany, UK and Canada.

3. Bio-oil Round Robin
The results of the Bio-oil viscosity and aging Round Robin from the 15 participating laboratories were reviewed at the meeting. It was apparent that dynamic viscosity measurements were less consistent compared to kinematic viscosity. The issue could be either the method itself and its application to bio-oil or, more probably, the experience level of the users of the method. The aging method gave consistent results within a given laboratory but was much more variable when comparing between laboratories. The potential reasons included variations in the heating oven and sample/container size. More information will be requested

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Task 34 Pyrolysis meeting...continued

from the participants.

Norms and Standards
ASTM—reported that an expansion of the ASTM burner fuel standard, D7544, is being balloted which will expand the standard to a second category of bio-oil that is higher quality (lower solids and ash). There was discussion about future standards, such as further refined burner fuel or for turbine or diesel fuels.

REACH—Status was reviewed. The registration that has been initiated with 34 companies filing includes many slow pyrolysis companies interested in the aqueous condensate. A company has identified itself as interested in being the co-ordinator. The task has agreed to support the effort by providing input as requested, such as for the chemical safety report. Further, the task believes that the registration should be divided into a slow pyrolysis group and a fast pyrolysis group, along the lines of the two CAS numbers which are now in existence.

MSDS—The several available need to be co-ordinated. The Biotox results need to be reviewed to identify fast pyrolysis results that can be used in an improved MSDS. The flash point also needs to be removed from the document with the addition of the information that bio-oil does not support sustained combustion.

Topics for Group Assignment
SOTA—The paper based on the country reports remains under development. The outline has been determined and some input has been received. This should be submitted for publication by the end of the year.

Analysis and methods development—The topic of sulfur analysis remains of interest to the task. The draft paper on the subject of analytical methods and results remains incomplete. Nitrogen analysis has been added to the scope of the paper.

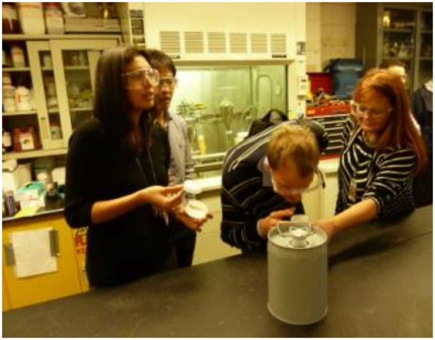
Materials—Corrosion remains an important topic. Only a limited amount of information is available. VTT in Finland has developed a test rig for making measurements. Oak Ridge National Laboratory in the US has a research project underway with tests of bio-oil from several sources being evaluated with a range of steels. Hydrotreated bio-oil will be added to the study in the near future.

Next meeting – It was decided that it will be the week of April 12-16, 2012, in Ottawa, Canada.

Doug Elliott
Task 34 Leader

The Task meeting included a visit to the PNNL laboratory *(photo middle of top row)* when a demonstration of the fast pyrolysis reactor was given by Daniel Santosa *(photo top left).*

Further demonstrations of the facilities were given by Mariefel Olarte *(photo top right and bottom right).* Alan Zacher explained about high pressure processing *(photo middle bottom row).*



Lignin pyrolysis for phenols: An integral component of two biorefinery projects in Germany

Dietrich Meier provides an insight into biorefinery research conducted in Germany

Biorefinery concepts based on lignocellulosic feedstocks are gaining increasing importance, as they could help to 1) broaden the basis for renewable feedstocks, 2) decrease the dependence on fossil resources, and 3) delay or even stop global warming of the atmosphere. Moreover, the use of lignocellulosic material in biorefineries avoids conflicts with the food industry, as human beings cannot digest this material. There are two reasons for this: firstly the accessibility of polymeric carbohydrates is limited since they are embedded in the lignin matrix, restricting enzyme access and attack; secondly the (ß) 1-4 glucosidic bond of cellulose cannot be split by human enzymes, making sugar digestion impossible. On the other hand, these two obstacles also pose technical barriers to increased conversion efficiencies in biorefineries. The lignocellulosic matrix needs to be opened and destroyed to improve accessibility for solvents and enzymes.

As a consequence, one German biorefinery project was initiated in 2007 to investigate a lignocellulosic biorefinery concept based on processing beech and poplar wood for the production of platform chemicals. The project funded by the German Ministry for Food, Agriculture, and Consumer Protection (BMELV) via German Agency for Renewable Feedstocks FNR. The first phase included 15 partners (four industry, two SMEs, four research centres, five universities). The basic concept is illustrated in Figure 1.

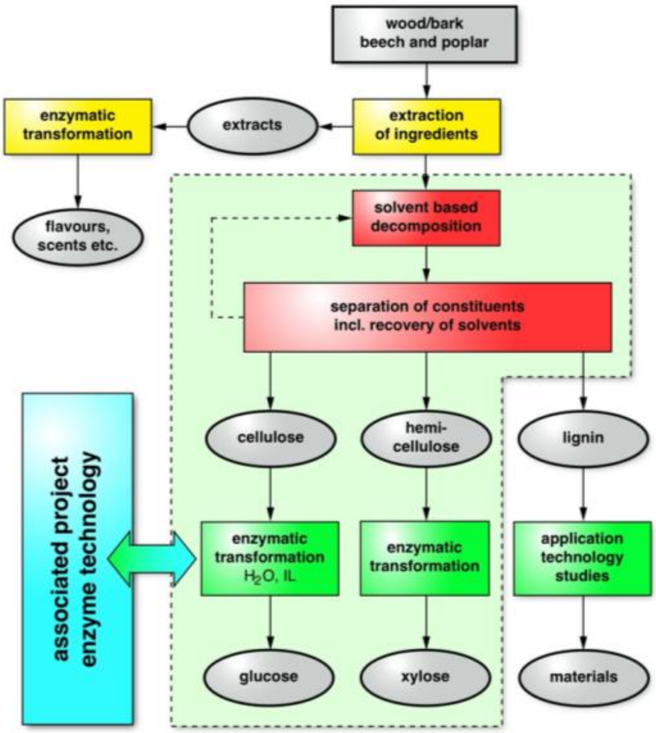


Figure 1: Lignocellulosic biorefinery concept.

Based on a review of literature the organosolv principle employing ethanol and water as a pulping agent was chosen as the basic procedure for component separation. The separation process should exhibit effective utilization of all wood components, namely cellulose, hemicelluloses, and lignin including the extractives. Indeed the process selected by the research consortium allows for separation of the extractives using the same solvent, which is required for the component separation into the wood polysaccharides and sulphur-free lignin. Optimization of pulping parameters was determined at 100g scale and verified at scales of 1kg and

Continued on page 28

Lignin pyrolysis for phenols...continued

10kg at vTI, Institute of Wood Technology and Wood Biology. A LCA study revealed that the use of lignin plays an important role for the economics of the concept.

Hence, in the second phase of the LCB project, lignin conversion into platform chemicals was integrated into the process scheme as (or in the form of) pyrolysis combined with catalytic hydroprocessing (hydropyrolysis, hydrocracking, hydrotreatment). Currently, lignin from the LCB project, lignin model compounds, and various catalysts are being screened at vTI using a modified Py-GC/MS system as well as a bench-top reactor system equipped with a fixed-bed micro-reactor and continuous feeding for hydroprocessing studies. During the course of the project a semi continuous autoclave system, which has previously been used, will be modified and tested.

Further information on the whole project can be found at: http://lignocellulose-bioraffinerie.de/

BIOREFINERY2021, a second lignocelluloses-based joint project funded by the German Federal Ministry for Education and Research (BMBF), aims for the development of a fully integrated and sustainable biorefinery. It commenced in 2009 and is divided into four modules:

- Module I - Process optimization
- Module II - Lignocellulosic feedstock
- Module III - High Value products from Lignocellulose
- Module IV - Integrated concepts

Lignin conversion is being performed under Module III. A circulating fluidized bed reactor (see Figure 2) is located at the Institute of Solids Process Engineering and Particle Technology at Hamburg University of Technology (TUHH) which is being used for this work.

The riser has an inner diameter of 8cm, the length is 200cm, and the throughput capacity is 10 kg/h. Aliquot samples are taken by means of a special probe located after the secondary cyclone. The probe is directly attached to the sample train using wash bottles filled with isopropanol.

Figure 3 shows the typical differently coloured solvent bottles after a run. Qualitative and quantitative analyses of liquid, solid, and gaseous samples are carried out at vTI, Institute of Wood Technology and Wood Biology. Process optimization including mass and energy balances is the main goal of the lignin pyrolysis task.

Further information on the whole project can be found at: http://www.biorefinery2021.com/cms/

Figure 2: Circulating fluidized bed reactor.

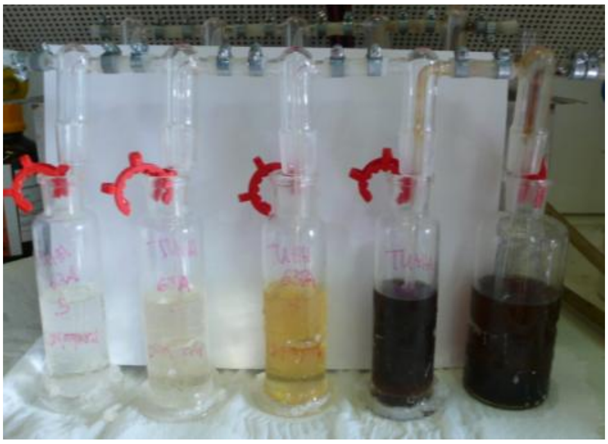


Figure 3: Typical differently coloured solvent bottles after a run.

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National Advanced Biofuels Consortium (NABC)

Update from John Holladay of Pacific Northwest National Laboratory in the USA

The National Advanced Biofuels Consortium (NABC) http://www.nabcprojects.org/ is developing cost-effective processes to produce biofuels that are compatible with today's transportation infrastructure. The NABC, co-led by the National Renewable Energy Laboratory and the Pacific Northwest National Laboratory, consists of 17 partners representing leading expertise and resources in advanced biofuels development across the national laboratories, academia, and industry.

NABC Strategy

The first year of research by the consortium was conducted from August 2010 to July 2011. Stage 1 efforts focused on determining whether technical and economic barriers could be overcome to develop a pilot-ready process in three years for six biofuels technology pathways. Over the first year, the NABC performed feasibility studies to determine which of the six approaches would move on to the next stage. The second stage will further develop the selected technologies to a pilot-ready state over two years.

Once commercialized, processes developed by the National Advanced Biofuels Consortium will help the United States increase energy security, reduce greenhouse gas emissions, and develop new economic opportunities.

Integrating biomass feeds into refineries

Biomass feedstocks must be processed into intermediates that are compatible with refinery streams before they are fed into traditional petroleum refineries. Successfully integrating these biomass feeds into refineries requires feeds that have low oxygen content, blend well with petroleum, and contain minimal contaminants that can poison refinery catalysts and degrade fuel streams.

The National Advanced Biofuels Consortium is investigating three proposed insertion points for advanced biofuels in a petroleum refinery.

Insertion Point 1. Biomass is converted into a bio-crude that can be co-processed with conventional crude oil.

Insertion Point 2. Biomass is upgraded into refinery-ready intermediates that are compatible with refinery streams that must go through further processing at the refinery.

Insertion Point 3. Biomass is upgraded to a near-finished fuel or blendstock that will be minimally processed at the refinery.

Process strategies

NABC has chosen to investigate six process strategies that have the highest potential to meet the project goals. All six processes involve new and innovative approaches that can dramatically advance the commercialization and adoption of advanced biofuels, as follows:

- Fermentation of sugars;
- Catalytic conversion of sugars;
- Catalytic fast pyrolysis;
- Hydropyrolysis;
- Hydrothermal liquefaction;
- Syngas to distillates.

In addition, NABC will perform

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National Advanced Biofuels Consortium (NABC)...continued

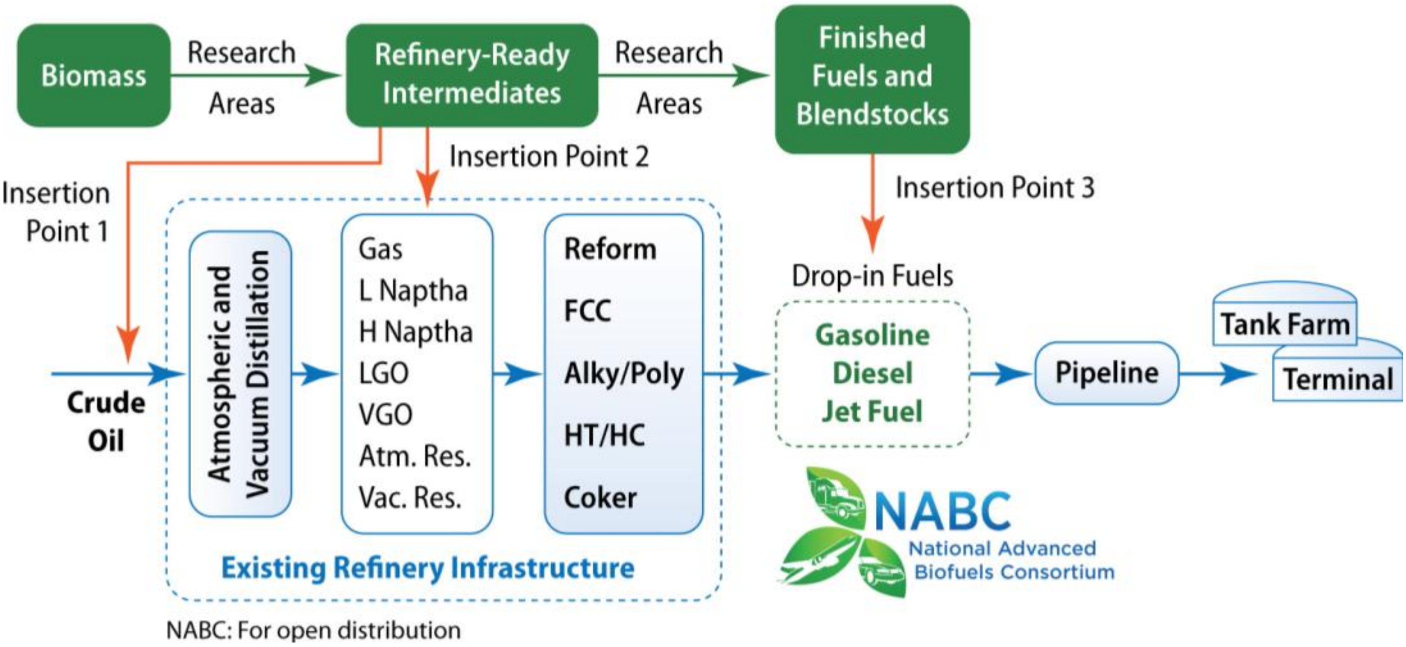

Figure 1: The NABC is evaluating three insertion points that take advantage of existing infrastructure to produce and distribute fuels.

cross-cutting research on feedstock logistics, pretreatments, separations, upgrading, engineering and sustainability analysis, and refinery integration.

In August, the National Advanced Biofuels Consortium (NABC) announced its initial selection of two "drop-in" biofuels technology pathways that will advance to the next development stage. Drop-in biofuels are fuels that can serve as direct replacements or supplements to existing gasoline, diesel and jet fuels, without any changes to existing fuel distribution networks or engines.

The pathways moving into Stage 2 under the NABC program will be funded with $26 million from DOE and will leverage an additional $12 million in cost share. The two technology pathways selected for Stage 2 development are:

- **Fermentation of Lignocellulosic Sugars** led by Amyris, and
- **Catalysis of Lignocellulosic Sugars** led by Virent.

The NABC has also identified two additional technology pathways that have demonstrated considerable promise for achieving drop-in biofuels but were missing key data to fully complete the feasibility study. These two technology pathways, **Catalytic Fast Pyrolysis** led by UOP and **Hydrothermal Liquefaction** led by PNNL, will be given three months to generate the missing data, at which point the NABC will then determine whether they are ready to proceed into stage II development.

Another important development from the NABC work is that GREET analysis of each of the technologies studied show greenhouse gas displacement relative to gasoline greater than 80% for each of the technologies evaluated.

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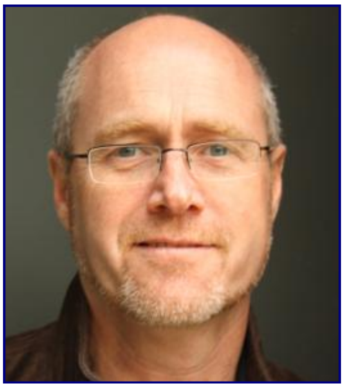
Overcoming the barriers



Mike Tooke (above) and Howard Jackson (below) of 2G BioPOWER in the UK give their perspective on the challenges of transforming waste biomass to upgraded pyrolysis oil

The journey of waste biomass to upgraded pyrolysis oil is akin to the 100 metre hurdles. Getting over, round, or breaking down these hurdles is 2G BioPOWER's raison d'être.

World population has hit seven billion increasing concerns over resources, and also increasing the production of waste which, whilst an issue, is perhaps also an opportunity.

Our ultimate aim is to convert the biogenic waste content, increasingly a commodity, into transport fuels, ideally "drop-in". The reticence of German car manufacturers to guarantee vehicles running on a slightly higher ethanol blend, E15, caused an understandable adverse German public reaction, hence our preference for a hydrocarbon solution.

However one does wonder what the market perception would have been if Formula 1 World Champion, Sebastian Vettel, had been running his Red Bull on E85! Fortunately motor sport governing body, the FIA, has seen the light and from 2012 fuels from biomass are allowed within the technical regulations. It's just a shame such fuels are not compulsory, but we do aim to stick 100% biofuel in an F1 car one day and add some sex appeal, after all "energy" deserves to be energised.

With the objective of developing commercial projects in the near term UOP-Envergent's RTP^{TM} fast pyrolysis technology with future UOP upgrade is highly attractive in combining both financial strength and experience brought to the table. Other technologies are being considered and can now be evaluated rapidly using the methods 2G BioPOWER has developed.

> *"The journey of waste biomass to upgraded pyrolysis oil is akin to the 100 metre hurdles."*

Producing a drop-in fuel is highly desirable, however size matters with UOP's upgrading technology and large quantities of pyrolysis oil are needed; an intermediate plan is required. As a result 2G BioPOWER's immediate focus is to produce waste-derived pyrolysis oil for the heat and power markets. However what is the most attractive proposition? A number of options have been modelled comparing scale, feedstocks and application. Starting from mass and energy flow, the models account for feedstock and product offtake prices in the markets allowing for [changing] UK incentives. Tools and methods 2G BioPOWER is now applying to evaluate other propositions.

Securing feedstock is key. UK waste wood feedstock arising is about 3.5-4.5 million tonnes

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Overcoming the barriers...continued

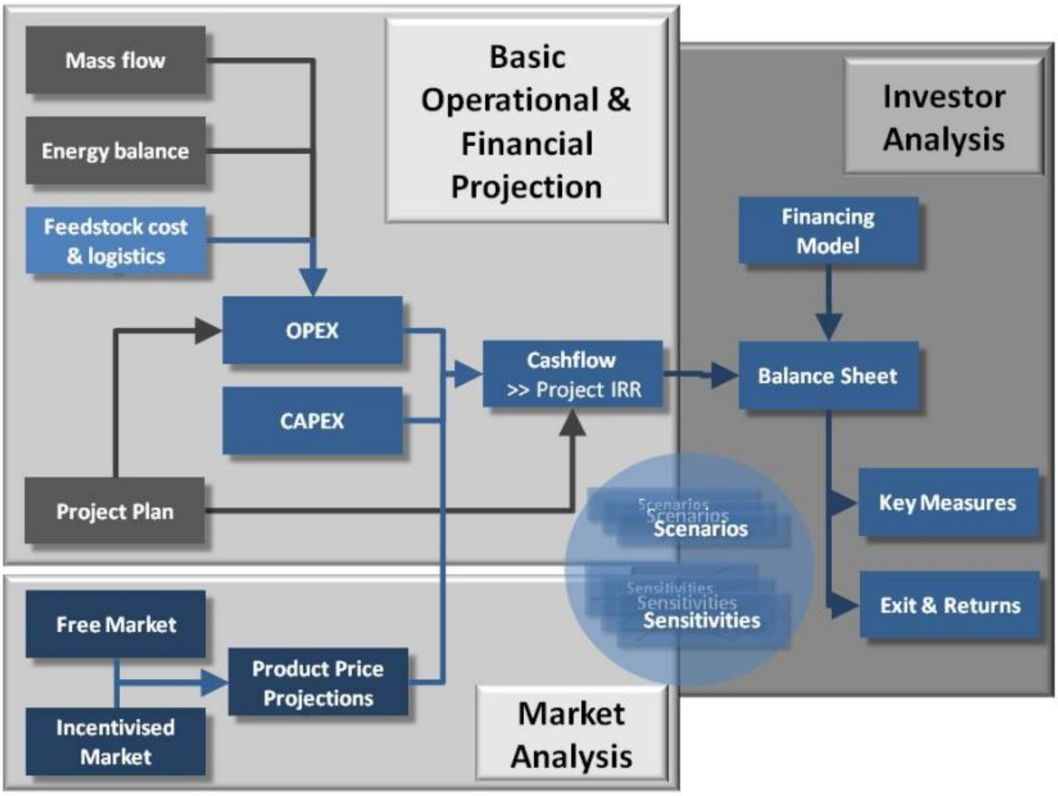

Figure 1: 2G BioPOWER modelling approach.

per year. As of 2011 sufficient biomass-to-power projects had been proposed to use ten times this quantity of biomass. However the recent revisions to ROC banding in the UK will tend to encourage co-firing and conversion rather than conventional biomass power plants, so many of these may well now not proceed.

Another major source of biogenic feedstock is municipal and commercial waste. Separation technologies now being proven at commercial scale, as demonstrated by Graphite Resources, have the capability to produce a waste-derived feedstock comprising more than 95% biogenic energy. 2G BioPOWER has also modelled the use of this technology which shows considerable promise.
Using fast pyrolysis to convert waste biomass to pyrolysis oil for subsequent use in embedded CHP applications makes energy sense. The most efficient co-firing power stations convert only 38% of the biogenic energy to power. Conversion to pyrolysis oil is about 60% efficient and a typical CHP installation would achieve 75% into heat and power – and overall conversion efficiency of 45%. Some CHP installations are even more efficient.

Power generation and CHP using pyrolysis oil are close to being realised commercially. For example UOP are working with a major partner to prove the use of pyrolysis oil with minimal pre-treatment in a diesel engine. The first commercial implementation will be in Envergent's 400 tpd RTP project in Canada.

The UK offers considerable support to such technologies with its ROC scheme providing approximately £90 per MWh subsidy to power projects employing advanced conversion technologies such as pyrolysis. After lobbying, the use of bioliquids is now being offered a similar level of support as biomass.

The UK's Renewable Heat Incentive has yet to provide support for bioliquids (although this has been proposed); however pyrolysis oil is likely only to be commercially viable in larger scale heating implementations, and following EU intervention the UK FiT support for implementations greater than 1 MWth is to be reduced from 2.7p to 1p per kWh.

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Overcoming the barriers...continued

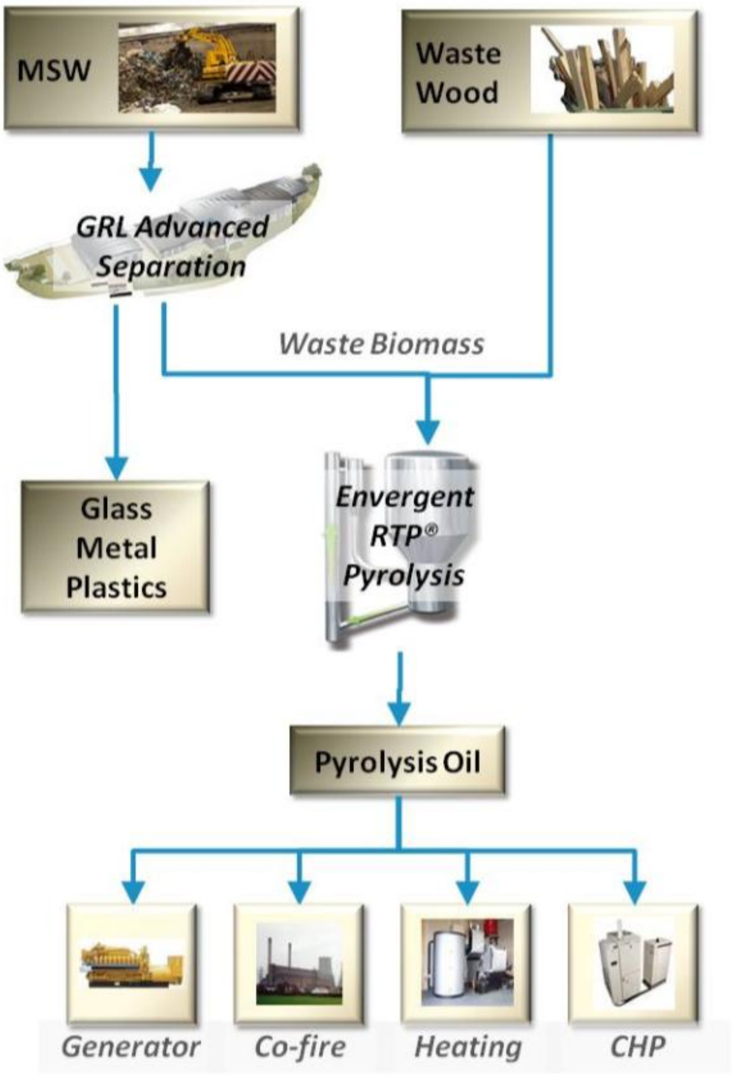

Figure 2: Initial pyrolysis project options.

Overall 2G BioPOWER has established that waste to energy (waste wood or waste biomass from MSW) is economically viable under UK incentives at 400 tonnes per day or more. Constructing a commercial scale fast pyrolysis project in the UK will develop UK logistics and operational experience.

However not even the blue-chip record of Honeywell-UOP and a complete EPC wrap is sufficient to overcome reticence by most banks to finance such a project.

However it is essential this type of step is made soon to ensure the UK is able to make best use of its biomass resources and to provide the foundation for upgrading projects that will deliver transportation biofuels from waste.

The financial market is risk averse; even more so when attempting something as yet unproven at scale. Use of market incentives that are open to competition (such as the UK's ROC for power) adds uncertainty to risk. The need for direct support from the government is clear.

The UK Government has been loath to back specific horses as "it doesn't pick winners", however is keen to support advanced conversion technologies. The message that focus and support is needed is now getting through.

Vinod Khosla has his own modus operandi: back every horse in the race and you're bound to win but more importantly you will also win every other race in the future. The US Government seems, at least partially, to be following his example. The UK's Green Bank is the UK's proposed vehicle for supporting such ventures. It can't come soon enough otherwise we will need to search out another Vinod Khosla.

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2G BioPOWER

Potential of fast pyrolysis applications within North American forest industries

Review from Iva Tews of Pacific Northwest National Laboratory (PNNL) in the United States

Pacific Northwest National Laboratory (PNNL), its partners Technical Research Centre of Finland (VTT) and National Renewable Energy Laboratory (NREL) conducted a market assessment of bio-oil production via forest residue fast pyrolysis in North America. Forest residue availability data collected and reported by VTT and their collaborator Poyry Management Consulting Oy is based on current residue information from chip and pulpwood based industry. Two application routes were developed based on the biomass availability and consequent technology application routes. These routes are designated as either near term and long-term applications for bio-oil production.

Near-term applications are focused on an integrated approach with current forest industries and bio-oil production for power, whereas long-term applications are more focused on bio-oil to fuels production in a standalone facility.

Near-term applications

The current forest industry is one of the main users of biomass and bioenergy in North America. This is why new bioenergy technologies can often be developed next to existing forest industry operations. Integration of the conversion process has many benefits such as raw material sourcing, integration of energy flows and the use of existing infrastructure and personnel.

VTT and Poyry worked together in developing a possible point of integration by investigating the conversion of power and heat boilers in the pulp and paper and sawmill industry for pyrolysis bio-oil production and utilization. By examining possible boilers of a certain size and age, a near-term technology insertion point for a fast pyrolysis bio-oil production route was identified. The primary product for this application is power, or combined heat and power

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"The forest industry is one of the main users of biomass and bioenergy in North America."

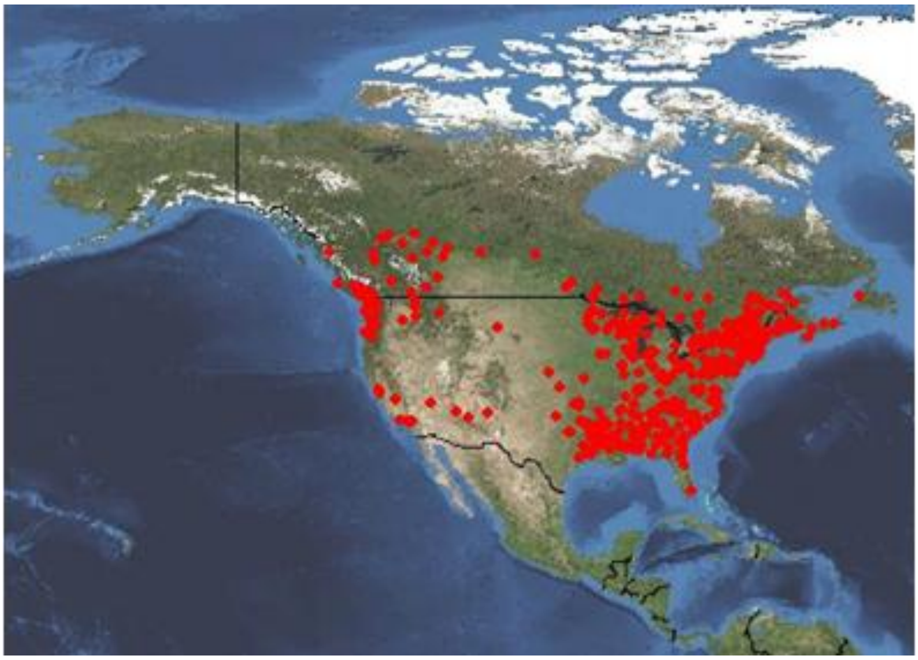

Figure 1: Distribution of North American pulp and paper and sawmill industry.

Potential of fast pyrolysis applications within North American forest industries...continued

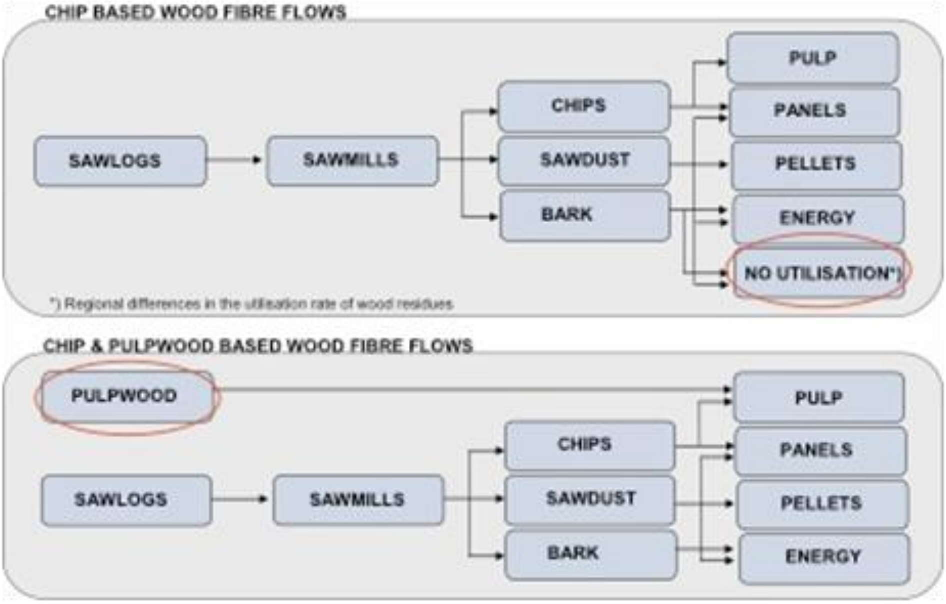

Figure 2: North American pulp and paper and sawmill industry process fiber flows.

generation.

Long-term processing applications
As the U.S. and other nations seek to use renewable fuels within their current infrastructure bio-oil production, stabilization, and consequent upgrading becomes essential. As part of this work and a long-term application of fast pyrolysis bio-oil production we modelled a distributed forest residue pyrolysis process and evaluated the cost economics and environmental impact of a standalone plant.

A Techno-Economic Analysis (TEA) was developed to identify process obstacles and possible research pathways towards overcoming them. Based on previously published work by Jones et. al.[1], a circulating fluidized bed reactor with a 250 metric tonne per day throughput was modelled using process modelling software (CHEMCAD®). Furthermore simulation results were used to obtain mass and energy balances which provided a basis for equipment sizing and cost,as well as development of the Life Cycle Analysis (LCA).

Within the first stage of this analysis both the TEA and LCA were developed around a raw pyrolysis oil production process. Our initial conclusions indicated that favourable economics and a reduction in the Global Warming Potential (GWP) from fossil sources makes this a potential route to biofuels. However complete process development and analysis to finished fuel such as gasoline, diesel or jet from forest residues will indicate the process viability. This research is still ongoing and the second phase will look at subsequent bio-oil upgrading to transportation fuel production.

Conclusions
Both near and future applications for bio-oil production can potentially be cost efficient. Production in the pulp and paper and sawmill industry represents a near term solution if the industries are willing to invest in upgrading of their boilers. Further research and analysis are necessary to understand the economic impacts of production of biofuels, however this route too looks promising. This work is still ongoing as data, models, and information are transferred between all three partners.

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Heterogeneously catalysed deoxygenation of pyrolysis oil in hot compressed water to produce fuel components

Udo Armbruster from the University of Rostock gives an overview of a new research collaboration in Germany focusing on the combination of two patented processes

In June 2011, a new research collaboration was established between academic research institutes (Von Thünen Institute in Hamburg (vTI) and Leibniz Institute for Catalysis in Rostock, LIKAT) and an SME based in the northern part of Germany. It aims at the combination of two patented processes, the ablative pyrolysis of biomass (BTO®, Pytec) and the CLC Process for heterogeneously catalysed deoxygenation in near-critical water. The feasibility of both processes has been validated in published studies and expertises.

The first process unit uses the kinetic energy of a rotating disk to transform woody biomass, being contacted with the disk (Figure 1), at high temperature and allows excellent heat control and product recovery to produce a stable pyrolysis oil. It has been successfully realised at a scale of 6 tons/day (Figure 2) and produces less char than comparable techniques (e.g. fluidised bed reactors).

The CLC process is an attractive option for downstream processing of such materials without consumption of external hydrogen. The process benefits from the aqueous reforming of a part of the fed carbonaceous material, which generates *in situ* hydrogen for subsequent hydro-deoxygenation. It also contains an internal hot recycle to establish rapid heating and feed activation, which helps to suppress the formation of coke almost completely. The heating step is crucial in the hydrothermal treatment of carbonaceous materials, as detrimental reactions like coking or polymerisation might run in this temperature range with high rates and deteriorate the overall efficiency of such treatment processes.

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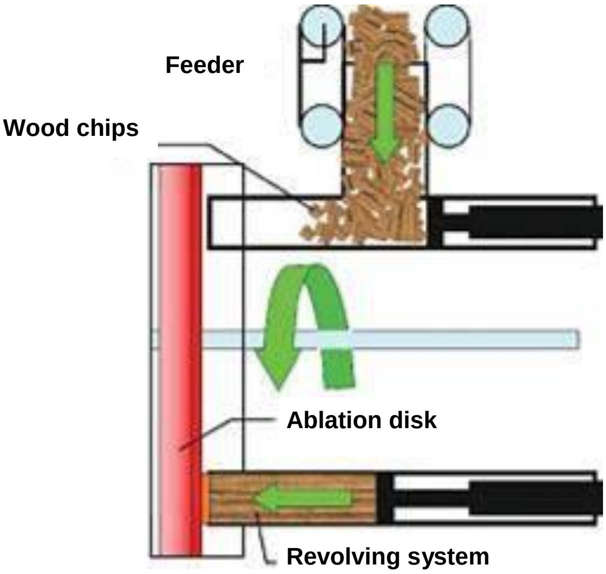

Figure 1: Basic principle of the PYTEC BTO® process.

Heterogeneously catalysed deoxygenation of pyrolysis oil in hot compressed water to produce fuel components...continued

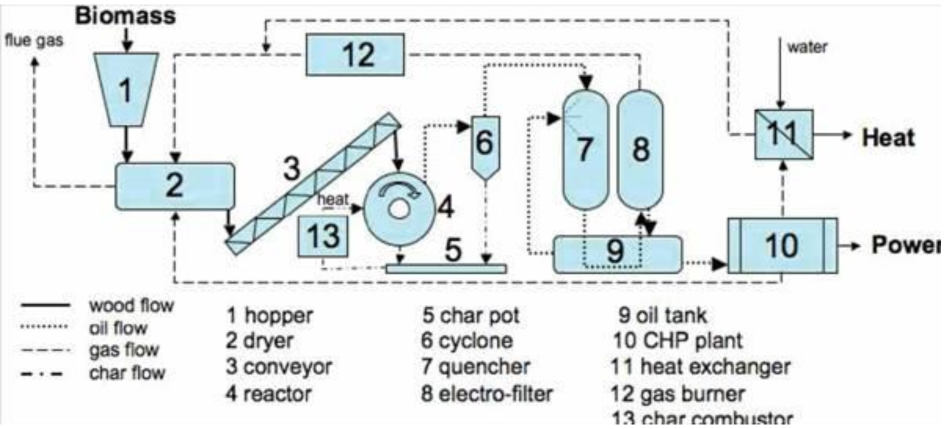

Figure 2: Overall scheme of the PYTEC BTO® process.

Typically, pyrolysis oil contains up to 50 wt-% of oxygen, and the overall process is expected to cut this percentage significantly. Currently, a demonstration plant to test this concept with a capacity of 1 kg/h is under construction in Hamburg, Germany.

Among the main tasks are:
- optimisation of reaction conditions, in particular hot recycle,
- development of hydrothermally stable active catalysts,
- co-feeding of biomass as additional hydrogen source.

The participating enterprises are responsible for the construction and operation of the demonstration plant. Von Thünen Institute has lengthy expertise in biomass pyrolysis and analysis of such complex materials by means of GC/MS, whereas Leibniz Institute for Catalysis will provide suitable catalysts and the corresponding physico-chemical analyses.

> *"Typically pyrolysis oil contains up to 50 wt-% of oxygen, and the overall process is expected to cut this percentage significantly."*

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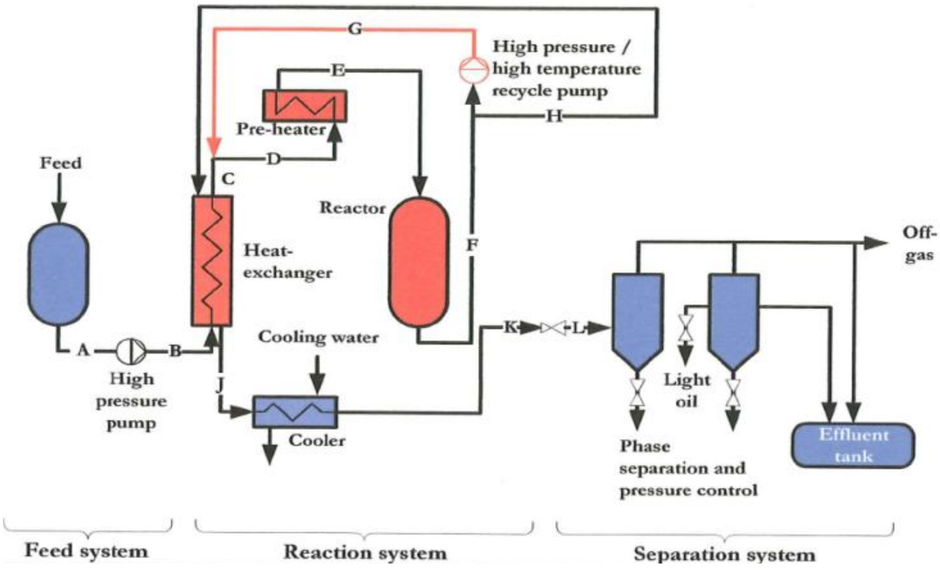

Figure 3: Overall scheme of the CLC process.

Slow pyrolysis research at the University of Edinburgh

Update from Ondřej Mašek regarding the latest developments at the UK Biochar Research Centre (UKBRC)

Climate change mitigation and adaptation are both pressing issues faced by society. The need to develop effective technologies to address these issues drives the pyrolysis research at the University of Edinburgh's UK Biochar Research Centre (UKBRC). The focus of this research is on slow pyrolysis, due to our interest in developing biochar and biochar-based products for atmospheric carbon sequestration and soil amendment, alongside other pyrolysis co-products.

Slow pyrolysis of biomass has been studied at the University of Edinburgh since late 2009, following the foundation of the UKBRC, funded mainly by the UK Engineering and Physical Sciences Research Council (EPSRC) as well as various industrial partners. The pyrolysis research team is a part of a larger interdisciplinary effort within the UKBRC that includes soil science and social sciences related to biochar and its deployment.

Figure 1: Laboratory-scale pyrolysis unit.

In its relatively short existence, the centre has been through a period of rapid growth both in terms of personnel and experimental facilities. The first challenge faced was to design a set of experimental facilities suitable for research on pyrolysis of different feedstock under a wide range of conditions. As a result we built two laboratory-scale units for fundamental research that allow us to conduct pyrolysis at temperatures up to 1000°C.

The first unit is a fixed- or fluidised-bed pyrolysis setup, heated using an IR image furnace, with capacity of approximately 50g of feedstock. This unit allows us to study processes occurring at different stages of pyrolysis and evaluate all co-products both qualitatively and quantitatively. For example, using a mass spectrometer we can analyse the composition of gases evolving in real time during pyrolysis.

The second unit is an auger-driven pyrolysis apparatus with throughput of up to 3-5 kg/h, operating in continuous mode. The unit is heated by a split-tube electric furnace and can run at temperatures of up to 850°C. This setup allows us to conduct more applied research, studying processes occurring in continuous pyrolysis as opposed to batch pyrolysis. Furthermore, it is also suitable for scale-up of findings from our basic research. As with the batch unit, we can also collect and assess (qualitatively and quantitatively) all pyrolysis co-product streams from the

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Slow pyrolysis research at the University of Edinburgh...continued

continuous unit.

The latest development in terms of building experimental capacity has been the design and installation of a pilot-scale continuous slow pyrolysis unit. In early 2011 we installed a new rotary kiln pyrolysis unit with throughput of up to 50 kg/h on the King's Buildings campus of the University of Edinburgh. The unit is housed in a dedicated new building that allows for comfortable operation of the unit, as well as storage of feedstock and products. The unit is based on an electrically heated (50 kW) rotary kiln with diameter of 250mm and length of 3m. As the main purpose of the unit is to produce solid products, i.e. biochar, it is equipped with active indirect cooling of the solids discharge system that ensures safe handling of the final product and maintains its quality.

At this moment, the unit is equipped with a pyrolysis liquid condensation system that allows separation of pyrolysis liquids only from a slip stream of the pyrolysis gas. The slipstream is used for analytical purposes so that the performance and energy and mass balance of the system can be monitored. In a second phase of development, a new larger separation unit will be developed and installed which will allow collection of larger quantities of pyrolysis liquids.

In its current form, the pyrolyser allows for connection with downstream processes such as gas cleaning and/or engines and fuel cells, thus facilitating research on direct coupling of pyrolysis and electricity generation.

Figure 2: Pilot-scale pyrolysis unit at the University of Edinburgh.

Current projects in progress at UKBRC include:

- Fate of contaminants in the pyrolysis of virgin and non-virgin biomass;
- Conversion of organic residues to biochar, gas and pyrolysis liquids;
- Development of 'specified' biochar, i.e. biochar optimised for specific use;
- Value added products from pyrolysis liquids;
- Integration of biochar and biorefineries;
- Modelling of pyrolysis processes.

The key objective of the research team is to develop viable systems for co-production of biochar and valuable co-products at different scales to optimize carbon abatement.

Our results so far have shown that for woody biomass, the yield of stable carbon (as related to environmental stability and measured using enhanced oxidation) is nearly independent of temperature in the range examined, i.e. 350-650°C [1]. Our work on organic residues has also shown some interesting results, for example, alkaline pyrolysis liquids (pH 8) from some organic residues as opposed to acidic liquids (pH 2.2) from pyrolysis of virgin biomass.

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Fast pyrolysis-catalytic steam gasification of biomass in a screw kiln reactor at the University of Leeds, UK

Update from Paul Williams (above) and Chunfei Wu (below) from the University of Leeds in the UK

Introduction

The thermal conversion of biomass to synthesis gas (syngas) via gasification is a favourable option for the utilization of biomass since the syngas can be stored, easily transported and the end-use of the gas can be de-coupled from the production process. Non-catalytic conventional biomass gasification requires high gasification temperatures often above 900°C in order to reduce the tar content (condensable hydrocarbons) of the syngas. However, high temperatures also lead to a reduced total energy efficiency of the process. Catalysts, particularly nickel based catalysts, have been utilized as an effective approach to reduce the tar content of syngas, while reducing the need for very high temperatures.

Among various reactors, the continuous screw kiln has been proposed to be a preferred reaction system for industrial commercialization. The screw kiln reactor is suggested to have the potential to be used for the processing of complex chemical and physical feedstocks. Furthermore, the screw kiln reaction system might reduce the over-cracking of raw materials, and generates comparatively narrow products that would be well reformed in a second stage to produce hydrogen gas.

Screw kiln reaction system

The screw kiln continuous reaction system at the University of Leeds consists of two stages (Figure 1). A first stage screw kiln fast pyrolysis reactor where pyrolysis of the biomass occurs since the feedstock is fed directly into hot zone of the reactor. The evolved pyrolysis gases are then passed to a second stage fixed bed reactor where gasification of the pyrolysis gases takes place in the

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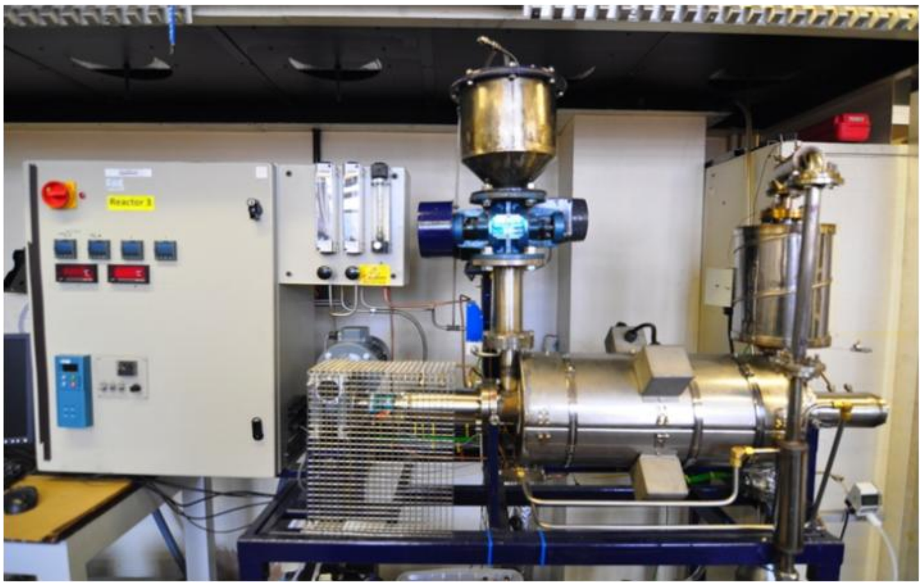

Figure 1: The screw kiln reaction system.

Fast pyrolysis-catalytic steam gasification of biomass...continued

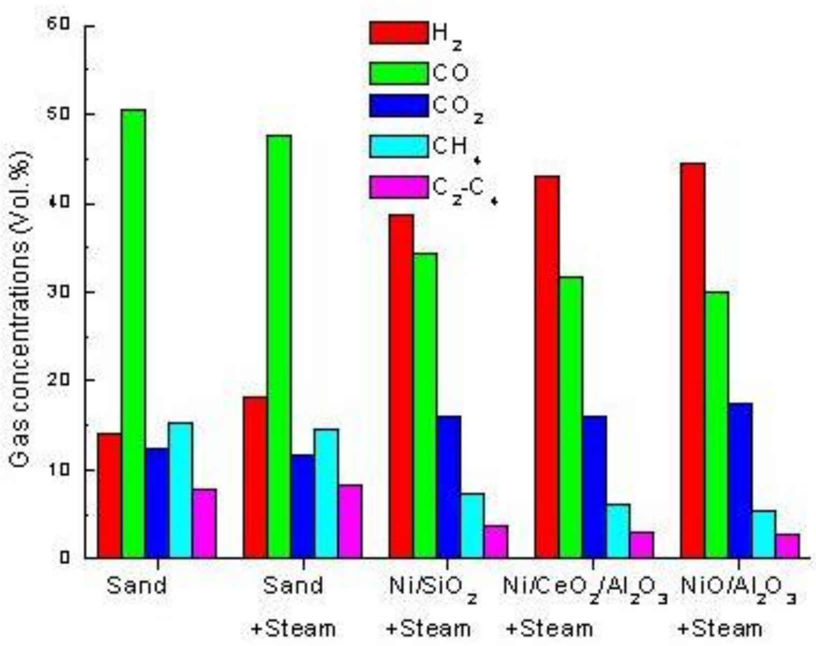

Figure 2: Gas concentrations of pyrolysis/gasification of waste wood with different catalysts.

presence of a catalyst and steam. The screw kiln reactor is 54cm long x 6.2cm diameter, constructed of stainless steel and heated by an electrical furnace to the fixed pyrolysis temperature. The second stage fixed bed catalytic gasification reactor is 26cm high x 2.5cm diameter, constructed of stainless steel and operated at a fixed gasification temperature.

Experiments have been carried out using wood waste in the horizontal screw-kiln reactor at 500°C and further catalytic steam gasification of the pyrolysis gases in the second stage reactor at 750°C. The product gases were passed through a series of condensers to trap any oil/tar, and the non-condensed gases were collected with gas sample bags and further analysed by gas chromatography. The influence of catalyst composition was investigated using three nickel based catalysts; 20 wt.% Ni/ CeO_2/Al_2O_3 (20 wt.% CeO_2 wt.%); 20 wt.%Ni/Al_2O_3; 20 wt.% Ni/SiO_2 catalysts.

Results and discussion

Figure 2 shows that the introduction of the different catalysts had a significant influence on the gas compositions. The H_2 and CO_2 compositions showed an increase, while the CO and CH_4 and C_2-C_4 compositions showed a decrease, with the introduction of the catalysts. Of most significance, the yield of hydrogen was substantial. There is much interest in producing hydrogen from sustainable sources, such as biomass rather than fossil fuels.

The NiO/Al_2O_3 catalyst resulted in a H_2 and CO_2 yield increase to 44.4 and 17.4 vol% respectively. and CO decrease to 29.9 vol% compared to the non-catalytic investigations. These results were only slightly different to that obtained for the NiO/CeO_2/Al_2O_3 catalyst (H_2 43.1 vol%) as shown in Figure 2. A comparison of H_2 yield from the NiO/Al_2O_3 and NiO/CeO_2/Al_2O_3 catalysts, indicates a possible reduction in the catalyst activity, for the NiO/CeO_2/Al_2O_3 catalyst. We have shown that a high content of CeO_2 addition to Ni catalysts results in reduced H_2 production due to catalyst sintering with high CeO_2 concentrations. This may explain the slight reduction in H_2 yield for the NiO/CeO_2/Al_2O_3 catalyst with a high CeO_2 content of 20 wt% used in this work.

Conclusion

Thermal degradation of biomass waste can be processed successfully in a screw kiln fast pyrolysis coupled with gasification in the presence of a catalyst and steam. The system can be used for syngas production with a high yield of hydrogen by catalytic reforming in the secondary gasification reactor.

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Review—tcbiomass 2011

A summary by IEA Task 34 Pyrolysis leader Doug Elliott

tcbiomass 2011, the international conference on thermochemical conversion science, was held in Chicago at the Westin Chicago River North Hotel on 28-30 September 2011. It was attended by the Task 34 national team leaders among the over 360 registrants.

tcbiomass 2011 was organized by GTI under the leadership of Terry Marker and the scientific panel with Vann Bush and Kyriakos Maniatis as conference co-chairs.The conference agenda included five keynote speakers:

- Kyriakos Maniatis—EU perspective
- Hans Sohlström—UPM and Bioenergy—Forest Products Industry
- Valerie Sarisky-Reed—U.S. DOE perspective
- Dave Cepla—Pyrolysis project drivers today and in the future
- Paul Nash—Alternative fuels—Targeting carbon-neutral aircraft operations

Thirty-eight technical presentations were organized into parallel sessions including:

- Gasification (2 sessions including 13 presentations)
- Pyrolysis (2 sessions including 13 presentations)
- Upgrading (6 presentations)
- Pretreatment and char (6 presentations)
- The conference also included 110 poster presentations in the same topic areas—27 gasification, 54 pyrolysis, 19 upgrading (mostly bio-oil), and 10 pretreatment and char.

Presentations and many of the posters are available on the conference website *tcbiomass2011*

The attendees at the conference represented 24 countries and 185 organizations. Continuing a trend in the recent thermochemical conversion conferences, the bulk of the presentations and posters related to pyrolysis.

The conference was reportedly a great success and one of the many highlights was the presentation of the Don Klass award, which was awarded to Suresh Babu for Excellence in Thermochemical Conversion Science to recognize his innovative contributions in the field of bioenergy.

tcbiomass2011 also hosted a competitive student poster contest to help connect today's top engineering students with global bioenergy experts. From the 29 poster contestants the 1st Place went to Kaige Wang, from Iowa State University on "Pyrolysis of Lipid-rich Biomass for Fuel and Chemical Production" and 2nd Place was Jatara Wise, from Texas A&M University on "Mineral Nutrient Recovery in Pyrolysis Co-products for Varied Feedstocks.

www.gastechnology.org/ tcbiomass2011

Country Update — Canada

Focus on ICFAR

On September 26 2011, the Institute for Chemicals and Fuels from Alternative Resources (ICFAR) at the University of Western Ontario (London, Ontario, Canada), hosted a one-day Workshop of Thermochemical Biomass Conversion. The workshop consisted of a series of short presentations delivered by 22 students describing their research work at ICFAR, and of keynote lectures by Tony Bridgwater, Dietrich Meier, Guus van Rossum and Marcel Schlaf.

ICFAR opened its doors in October 2009 (http://www.icfar.ca/). Over the past two years, it has grown to become a very large research and development centre, focusing on biomass thermochemical conversion technologies (torrefaction, pyrolysis, gasification, hydrothermal conversion, supercritical water gasification and upgrading processes). The Institute, originally founded by Franco Berruti and Cedric Briens, has recently become the home of the NSERC-FPInnovations Industrial Research Chair in Forestry Biorefinery (Charles Xu).

Today, the research team consists of three full time faculty members, 30 graduate students at the Master and PhD levels, seven postdoctoral fellows, three technical support staff and three administrative staff members. The Institute carries out R&D activities in collaboration with industrial institutions worldwide and it also receives considerable government grants. Technology transfer and commercialization are also goals of the Institute.

Agri-Therm is one of the successful spin-offs of the activities of ICFAR (http://www.agri-therm.com/). Agri-Therm has been developing a 10 t/day mobile pyrolysis technology for the production of bio-oil and bio-char from a variety of agricultural and forestry residues. Currently, the second-generation (pre-commercial) of the mobile converter is being built and it will be commissioned in 2012. It is anticipated that the technology will become commercially available by the end of 2012.

Canadian Event

13—15 June, 2012

Explore innovation, discover emerging ideas, learn from the experience of others, and conduct business in the wood-based bioenergy capital of Canada.

The International Bioenergy Conference and Exhibition is Canada's longest-running conference devoted to the global bioenergy sector.

This leading event provides opportunities for bioenergy experts, existing businesses and organisations, and new entrants to come together to explore leading-edge concepts and current applications in the bioenergy sector.

For further information contact:

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Country Update — Finland

Industrial consortium

Metso, UPM, Fortum and VTT have developed the world's first integrated bio-oil production concept to provide an alternative to fossil fuels.[1] The consortium has constructed an up to 7 tpd bio-oil production pilot unit integrated with a conventional fluidized-bed boiler. Proof-of-concept has been carried out: more than 100 tonnes of bio-oil has been produced from sawdust and forest residues at high availability. Around 40 tonnes of bio-oil has been combusted in Fortum's 1.5 MW district heating plant with high efficiency. Flue gas emissions were close to those of heavy fuel oil.

VTT (Technical Research Centre of Finland)

Anja Oasmaa is serving as the national team lead for Finland. The biomass pyrolysis research is focused on three areas:

1. The industrial project supports the industrial consortium in their effort to demonstrate fast pyrolysis oil production and long-term use.
2. The national Tekes project aims to create the basic tools for commercialization of fast pyrolysis oil production and use. This involves the work on MSDS, initialization of standardization in Europe under CEN, developing and validifying test methods[2], and on-line methods for process quality control. Stability[3] and acidity[4] issues of pyrolysis oils have been studied in more detail as well as chemical characterisation. The work involves also work on modelling of biomass pyrolysis. Experiments are conducted in circulated fluid-bed (CFB) and bubbling fluid-bed (BFB) pyrolyzers (20 kg/h), 1 kg/h fluid-bed unit, and continuous-flow hydrotreatment unit (20–30 g/h).
3. Slow pyrolysis research carried out during 2008-2010[5] in Finland as a joint project of VTT, MTT Agrifood Research and University of Helsinki, is continuing within a new joint project "Overall concepts for utilisation of slow pyrolysis products". The project aims at developing new distributed biorefineries and comprehensive concepts based on slow pyrolysis for SMEs. The goal is an optimised slow pyrolysis process for new applications of the products.

ÅA (Åbo Akademi University)

At ÅA, pyrolysis, and gasification of black liquor (biomass bio-product from pulping industry) are being studied in laboratory-scale units. The purpose is to better understand the fate of the pulp cooking chemicals, sulphur and sodium, in novel thermal conversion processes being planned. Pyrolysis oil production from woody biomasses and catalytic upgrading of the pyrolysis vapors is studied using a special type of dual reactor laboratory system.[6]

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[3] Oasmaa, Anja; Korhonen, Jaana; Kuoppala, Eeva. 2011. Energy & Fuels. ACS Publications, vol. 25, 7, pp. 3307-3313

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[5] Fagernäs, L. 2010. Slow pyrolysis research in Finland. IEA Bioenergy Agreement Task 34 Newsletter - PyNe, 28, ss. 32-33

[6] Aho, A.; Kumar, N.; Lashkul, A. V.; Eränen, K.; Ziolek, M.; Decyk, P.; Salmi, T.; Holmbom, B.; Hupa, M.; Murzin, D. Yu. Fuel (2010), 89(8)

Country Update — Germany

KIT – Karlsruhe Institute of Technology, Karlsruhe is developing the bioliq® process which comprises fast pyrolysis of straw in a twin screw reactor, slurry preparation by mixing bio-oil with char, slurry gasification to syngas in a pressurized entrained flow gasifier, and direct synthesis of DME (Dimethylether). The pyrolysis unit was operated this year in two campaigns. The heat carrier circle has been operated for 1000 hours and is dominated by the staff.

Problems are encountered with the circulation of the tar as quenching medium. Obviously this is not a principle problem but a consequence of lacking operating experience. The formation of larger agglomerates led to blockage of spray nozzles. This problem will be solved by installing a deagglomarator.

For the preparation of the biosyncrude there is a new partner: MAT Mischanlagentechnik GmbH, Immenstadt. This company owns an intelligent process for the colloidal decomposition of particles, well suited for an energy efficient application of the pyrolysis char.

CHOREN Industries GmbH, Freiberg. CHOREN is under controlled insolvency. With “CHOREN Components GmbH“, the first company of the CHOREN Group could be successfully transferred to an investor. For the other two insolvent companies of the group, CHOREN Industries GmbH (CI) and CHOREN Fuel Freiberg GmbH & Co. KG (CFF), there is progress in terms of finding new investors as well. Meanwhile, the insolvency proceedings for all three companies of the CHOREN Group was opened on September 30, 2011.

Fraunhofer UMSICHT, Oberhausen develops applied and custom-made process engineering technologies. Within their biorefinery activities "Fraunhofer UMSICHT” is currently establishing a technical centre for biomass including a pilot plant for ablative fast pyrolysis.

vTI-HTB – Institute of Wood Technology and Wood Biology, Hamburg has been involved in two German biorefinery projects (1) Lignocellulose Biorefinery, (2) Biorefinery 2021. In both projects vTI is dealing with pyrolysis of lignin for the production of monomeric phenols. A Py-GC/MS screening unit has been developed for testing lignins and catalysts.

Other German news

See the following pages for further updates from Germany

Article title	Contributor	Pages
Lignin pyrolysis for phenols: An integral component of two biorefinery projects in Germany	**Dietrich Meier** Johann Heinrich von Thünen-Institute (vTI)	27-28
Heterogeneously catalysed deoxygenation of pyrolysis oil in hot compressed water to produce fuel components	**Udo Armbruster** Leibniz Institute for Catalysis at University of Rostock	36-37

Country Update — UK

Research activities in fast pyrolysis	
Aston University Bioenergy Research Group (BERG)	• Fast pyrolysis of biomass and waste in continuous fluid bed and ablative reaction systems for bio-oil • Analytical pyrolysis • Catalytic and chemical upgrading • Nitrogenolysis • System studies • Techno-economic analysis
University of Leeds	• Fast pyrolysis in fluid beds • Analytical pyrolysis
University of Nottingham	• In bed upgrading of fast pyrolysis oils with metals
University of Southampton	• Development of computational models of fast pyrolysis reactors and liquid collection for process design, optimization and scale-up
University of York	• Utilisation of biomass through microwave pyrolysis to produce energy products including bio-oils and biochars
Demonstration activities in fast pyrolysis	
Centre for Process Innovation	• Demonstration scale processing of biomass derived products for energy and chemicals • Scale up • Commercial assessment of new opportunities
Biomass Engineering Ltd	• Fast pyrolysis plant (FPP) rated at 250 kg/hour feedstock input • Designed to convert sawdust from clean wood into pyrolysis oil • Purpose built reactor that utilizes fluidized bed technology • The FPP is expected to be installed, commissioned and producing pyrolysis oil by the end of 2011/early 2012
Commercial applications in fast pyrolysis	
2G BioPOWER Ltd	• Advanced biofuels from municipal and commercial waste • Focus is on the use of pyrolysis and upgrading based on Envergent RTP™ (Rapid Thermal Processing) pyrolysis technology and upgrading via hydroconversion from UOP • Projects are currently under development in the South East and North East of England
Conversion and Resource Evaluation (CARE) Ltd	• Design and construction of fast pyrolysis plants for biomass and wastes at 0.5, 5 and 250 kg/h for the production of liquids for subsequent upgrading to a blendate for liquid transport fuels • Techno-economic assessment of the production of the blendate from a 100,000 t/y input integrated biomass fast pyrolysis process • Design and specification of fast pyrolysis liquids collection system for a commercial fast pyrolysis system

Country Update — USA

PNNL (Pacific Northwest National Laboratory)
Upgrading by hydroprocessing remains a key component of the research into effects of operating parameters and catalyst composition on fouling of the catalyst bed (a recent presentation by Zacher et al and a poster by Elliott et al at *tcbiomass 2011*). The three new projects at PNNL, fixed catalyst bed processing with UOP and Albemarle, the Grace-led effort to develop a new catalytic reactor system, and the Battelle-led team to develop catalytic pyrolysis have all been delayed in start-up due to contractual issues. The three-year projects are now underway and have the goal to allow extended operation (>1000 hr) of hydrotreating of fast pyrolysis bio-oil.

PNNL will begin the planned revision to the 2009 Pyrolysis and Upgrading Design Report with the updated design case slated for completion in 2013. The revision will draw upon several sources, including such DOE funded work as 1) the stabilization of bio-oil solicitation, 2) the NABC which has research into fundamental pyrolysis, catalytic-pyrolysis and hydro-pyrolysis, 3) the upgrading solicitation projects which focus on improving the conversion of raw pyrolysis oil to hydrocarbon fuel, 4) the pyrolysis Integrated Bio-refinery demonstration, as well as international collaboration projects, and industry and university research.

NREL (National Renewable Energy Laboratory)
NREL continues its efforts in catalytic fast pyrolysis and mild hydrotreating. Catalytic fast pyrolysis studies in both micro scale and bench scale have confirmed the possibility of producing oil consisting of mainly hydrocarbons. Hydrotreating studies compared the activities of traditional petroleum NiMo catalyst and precious metal catalyst in producing refinery intermediates with low-oxygen and low acid contents, good volatility and miscibility in hydrocarbons. The research results were presented at the recent *tcbiomass* conference in Chicago.

Iowa State University
Iowa State University is exploring ways to maximize the production of monomers from both carbohydrate and lignin from the pyrolysis of biomass. Ideally, cellulose will be depolymerized to levoglucosan or other monosaccharides while lignin will be depolymerized to phenolic monomers. Thermal depolymerization of cellulose has been encouraged through passivation of alkali and alkaline earth metals, which otherwise catalyze homolytic fission of pyranose rings.

Thermal depolymerization of lignin appears to occur readily during pyrolysis, but the resulting monomers rapidly reoligomerize in secondary reactions to produce less desirable polyaromatics of three to four rings, which appears to be acid catalyzed. This work was reported at the recent *tcbiomass* conference in Chicago.

Washington State University/ Pullman
The biomass thermochemical conversion group includes seven PhD students covering a wide range of research topics from fundamental studies of cellulose and lignin thermochemical reactions to the development of new strategies to fully utilize bio-oil. This group is evaluating the potential of intermediate pyrolysis reactors for the balanced production of bio-oil and bio-char. The yields and composition of bio-oils obtained in an Auger reactor

Continued on page 48

Country Update — USA ...continued

operating with small particles have been thoroughly investigated. The effect of biomass pretreatment and the use of an additive to enhance the production of precursors of transportation fuels, and to reduce grinding energy have also been studied. This group is also evaluating new strategies to refine pyrolysis oils that combine biological and thermochemical conversion steps.

Washington State University/ Tri-Cities

Washington State University's Center for Bioenergy and Bioproducts operates microwave assisted reactors in both torrefaction and pyrolysis modes. The microwave pyrolysis offers a fast and efficient way of generating pyrolysis vapors to evaluate the upgrading performance of the catalysts developed at PNNL compared to commercial catalysts.

Novel microwave pyrolysis and fixed-bed catalysis schemes are also being studied using various biomasses for the production of phenols, aromatics, and deoxygenated hydrocarbon oils.

Event — USA

The 5th annual **International Biomass Conference & Expo** will take place April 16-19, 2012, at the Colorado Convention Center in Denver, Colorado. This dynamic event unites industry professionals from all sectors of the world's interconnected biomass utilization industries—biobased power, thermal energy, fuels and chemicals.

International Biomass Conference & Expo is where future and existing producers of biobased power, fuels and thermal energy products go to network with waste generators and other industry suppliers and technology providers. It's where project developers converse with utility executives; where researchers and technology developers rub elbows with venture capitalists; and where Fortune 500 executives and influential policy makers sit side-by-side with American farmers and foresters.

2012 International Biomass Conference & Expo program will include 30-plus panels and more than 100 speakers, including 90 technical presentations on topics ranging from anaerobic digestion and gasification to pyrolysis and combined heat and power, all within the structured framework of six customized tracks:

- **Track 1:** Crop Residues
- **Track 2:** Dedicated Energy Crops
- **Track 3:** Forest and Wood Processing Residues
- **Track 4:** Livestock and Poultry Wastes
- **Track 5:** MSW, Urban Wastes and Landfill Gas
- **Track 6:** Food Processing Residues

Visit www.biomassconference.com/ema for further information

See Worldwide Events section on pages 49 and 50 for details of other forthcoming conferences and exhibitions around the globe

Worldwide Events

JANUARY 2012

16th-18th
Pacific West Biomass Conference & Trade Show
San Francisco, California, USA

23rd-24th
9th International Conference on Biofuels "Fuels of the Future 2012"
Berlin, Germany

25th-26th
2nd Annual Global Biofuels Summit
Barcelona, Spain

FEBRUARY 2012

2nd-5th
Bioenergy Expo 2012
Verona, Italy

7th
Carbon Capture and Storage: demonstration programmes and the 2050 roadmap
London, UK

21st-25th
BiogasWorld
Berlin, Germany

22nd-23rd
Energy from Waste
London, UK

22nd-24th
National Ethanol Conference
Orlando, Florida, USA

23rd-24th
3rd Biomass Trade & Power
Brussels, Belgium

28th-29th
Bioenergy Expo 2012
Atlanta, Georgia, USA

28th February-1st March
Bio4Bio 'Advanced Biofuels in a Biorefinery Approach'
Copenhagen, Denmark

29th February-2nd March
World Sustainable Energy Days 2012
Wels, Austria

29th February-1st March 2012
European Pellet Conference 2012
Wels, Austria

MARCH 2012

13th-15th
World Biofuels Markets 2012
Rotterdam, the Netherlands

20th-22nd
Green Polymer Chemistry
Cologne, Germany

25th-29th
BIONATURE 2012
St Maarten, the Netherlands Antilles

28th-30th
8th South-East European Congress & Exhibition on Energy Efficiency & Renewable Energy
Sofia, Bulgaria

29th-31st
CEP 12 Clean Energy & Passivehouse
Stuttgart, Germany

APRIL 2012

2nd-5th
Bioenergy Russia Moscow 2012
Moscow, Russia

11th-12th
European Biomass to Power
London, UK

16th-18th
Technoport RERC (Renewable Energy Research Conference 2012)
Trondheim, Norway

16th-19th
International Biomass Conference & Expo
Denver, Colorado, USA

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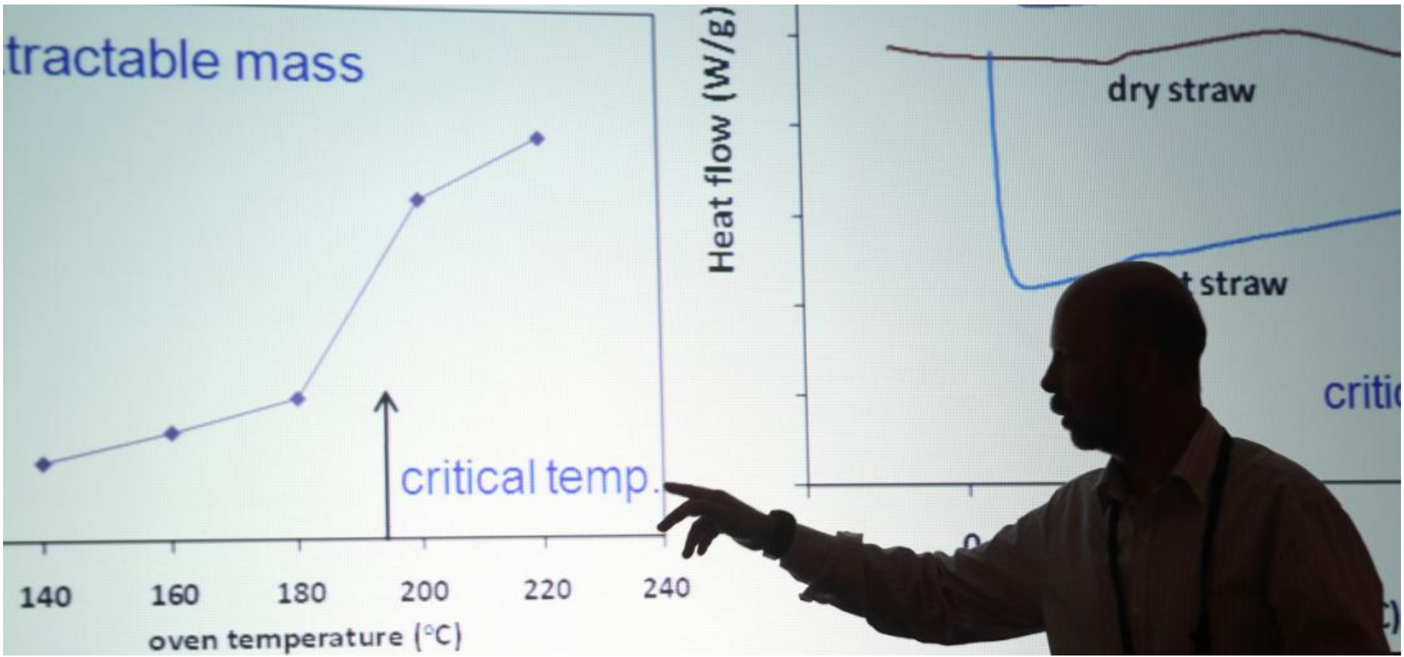


Worldwide Events...continued

APRIL 2012...continued

24th-25th
3rd International Conference on Biomass and Waste Combustion
London, UK

25th-26th
European Algae Biomass
London, UK

25th-28th
2nd World Congress of Bioenergy - 2012 (WCBE - 2012)
Xi'an, China

29th April-2nd May
World Congress on Industrial Biotechnology & Bioprocessing
Orlando, Florida, USA

MAY 2012

8th-10th
IEA Bioenergy ExCo 69
Istanbul, Turkey

17th-19th
Renexpo Central Europe
Budapest, Hungary

21st-25th
19th International Symposium on Analytical and Applied Pyrolysis
Linz, Austria

29th-31st
World Bioenergy 2012
Jönköping, Sweden

JUNE 2012

4th-7th
International Fuel Ethanol Workshop & Expo
Minneapolis, Minnesota, USA

13th-14th
European Biodiesel 2012
Krakow, Poland

13th-15th
International Bioenergy Conference & Exhibition 2012
British Columbia, Canada

18th-22nd
20th European Biomass Conference and Exhibition
Milan, Italy

25th-27th
3rd AEBIOM Bioenergy Conference 2012
Brussels, Belgium

JULY 2012

1st-6th
15th International Congress on Catalysis
Munich, Germany

AUGUST 2012

27th-30th
The EWLP 2012—12th European Workshop on Lignocellulosics and Pulp
Espoo, Finland

SEPTEMBER 2012

24th-26th
tcbiomass 2012— Symposium on Thermal and Catalytic Sciences for Biofuels and Biobased Products
North Carolina, USA

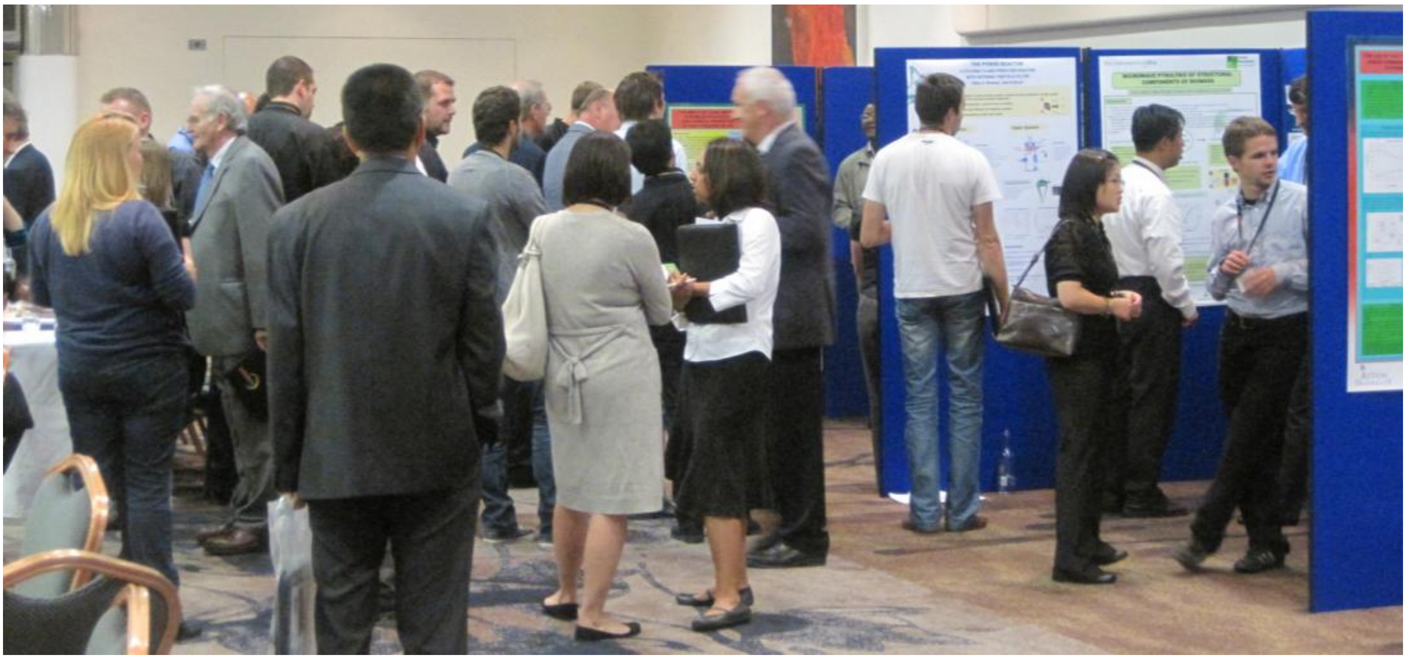
OCTOBER 2012

23rd-25th
4th Nordic Wood Biorefinery Conference
Helsinki, Finland

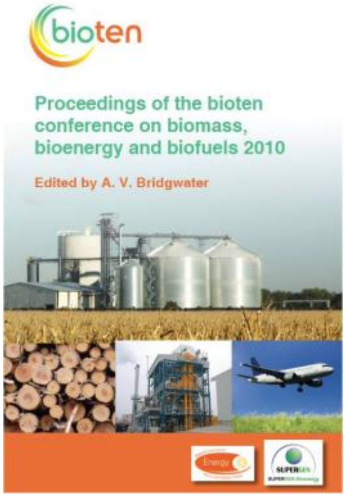
NOVEMBER 2012

12th-16th
IEA Bioenergy ExCo 70
Vienna, Austria

13th-16th
BioEnergy Decentral
Hanover, Germany



Publications



bioten

Proceedings of the bioten conference on biomass, bioenergy and biofuels 2010

Edited by A. V. Bridgwater

New books

Proceedings of the Bioten conference on biomass, bioenergy and biofuels 2010
Edited by A.V. Bridgwater
Published by CPL Press in October 2011

Contents include:
Biomass, Bioconversion and Systems
- Biomass
- Biological Conversion
- Systems

Thermal Conversion
- Pyrolysis
- Gasification
- Combustion

Energy & Environmental Science

PAPER

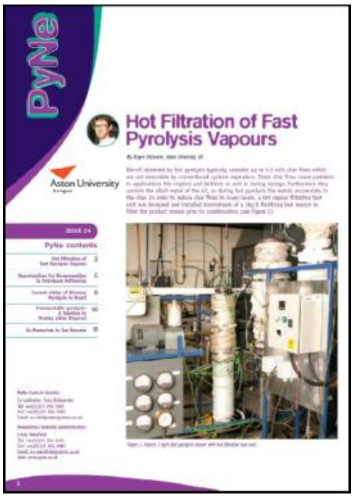
Revealing pyrolysis chemistry for biofuels production: Conversion of cellulose to furans and small oxygenates†

New papers

Revealing pyrolysis chemistry for biofuels production: Conversion of cellulose to furans and small oxygenates

Authors: Matthew S. Mettler, Samir H. Mushrif, Alex D. Paulsen, Ashay D. Javadekar, Dionisios G. Vlachos and Paul J. Dauenhauer
http://pubs.rsc.org/en/Content/ArticleLanding/2012/EE/C1EE02743C

Review of fast pyrolysis of biomass and product upgrading
Author: A.V. Bridgwater
http://www.sciencedirect.com/science/article/pii/S0961953411000638



PyNe

Hot Filtration of Fast Pyrolysis Vapours

Aston University

Past newsletters

Past editions of the PyNe newsletter can be found in the 'Newsletter & Publications' section of the PyNe website at www.pyne.co.uk

Further Information

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IEA Bioenergy

Task 34 Pyrolysis

PyNe
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