IEA Bioenergy

Task 34 - Pyrolysis

Welcome to Task 34

PyNe Issue 33

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By Doug Elliott, Task 34 Leader

The IEA Bioenergy Task 34 for Pyrolysis has started up its work in the new triennium, from 2013 to 2015. Current participants in the Task are Finland, Germany, Netherlands, Sweden and UK, with leadership provided by the USA. This newsletter is produced by the Task to stimulate the interaction of researchers with commercial entities in the field of biomass fast pyrolysis.

Task 34 National Team Leaders at task meeting held on 16-18 April 2013 at Karlsruhe Institute of Technology, Germany. See page 2 for their contact details.

Aims and 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.

The following are the Priority Topics identified for the triennium by the Task:

- Review of bio-oil applications;
- Bio-oil standardization;
- Round Robin for analytical method development;
- Technoeconomic assessment of thermochemical liquefaction technologies.

In this issue

There are several articles from the participants describing the latest developments in fast pyrolysis including from the Netherlands, the developments in hydrodeoxygenation of bio-oil and initial results from turbine testing

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Inside this issue

Welcome ..continued

with bio-oil; from Germany, the development of on-line measurements in fast pyrolysis and the Bioboost system; and from the USA we have contributions from Utah State, Washington and Maine Universities and from GTI describing their hydropyrolysis developments.

In this issue we have additional contributions from Austria on the Biocrack process; from Canada, a note describing fast pyrolysis of milkweed residues; and from the UK, an article about work at Aston University. There is also an updated calendar of events of interest to the biomass pyrolysis community.

In the past you may have seen the short introductory articles from the national team leaders from each of the participating countries summarizing the particular biomass pyrolysis efforts in their countries. These have been moved to direct links on our webpage - please use the tab for 'Developments' for Country Report Updates.

In addition, you may be interested to read the journal publication prepared by the task participants, "State-of-the-Art of Fast Pyrolysis in IEA Bioenergy Member Countries" by Dietrich Meier, Bert van de Beld, Tony Bridgwater, Doug Elliott, Anja Oasmaa, and Fernando Preto in Renewable and Sustainable Energy Reviews, 20, 619-641.

Similarly, in the past we have included an overview of the latest Task meeting with information on the developments within each of the Priority Topics. These summaries will now be found on the website by using the 'Task 34 Meetings' tab and linking to the relevant meeting's Summary Minutes. We hope you find the website (www.pyne.co.uk) useful.

Doug Elliott
Task 34 Leader

Members of IEA Bioenergy Task 34: 2013-2015

USA
Doug Elliott
Pacific Northwest National Laboratory (PNNL)
902 Battelle Boulevard
P.O. Box 999
Richland
Washington, 99352
USA
T: +1 509 375 2248
E: dougc.elliott@pnnl.gov

Doug Elliott

Task 34 Leader

Finland
Anja Oasmaa
VTT Technical Research Centre of Finland
Liquid Biofuels
Biologinkuja 3-5, P.O. Box 1000, Espoo, FIN02044
VTT, FINLAND
T: +358 20 722 5594 E: anja.oasmaa@vtt.fi

Germany
Dietrich Meier
Johann Heinrich von Thünen-Institut (vTI) Institute
of Wood Technology and Wood Biology (HTB)
Leuschnerstr. 91, D-21031 Hamburg, GERMANY
T: +49 40 73 962517 E: dietrich.meier@vti.bund.de

Netherlands
Bert van de Beld
BTG Biomass Technology Group BV
Josink Esweg 34, 7545 PN
NETHERLANDS
T: +31 53 486 1186   E: vandebeld@btgworld.com

UK
Tony Bridgwater
Aston University Bioenergy Research Group
School of Engineering and Applied Science,
Birmingham B4 7ET, UK
T: +44 121 204 3381 E: a.v.bridgwater@aston.ac.uk

Sweden - to be announced shortly

Pyrolysis activities at the University of Maine's Forest BioProduct Research Institute

William DeSisto provides an overview of the formate-assisted pyrolysis method developed at the University of Maine, USA

In the State of Maine, biomass is harvested in forests and used primarily by the pulp and paper industry. As a result, there are many opportunities to partner with harvesters and pulp and paper mills in biomass conversion technologies. One opportunity is to take advantage of existing harvesting operations and utilize forest thinnings and residues as a biomass source for pyrolysis to fuels and chemicals.

For pyrolysis technologies to be successful, both capital and operating costs must be kept low, due to the relatively small scale of operations forced by the high cost of biomass transportation. Another challenge with pyrolysis technology, particularly in relationship to fuel production, is the removal of the large amount of oxygen in the biomass.

At the University of Maine's Forest BioProduct Research Institute (FBRI), we are focused on developing new approaches to removing oxygen from biomass during the conversion process. Our particular focus is on developing processes that are robust and relatively simple, and on removing significant quantities of oxygen without using precious metal catalysts and elevated pressures.

In our research team, we have recently discovered a breakthrough in concentrating biomass into liquid form while removing significant quantities of oxygen using a fast pyrolysis method. In our method, formate-assisted pyrolysis (FAsP), we add an alkaline-earth salt of formic acid to the feedstock. The formate thermally decomposes along with the biomass during processing, creating reactive hydrogen and carbon monoxide which remove oxygen from the biomass. In addition, and perhaps even more important, is the increase in yields we observe relative to competing processes.

We believe this is due to the in-situ deoxyhydrogenation that stabilizes intermediate molecules which could either polymerize during pyrolysis or condense resulting in char formation. We have shown this for wood and for lignin, which is a notoriously recalcitrant byproduct of the pulping industry that is currently used as a fuel for process heat source.

> **'We have recently discovered a breakthrough in concentrating biomass into liquid form while removing significant quantities of oxygen using a fast pyrolysis method.'**

The new FAsP method has the potential to produce liquid hydrocarbons meeting target levels of less than 8% oxygen, higher heating values greater than 40 MJ/kg, and overall energy yield greater than 40% of theoretical in the oil product, while avoiding expensive/short-lifetime catalysts, hydrogen, and processing at excessive pressures. Because of its inherent robustness, FAsP is flexible regarding process scale and biomass specificity, both critical because biomass is less densely concentrated in nature than fossil fuels.

In the FAsP method, calcium formate is mixed with biomass (lignin and pine sawdust) and pyrolyzed in a bench-scale, fluidized bed, fast pyrolysis reactor with a solid feed rate of approximately 0.5 kg/hr. Typical pyrolysis conditions include temperatures of ~500ºC and residence times on the order of 1-5 seconds. Solid char product that contained calcium carbonate was separated using a hot gas filter. Liquid was collected in a condenser and electrostatic precipitator in series. The liquid oil from FAsP separated from a less-dense aqueous phase.

Mass ratios of calcium formate to lignin ranged from 0.7-1.4 for lignin. In the liquid oil product, the O/C ratio was reduced from 0.19 (fast pyrolysis without calcium formate) to 0.067 (with calcium formate), while the liquid product yield increased from 23 to 32.5 wt%. Products identified by Gas Chromatography Mass Spectrometry (GC-MS) include a significant quantity of alkylated phenols. Carbon 13 Nuclear Magnetic Resonance (^{13}C NMR)

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Pyrolysis activities at University of Maine *...continued*

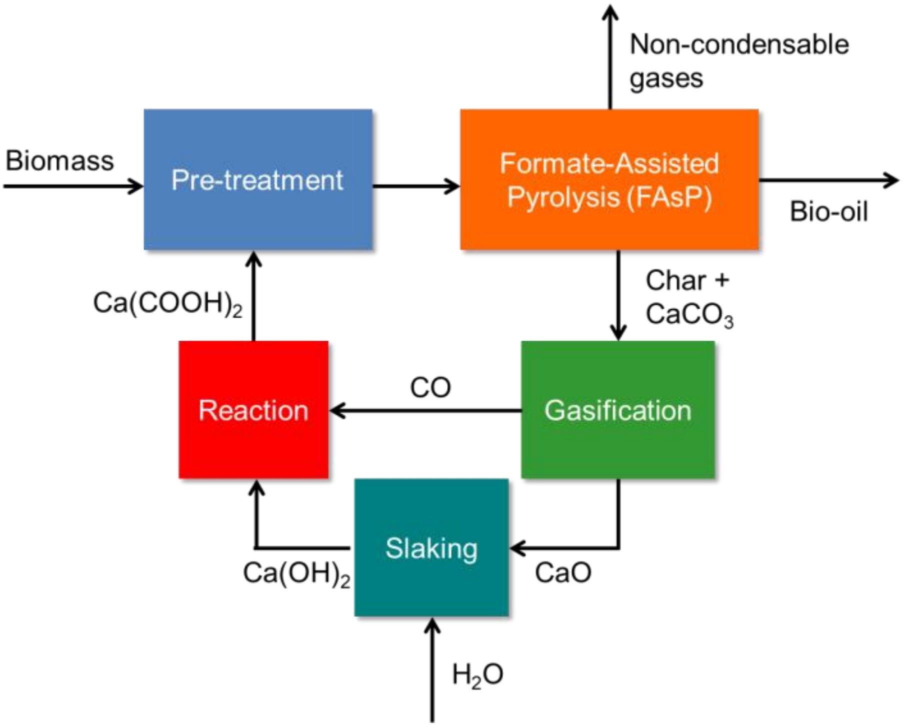

Figure 1: Conceptual flow diagram for production of calcium formate from pyrolysis residue. Char from FAsP can be gasified to produce carbon monoxide, which is then contacted with calcium hydroxide. Calcium hydroxide is regenerated by slaking calcium oxide, which is the resulting product of high temperature oxidation of calcium carbonate.

analysis indicated a significant reduction in methoxy/hydroxyl functionality, indicating that methoxy functionality from guaiacol-like compounds was reduced during pyrolysis.

Mass ratios of calcium formate to pine sawdust ranged from 0.11-1.4. In the liquid oil product, the O/C was reduced from 0.28 to 0.16 upon addition of calcium formate to the feed. The energy yield in the FAsP pine sawdust oil was 33.2%. GC-MS analysis indicated major peaks for cyclopentanones and alkylated phenols. ^{13}C NMR indicated a significant reduction in methoxy/hydroxyl groups, similar to lignin FAsP oil.

The key challenges to rapid commercialization of FAsP technology include optimizing liquid yields and compositions, verifying that minimal upgrading will be necessary for refinery insertion, and integrating formate salt production. We envision that formate salts (not formic acid) will be produced by using carbonylation of lime rather than by neutralizing formic acid which is commercially produced by hydrolysis of methyl formate.

Conceptual integration of the calcium recovery cycle with gasification of FAsP byproducts is shown in Figure 1, and material balances indicate that sufficient carbon exists to provide the required calcium formate, therefore, eliminating the need to purchase formic acid. Interestingly, the process could take advantage of processes such as lime kilns and slakers which are common to pulp mills and biorefineries.

Future directions of the work will include understanding fundamental reactions occurring during FAsP, as well as increasing the overall energy yield of the process.

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Contact
William DeSisto
Department of Chemical and Biological Engineering and Forest BioProduct Research Institute
University of Maine
Orono
ME 04469
USA

T: +1 207 5811561
E: WDeSisto@umche.maine.edu

www.umaine.edu

The BDI bioCRACK pilot plant at OMV refinery Schwechat

Peter Pucher of BDI summarises a joint venture with OMV in Austria

Figure 1: The integrated pilot plant at OMV refinery Schwechat.

BDI – BioEnergy International AG is a market and technology leader in the construction of customized biodiesel plants using multi-feedstock technology. In 2007, BDI started its research activities in the biomass-to-liquid area. The developed 'bioCRACK' technology produces mineral diesel with renewable shares that can be easily upgraded to EN590 quality with existing refinery units. This concept fulfils two fundamental tasks: Producing diesel to meet the growing demand, while simultaneously increasing the biogenic share. Pyrolysis oil and bio-char are additional valuable by-products of this unique conversion process.

OMV and BDI - BioEnergy International AG have been jointly involved in the innovative bioCRACK pilot plant project since 2009 (see Table 1). The bioCRACK pilot plant at the OMV refinery Schwechat is the first of its kind worldwide and converts solid biomass, such as wood chips and straw, directly into diesel fuel (see Figure 1). It is fully integrated into the existing plant and uses a refining by-product as heat carrier oil for underlying in the refinery liquid phase pyrolysis process.

Figure 2 shows the concept for refinery integration. The key-product - a raw fuel fraction - consists of cracked hydrocarbons and converted biomass. It contains a biogenic share in the range of 5 to 20% and can be upgraded with existing refinery utilities into diesel fuel according to the EN590 standard. An advantage of this process is that in the past heavy mineral oil was used mainly for the production of petrol, but now it can be used for the production of diesel, which is in strong demand, especially in Europe.

The uncracked heavy oil fraction will go its conventional way to a fluidized catalytic cracking unit to be converted to gasoline and lower hydrocarbons. This stream contains renewable carbon from the biomass and will hence contribute to a more sustainable carbon balance of the refinery. Currently, the side products pyrolysis oil and biochar have no established way in the refinery integration concept. In cooperation with external research partners, BDI is currently investigating a further upgrade of this sustainable energy carrier to increase the percentage of renewable carbon to be transferred to value added products.

Interested parties are welcome to test our pyrolysis oil - which is free of solids and poor in tars - in their upgrading facilities.

Acknowledgement
This project is funded by the Austrian Climate and Energy Fund as part of the 'New Energies 2020' research and technology programme. The author would like to thank project partner OMV Refining and Marketing GmbH for their support.

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The BDI bioCRACK pilot plant ...*continued*

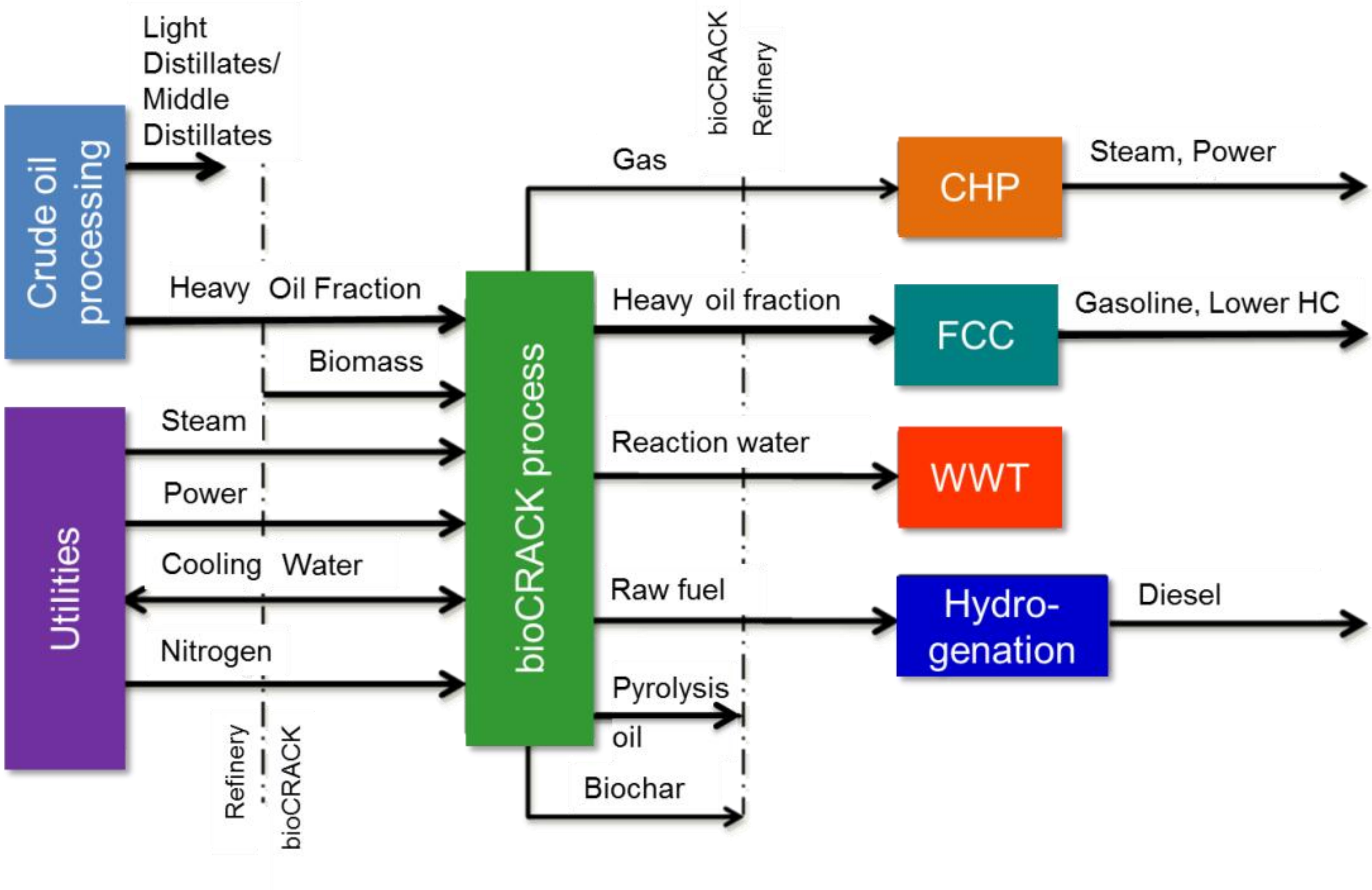

Figure 2: Process flow sheet of the bioCRACK refinery integration concept.

Table 1: Key facts and figures relating to the BDI bioCRACK pilot plant.

Project Owner	BDI - BioEnergy International AG
Project Name	bioCRACK
Location (City, Country)	Schwechat/Vienna
Technology	Thermochemical
Raw Material	Lignocellulosics
Input Capacity	2.4 t/d
Product(s)	Raw diesel, bio-oil, bio-char
Output Capacity in [t/a]	500 t/a raw diesel
Facility Type	Pilot
Investment	7 million EUR
Project Funding	2 million EUR
Status	Operational
Start-up Year	2012

Contact
Peter Pucher
BDI – Bioenergy International AG
Parkring 18
8072 Grambach/Graz
Austria

T: +43 316 4009 1513
E: peter.pucher@bdi-bioenergy.com

www.bdi-bioenergy.com

Products from fast pyrolysis of beetle-killed trees

Fernando Resende of the University of Washington, USA details the pyrolysis products identified at different stages of degradation of lodgepole pine

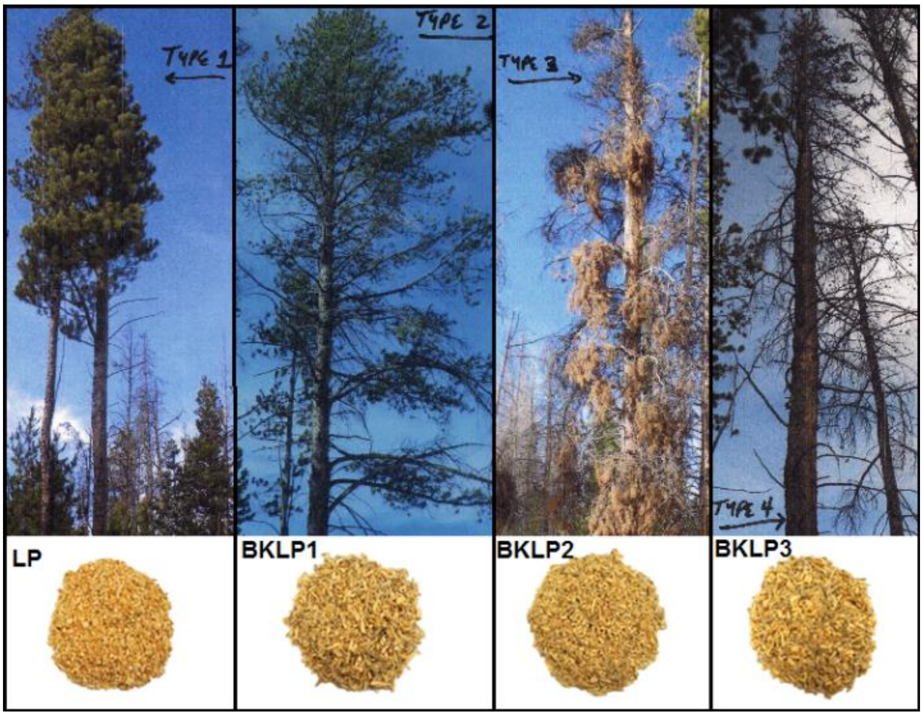

Figure 1: Four stages of degradation of lodgepole pine.

The mountain pine beetle (MPB, or *Dendroctonus ponderosa*) is one of the most damaging bark beetles attacking lodgepole pine (*Pinus contorta var. latifolia*). MPB inhabits areas in the north American continent that go from northern Mexico to north-western British Columbia in Canada, and from the Pacific Coast east to the Black Hills of South Dakota[1].

In recent years, drought, warmer winters and aging forest have led to a beetle epidemic with high levels of tree mortality, generating a fire hazard in forests within the USA and Canada. This epidemic has affected more than 4 million acres[2].

The most important characteristic of the trees attacked by the beetle are the loss of moisture over time. This is a concern to the solid-wood industry sector, because it causes cracking of wood (checking), adversely affecting product quality, especially below 30% moisture. Checking becomes an issue for beetle-affected wood within 2 years of death[3].

The conversion of beetle-killed trees into bio-oil via fast pyrolysis presents an opportunity to reduce the volume of accumulated dead trees, avoiding a wildfire hazard while simultaneously producing a high-value product in the bio-oil. The dry, affected wood is an excellent feedstock for fast pyrolysis, since drying costs are minimized or even eliminated. Fast pyrolysis also produces biochar, which can be economically used on-site as a solid amendment.

In addition, fast pyrolysis can essentially convert any form of biomass into bio-oil. The process is essentially feedstock agnostic and our working hypothesis is that the quality of the bio-oil product is not affected by the beetle attack to the wood.

We are evaluating the fast pyrolysis products of lodgepole pine at four stages of degradation, as identified in Figure 1:

- Green uninfected or minimally infected tree (LP);
- Partially green terminally infected tree (BKLP1);
- Standing dead with red needles and bark intact (BKLP2);
- Standing dead with loss of small branches, no needles and some bark loss, two to four years after death (BKLP3).

Figure 2 shows the chromatograms and top 20 pyrolysis products identified for the four stages of degradation. The main products are mequinol, 2-methoxy-p-creosol, 2-methoxy-vinyl-4-phenol, and 2-methoxy-4-(1-propenyl)-phenol. Clearly, the attack of the beetle does not affect the pyrolysis products, even for trees that have been dead for years.

An ablative bench-scale pyrolysis unit is currently being designed

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Products from fast pyrolysis of beetle-killed trees...*continued*

and will be constructed in our laboratory during the second half of 2013. Ablative units do not require grinding of wood particles to very small particle sizes, and are an excellent option for small scale reactors such as mobile units. The use of mobile pyrolysis units that can convert wood into bio-oil on-site is essential to make fast pyrolysis an economically viable option to dispose beetle-killed trees. Our approach will allow evaluation of the feasibility of mobile ablative pyrolysis units for the conversion of beetle-killed trees into bio-oil.

Support

This research is supported by the National Institute of Food and Agriculture (NIFA) of the US Department of Agriculture (USDA), under Award Number 2012-34638-2020.

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Contact

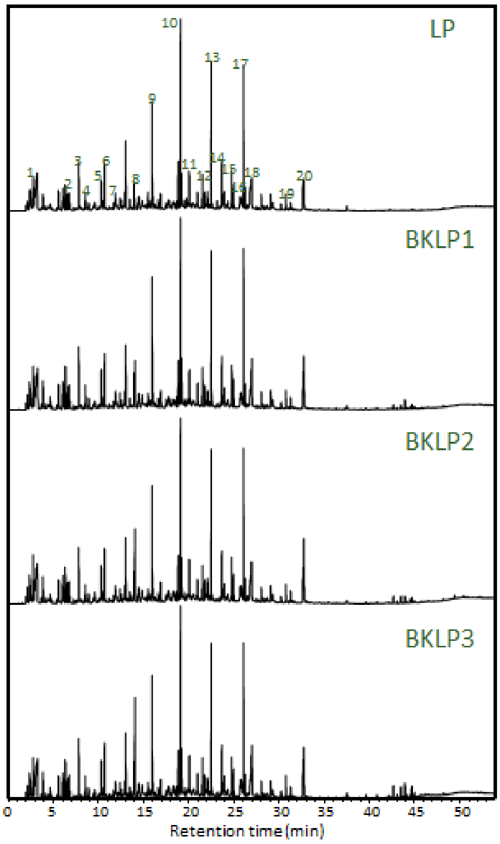
Fernando Resende
University of Washington
Box 352100, Seattle, WA 98195
USA

T: +1 206 221 1580
E: fresende@uw.edu

http://depts.washington.edu/sfrbbl/

BBL
Biofuels and Bioproducts Laboratory
University of Washington School of Environmental and Forest Sciences

UNIVERSITY of WASHINGTON



No.	Compound	Formula
1	Formic acid	CH_2O_2
2	2,3-dihydro-5-methyl-Furan	C_5H_8O
3	Furfural	$C_5H_4O_2$
4	2-Furanmethanol	$C_5H_6O_2$
5	2(5H) - Furanone	$C_4H_4O_2$
6	1,2-Cyclopentanedione	$C_5H_6O_2$
7	Phenol	C_6H_6O
8	β-Phellandrene	$C_{10}H_{16}$
9	Mequinol	$C_7H_8O_2$
10	2-methoxy-*p*-Creosol	$C_8H_{10}O_2$
11	5-Hydroxymethylfurfural	$C_6H_6O_3$
12	*p*-Ethylguaiacol	$C_9H_{12}O_2$
13	2-Methoxy-4-vinylphenol	$C_9H_{10}O_2$
14	Eugenol	$C_{10}H_{12}O_2$
15	Vanillin	$C_8H_8O_3$
16	1,6-anhydro-β-D-Glucopyranose	$C_6H_{10}O_5$
17	2-methoxy-4-(1-propenyl)- Phenol	$C_{10}H_{12}O_2$
18	1,6-Anhydro-β-D-talopyranose	$C_6H_{10}O_5$
19	2-Ethoxy-6-(methoxymethyl)phenol	$C_{10}H_{14}O_3$
20	γ-Hydroxyisoeugen	$C_{10}H_{12}O_3$

Figure 2: Fast pyrolysis products of affected lodgepole pine.

Direct production of gasoline and diesel from biomass using Integrated Hydropyrolysis and Hydroconversion (IH^2)

Terry Marker of the Gas Technology Institute (GTI) in USA provides an insight into a new process known as IH^2

> **‘IH^2 makes high quality hydrocarbon fuels from biomass economically and directly. Testing at the 50 kg/d scale has been very successful, so we expect to take the next step to demonstration scale soon.’**

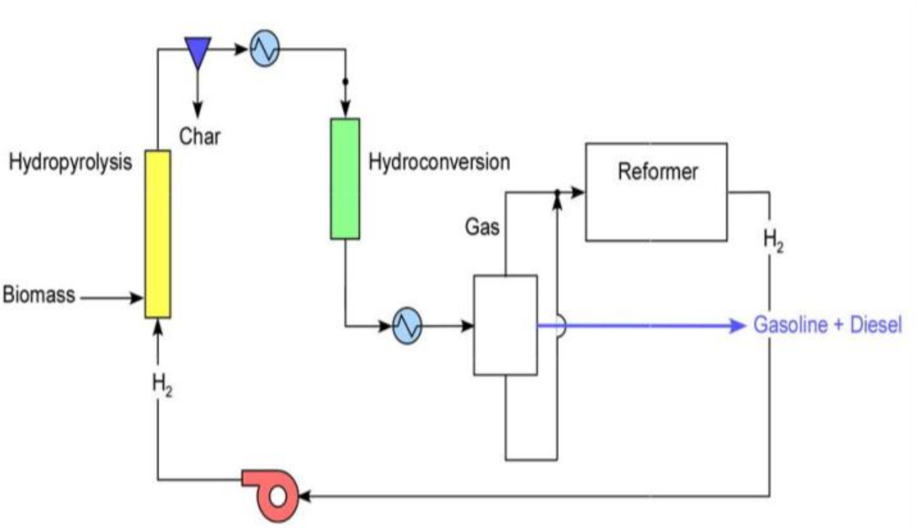


Figure 1: IH^2 system schematic, showing the overall process flow.

GTI is testing a new process called IH^2 to directly produce gasoline and diesel blending components from biomass. The IH^2 process used a first stage catalytic hydropyrolysis step integrated with a second stage hydroconversion step. This combination directly produces high quality hydrocarbon gasoline and diesel blending components. The hydrogen required for the IH^2 process is produced by reforming the C$_1$-C$_3$ products so no supplementary hydrogen is required. The IH^2 integrated process schematic is shown in Figure 1.

Initial economic analyses suggest that the IH^2 process has excellent economics and greenhouse gas reduction, and is an improvement compared to pyrolysis plus upgrading for producing transportation fuels from biomass.

The first stage catalytic hydropyrolysis step converts the biomass to hydrocarbons in a fluidized bed of catalyst under hydrogen pressure of 20 to 35 bar and temperatures of 370 to 475°C. Catalytic hydropyrolysis removes 80-90% of the biomass oxygen as water and CO$_X$, while minimizing undesirable acid-catalyzed polymerization, aromatization, and coking reactions which occur during standard fast pyrolysis. The second stage fixed bed hydroconversion reactorthen removes the remaining oxygen and converts the product to high quality hydrocarbon products.

Initial experiments had been conducted in a small scale mini bench unit (MBU) which feeds 1 lb/hr of biomass over a period of 3-6 hours. In 2012, IH^2 testing was moved to a 50 kg/day continuous IH^2 pilot plant. A schematic diagram of the IH^2 pilot plant is shown in Figure 2 and the actual pilot plant is shown in Figure 3.

The IH^2 50 kg/d continuous pilot plant produced similar yields and product quality to that found in the small scale testing.

Data from 750 hours of IH^2 pilot plant testing is shown in Figure 4.

The hydrocarbon liquid yields and

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Integrated Hydropyrolysis and Hydroconversion (IH^2)*...continued*

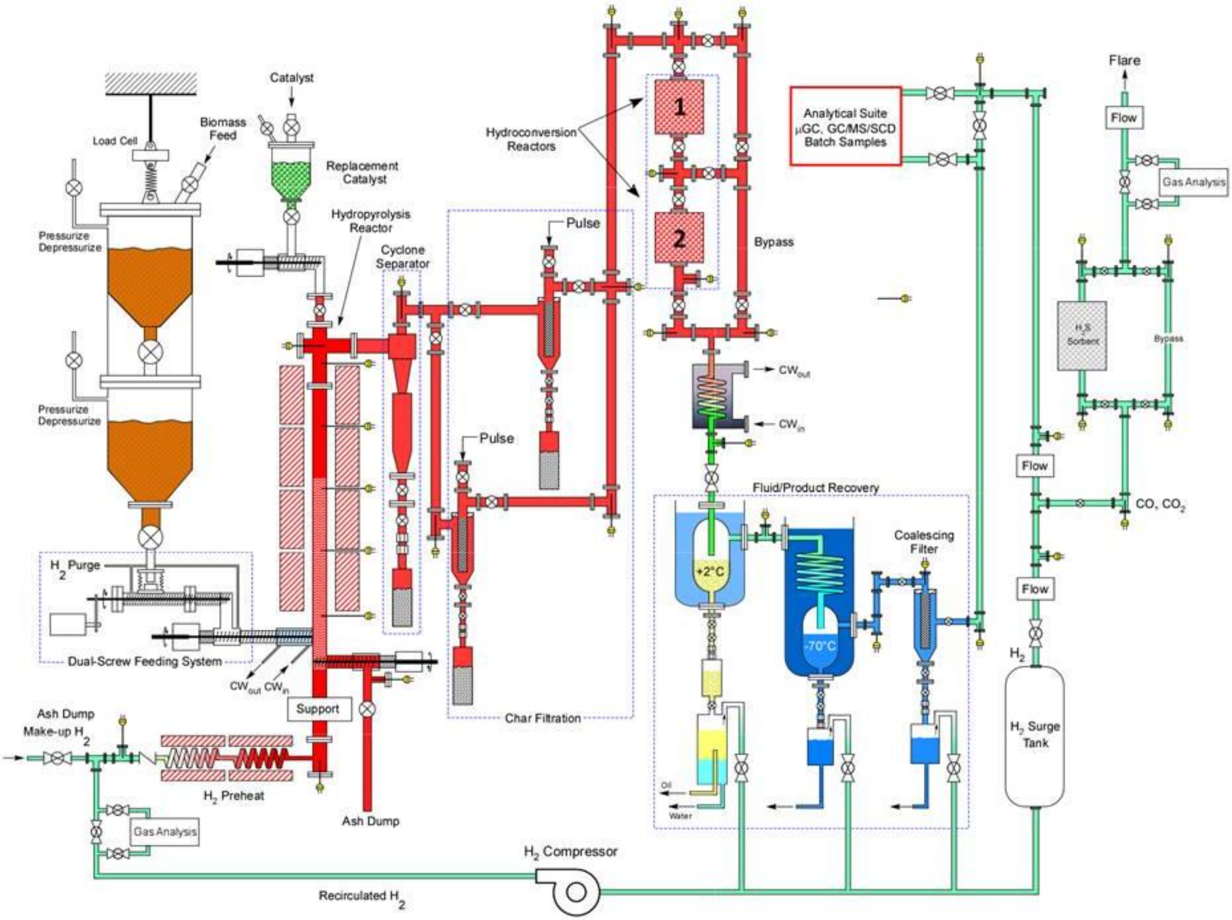

Figure 2: Schematic of GTI's 50 kg/day IH^2 pilot plant.

Figure 3: GTI's 50 kg/day IH^2 pilot plant.

Integrated Hydropyrolysis and Hydroconversion (IH^2)*...continued*

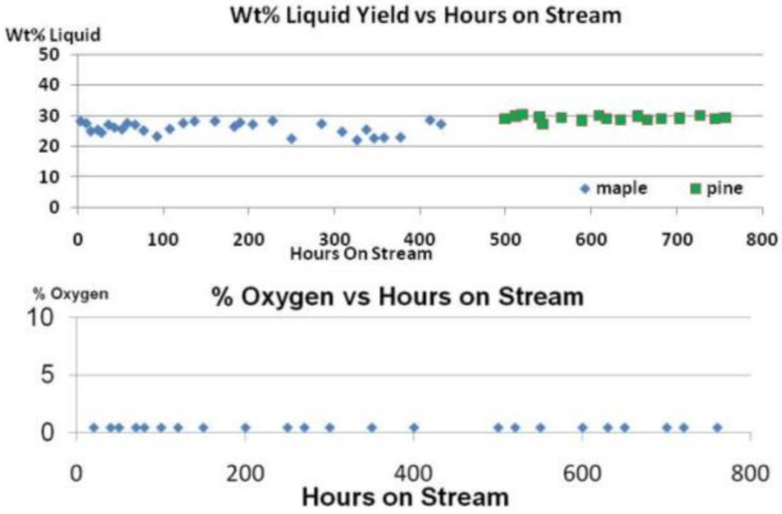

Figure 4: Continuous pilot plant yields and quality from GTI 50 kg/day pilot plant.


Gasoline-Range Hydrocarbons

Diesel/Jet-Range Hydrocarbons

Aqueous Product

Figure 5: IH^2 pilot plant product. Liquid products collected from continuous IH^2-50 testing with wood.

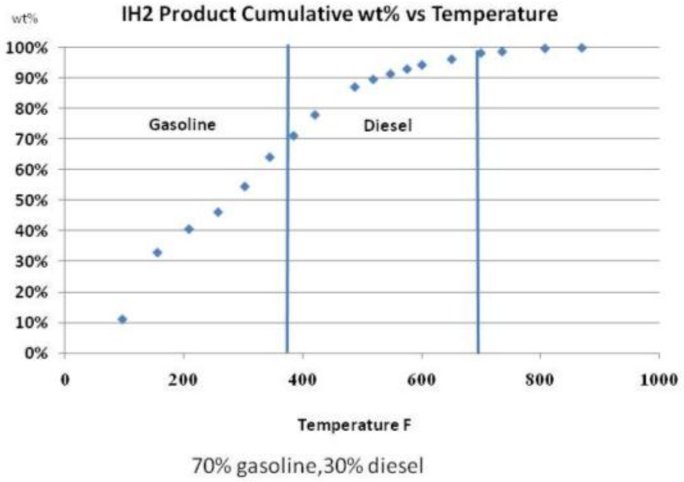

Figure 6: Boiling point distribution of the IH^2 product.

quality remained high and steady throughout the test. A picture of the products produced from the pilot plant is shown in Figure 5. Throughout the test the oxygen in the hydrocarbon product was less than 1% and the Total Acid Number (TAN) of the hydrocarbons was less than one.

The liquid hydrocarbon products from the pilot plant were in the gasoline and diesel range. As shown in Figure 6.

The IH^2 hydrocarbon product was fractionated into gasoline and diesel cuts. The gasoline cut is almost at "drop in" quality and has a high octane of 86. The diesel can be used as a blending component or further upgraded to improve its cetane number.

The IH^2 project was funded through DOE project DE-EE0002873 and DE-EE0004390. Other IH^2 DOE project partners include CRI Catalyst, Cargill, Johnson Timber, Aquaflow, Blue Marble Energy, NREL and MTU.

Contact

Terry Marker
Gas Technology Institute
1700 S Mount Prospect Road
Des Plaines Il 60018
USA

T: +1 847 544 3491
E: terry.marker@gastechnology.org

www.gastechnology.org

Application of pyrolysis oil in the OP16 gas turbine – feasibility study

An overview by Martin Beran (above) and Lars-Uno Axelsson (below) of OPRA Turbines in the Netherlands

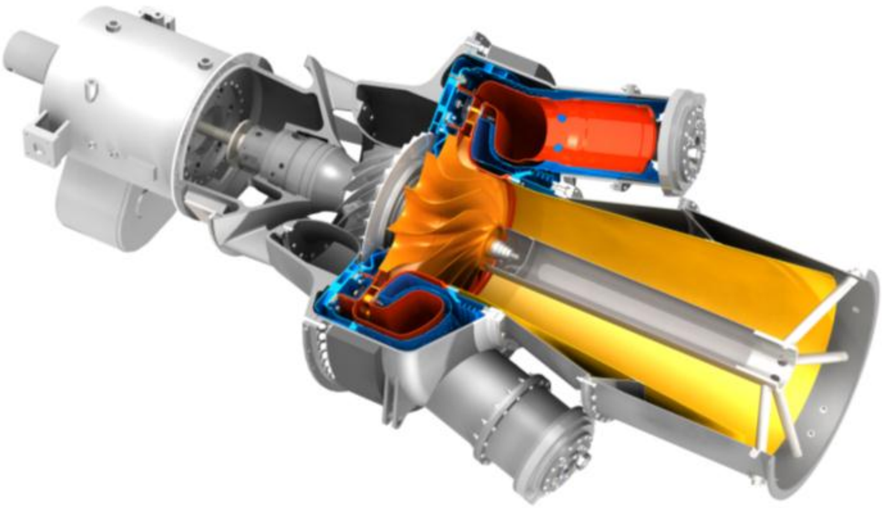

Figure 1: The OP16 gas turbine.

OPRA Turbines develops, manufactures, markets and maintains generator sets in the 2 MW power range using the OP16 series of gas turbines. The OP16 gas turbine, shown in Figure 1, is of an all-radial design, which provides robustness, reliability and highest efficiency in its class. A key feature of the OP16 gas turbine is the ability to utilize a wide range of fuels.

As part of OPRA's continuous effort to extend the fuel capability of the OP16, an R&D project was initiated focusing on utilizing pyrolysis oil. The overall aim of the R&D project was to develop a combustor suitable for efficient combustion of pyrolysis oil. The higher viscosity, lower energy density and limited chemical stability of the pyrolysis oil require different fuel handling compared to conventional liquid fuels. This article will present the initial phase of this R&D project - a feasibility study consisting of several test campaigns performed in OPRA's atmospheric combustor test rig. As a fuel for the experimental work pyrolysis oil from pine wood, provided by BTG Bioliquids BV, was used.

Test set-up

The properties of the pyrolysis oil used for the experimental investigation are provided in Table 1. The properties of diesel No. 2, which is a common liquid fuel for gas turbines, are included for reference. Due to the higher viscosity of the pyrolysis oil, a pintle airblast nozzle, designed by OPRA, was selected as the fuel injector.

The pintle airblast nozzle can handle liquid fuels with higher kinematic viscosity than a standard pressure nozzle. A major advantage of the pintle airblast nozzle is that it works with the pressure difference caused by the pressure loss across the combustor flame tube. This means that a pintle airblast nozzle does not need any external source of air or steam.

The OP16-3A gas turbine conventional combustor working in diffusion mode was used for the experiments. A benefit of this combustor is that the flame tube is very flexible for changes related to the effective flame tube area and the air split across the combustor.

(Continued on page 13)

Application of pyrolysis oil in the OP16 gas turbine...*continued*

Table 1: Comparison between pyrolysis oil and diesel No. 2.

Property	Pyrolysis oil	Diesel No. 2
Density at 15°C [kg/m3]	1150	840
Low Heating Value [MJ/kg]	18.7	42.7
Viscosity at 38°C [cSt]	17	1.9-4.1
Polymerization temperature [°C]	140	N/A
pH	2.5	4 to 7

Hence, with this flexibility the optimum condition for pyrolysis oil burning can be relatively easily defined with respect to the combustor loading. The combustor loading is an important parameter since it is closely related to the emission figures and combustion efficiency. The OP16-3A conventional combustor was adjusted in several steps to find the optimal configuration for pyrolysis oil burning.

Results from the tests

The first test was performed with the standard flame tube and without fuel pre-heating. The purpose of this test was to establish a baseline data set for further research. With the standard configuration it was found to be possible to keep a stable combustion process with a mixture of 25% pyrolysis oil and 75% ethanol. The residence time is related to the combustor volume. Due to the differences in fuel composition, especially the large amount of dilutants associated with the pyrolysis oil, the residence time for pyrolysis oil is longer than for fossil fuels. From the initial tests it became clear that the required combustor outlet temperature could not be reached.

The unburned fuel resulting from incomplete combustion formed sediment on the flame tube inner wall and in the exhaust duct. Based on the test results from this configuration, the combustor geometry was adjusted and an optimized geometry was found. To simulate the effect of a larger volume the effective area of the flame tube and the amount of air entering the combustor were decreased.

The pressure loss of the combustor is an important parameter governing the mixing process and the function of the airblast atomizer. Therefore, it was important to decrease the effective combustor area and air mass flow to maintain the same pressure loss as the original combustor. By decreasing the effective flame tube area and the inlet air mass flow, a significantly longer residence time was achieved. A significant improvement of the flame stability was achieved and no unburned fuel in the exhaust duct was observed. Due to the decrease of the combustor loading the full load condition was reached.

Figure 2: Flame tube interior.
Left: Original flame tube. The sediments on the walls are clearly visible.
Right: Optimized flame tube. Note the clean flame tube without any sediment.

Furthermore, it was found that with between 70% to 100% load, it is possible to burn 100% pyrolysis oil without the need of mixing it with ethanol. Based on this research, OPRA has been able to design a new combustor for burning pyrolysis oil and other low-calorific fuels. The new combustor is large enough to provide sufficient residence time for complete combustion of the pyrolysis oil.

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Contact

Martin Beran
E: m.beran@opra.nl

Lars-Uno Axelsson
E: l.axelsson@opra.nl

OPRA Turbines BV
Opaalstraat 60
7554 TS Hengelo
The Netherlands
T: +31 74 245 2121

www.opra.nl/en/

BioBoost – biomass based energy intermediates boosting bio-fuel production

A summary by Andreas Niebel of Karlsruhe Institute of Technology (KIT) in Germany

BioBoost is a European R&D project funded under contract 282873 within the Seventh Framework Programme by the European Commission.

Objectives

The overall objective of this project is to pave the way for de-central conversion of biomass to optimised, high energy density carriers, which can be utilised either in large scale applications for the synthesis of transportation fuel and chemicals or directly in small-scale combined heat and power (CHP) plants.

Concept

BioBoost studies the conversion technologies Fast Pyrolysis (FP), Catalytic Pyrolysis (CP) and Hydrothermal Carbonisation (HTC). Together, these technologies enable the flexible use of a wide range of biomass including wet, grassy and ash-rich feedstock, focusing on residues and waste as sources for bioenergy generation. These technologies offer various de-central conversion capabilities for the production of bio-oil, -char and -coal. FP and HTC plants in pilot size of 0.5-1 t/h are available within this project. Prior to the energetic use valuable chemicals like phenols or food flavourings from FP and CP, fertilisers and furfural from the HTC process are extracted as valuable side products.

The energy carrier may be transported to further use either “as produced” (oil, char, coal) or further processed to e.g. oil/char slurries or pellets and other suitable forms. BioBoost develops the best energy carrier regarding the mode of transportation, respective infrastructure, cargo handling, safety and economy. Among different sectors of application, all conversion products have been proven to be well suited for gasification and production of synthetic transportation fuels.

However, a respective central gasification facility has a high feedstock demand requiring a developed energy carrier market. Therefore, a market implementation plan is developed. In the ramping phase it proposes the use of energy carriers in available applications of the heat and power sector (CHP) or refineries. Later, a gasification plant would be phased into a developed bioenergy carrier market according to its economic and technical performance (Figure 1).

Overall strategy and work plan

The project comprising seven work packages addresses the complete value chains from feedstock potential, conversion processes, optimisation of transport and logistics to the exploitation of the energy carrier and its by-products. The techno/economic and environmental assessment integrates the complete supply chain (Figure 2).

During the first year the technical processes were defined and investigated. The feedstock potential has been determined, the procedures of the socio-economic and environmental assessment were defined and the logistics model was built up. First results are expected in the third quarter of 2013.

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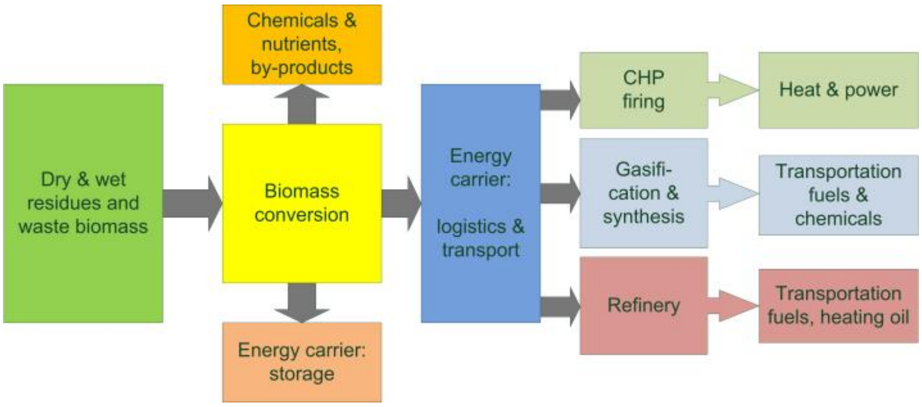
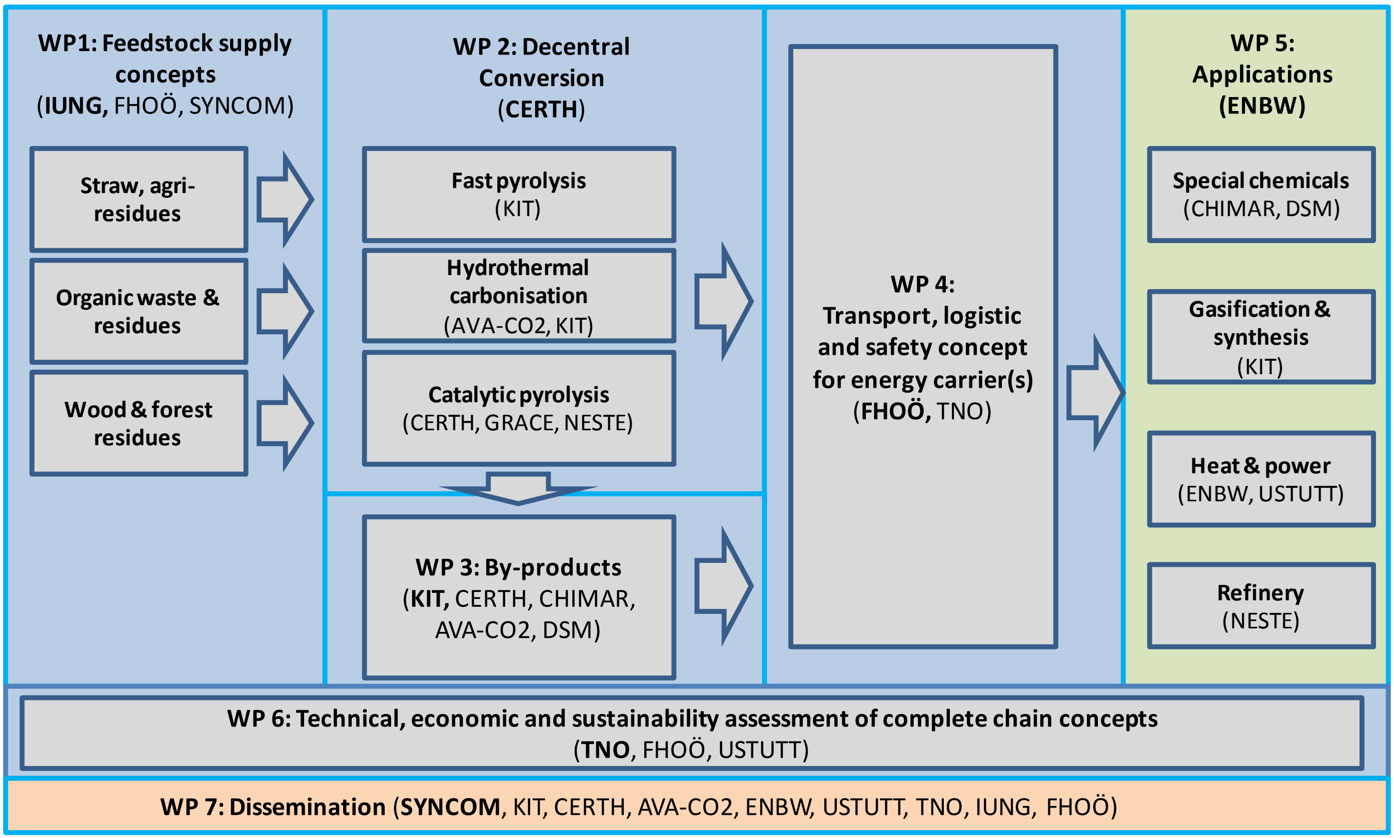


Figure 1: Overview of conversion routes to fuels and chemicals.

BioBoost – biomass based energy intermediates boosting bio-fuel production...*continued*


WP1: Feedstock supply concepts
(**IUNG,** FHOÖ, SYNCOM)

Straw, agri-residues

Organic waste & residues

Wood & forest residues

WP 2: Decentral Conversion
(**CERTH**)

Fast pyrolysis
(KIT)

Hydrothermal carbonisation
(AVA-CO2, KIT)

Catalytic pyrolysis
(CERTH, GRACE, NESTE)

WP 3: By-products
(**KIT,** CERTH, CHIMAR, AVA-CO2, DSM)

WP 4: Transport, logistic and safety concept for energy carrier(s)
(**FHOÖ,** TNO)

WP 5: Applications
(ENBW)

Special chemicals
(CHIMAR, DSM)

Gasification & synthesis
(KIT)

Heat & power
(ENBW, USTUTT)

Refinery
(NESTE)

WP 6: Technical, economic and sustainability assessment of complete chain concepts
(**TNO**, FHOÖ, USTUTT)

WP 7: Dissemination (**SYNCOM**, KIT, CERTH, AVA-CO2, ENBW, USTUTT, TNO, IUNG, FHOÖ)

Figure 2: Project structure including Work Packages (WP); parties involved (shown in brackets) and WP leaders (shown in brackets in bold).

Consortium

The BioBoost project consortium consists of 13 beneficiaries, plus one third-party contributor from six countries (Austria, Finland, Germany, Greece, the Netherlands and Poland):

1. Karlsruhe Institute of Technology (KIT);
2. Centre for Research and Technology Hellas (CERTH);
3. AVA-CO2-Forschung GmbH (AVA-CO2);
4. CHIMAR Hellas SA (CHIMAR);
5. EnBW Energie Baden-Württemberg AG (ENBW);
6. Nederlandse Organisatie voor Toegepast Natuurwetenschppelijk Onderzork (TNO);
7. GRACE GmbH & CO KG (GRACE);
8. Instytut Uprawy Nawozenia I Gleboznawstwa, Panstwowy Instytut Badawczy (IUNG);
9. FH OÖ Forschungs & Entwicklungs GmbH (FHOÖ);
10. Neste Oil Corporation (NESTE);
11. SYNCOM Forschungs- und Entwicklungsberatung GmbH (SYNCOM);
12. DSM Chemical Technology R&D BV (DSM);
13. University of Stuttgart (USTUTT).

Project facts	
Start	01/2012
Duration	42 months
Total budget	7.3 million EUR
Funding	5.1 million EUR
Website	www.bioboost.eu/

Contact

Andreas Niebel
Karlsruhe Institute of Technology (KIT)
Institute of Catalysis Research and Technology (IKFT)
Hermann-von-Helmholtz-Platz 1
76344 Eggenstein-Leopoldshafen
Germany

T: +49 721 60 82 36 31
E: andreas.niebel@kit.edu

www.ikft.kit.edu/

BioBoost

KIT
Karlsruhe Institute of Technology

Milkweed pyrolysis

An overview by Jan Piskorz (top) and Piotr Majerski (middle) of Resource Transforms International and Hooshang Pakdel (bottom) of Pyrovac Inc. in Canada

Figure 1: Monarch butterfly on milkweed.

In the past, extraction of phytochemicals by pyrolysis was investigated at the authors' laboratories (see references 1,2,3 and 4 for further details). Compounds of interest were plant-derived bio-molecules like cannabinoids, taxanes, nicotine, caffeine, limonene, betulin, fatty acids and resin acids, steroids and sugars.

One of the "medicinal" plants, popular in the folklore/tradition of indigenous groups of North America Indians (Mohawks, Cherokee) is a milkweed. The natives reportedly, used milkweed as a source of food (flower buds, young shoots and seed pods), fibre and medicine (anti-fertility concoction, warts/ulcer remedy). *Asclepia Syriaca*, a common milkweed, is a North American native, abundant and perennial plant.

It is named for its milky juice and is known to contain alkaloids, latex and several cardenolides (toxins). It grows to a height of approximately 1 metre.

Milkweed leaves are the sole food source of Monarch butterfly larvae. This common wild plant is often grown in gardens by butterfly lovers. The migration of millions of Monarchs (see Figure 1) from Canada to Mexico is a celebrated naturalist event in September every year. Full grown stems of milkweed (see Figure 2) decorate borderlands of creeks, farmers' fields, pastures, woodlots and roadsides.

Every autumn, the stems contribute to soil humus content by lignin degradation and to atmospheric carbon dioxide by holocellulose oxidation. Milkweed white fibrous filaments from seed follicles have good insulation qualities. In the past, these filaments were contemplated commercially as a hypoallergenic filling for pillows as well as a substitute for kapok fibre.

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Milkweed pyrolysis

...continued

Results

Feed

Milkweed stems with partially empty seed pods were collected from the Waterloo countryside in autumn 2012. Plants were dried and ground to pass through a 1.00 mm sieve.

The moisture and the ash were determined as follows:

- Moisture - 4.4 wt%, as used;
- Mineral ash - 3.7 wt%, on dry basis.

The ash (grey solids) in water exhibited some solubility/alkalinity - pH ~10.

Pyrolysis

The bench scale, fluid bed continuous fast pyrolysis test was carried out (similar to the one developed for hydrous fast pyrolysis - see Pyne 27, pp. 24-26).

The pyrolysis recovery train consisted of two ice-water condensers, one electrostatic precipitator and one drierite-dessicant column. This set up allowed for carrying out a complete material balance.

Under the pyrolysis condition used, two condensates were collected:

1. Aqueous fraction containing most of the stopped/condensed water-soluble-organics. This fraction was analyzed quantitatively by HPLC, K-F, Brix.
2. Oil fraction (water dissolved in organic phase). This fraction was removed with the addition of methanol and evaluated by K-F and GC-MS.

Characterization

Aqueous fraction (24.6 g, Brix=12)

Water - 86.7 wt%
Hydroxyacetaldehyde - 2.5 wt%
Acetic acid - 3.1 wt%
Acetol - 2.0 wt%
Glyoxal, levoglucosan, formaldehyde, formic acid and furfural were each also identified in concentrations below 1.0 wt%.

Oil fraction

Oligomeric lignin as water insoluble fraction extracted and contributed to 26.29% by weight of maf feed basis.

Table 1: Selected conditions/parameters of pyrolysis.

Temperature (°C)	480
Duration, min	45
Milkweed feed rate, g/hr	54
Steam feed rate, g/min	0.5
Nitrogen, l/min (room tp)	8.5
Apparent vapour residence time, s	~1

Table 2: Material balance, in wt% on dry ash free basis.

CHAR/solids	18.50
WATER (pyrolysis water only)	23.27
ORGANICS (condensed/captured)	39.90
GAS – includes experimental losses (by difference)*	18.22
Total above	100

*Mostly carbon dioxide and carbon monoxide.

The following volatile degradation products and natural waxy and phyto-chemicals were identified in the oil phase:

Degradation products

- 2-methoxy-4-(1-propenyl) phenol
- 2, 6-dimethoxyphenol
- 4-ethyl-2-methoxyphenol
- 2-methoxyphenol
- 4-methylphenol
- 1, 4-methoxyphenylethanone
- 1, 2-Benzenediol
- 2, 6 dimethyl-3-(methoxymethyl)-p-benzoquinone
- Levoglucosan
- Acetol
- Furfural

Waxy products

- Methyl-9,12-Octadecadienoate
- 9-Octadecenoic acid
- Methyl-7,10-Octadecadienoate
- 3-(2-pentenyl)-1,2,4-cyclopentane trion,
- 9-Octadecanoic acid
- Hexadecanoic acid
- Hexatriacontane
- 3-butenylpentylether
- 1-Hexadecene

Phyto-chemicals

- Phytosteroids
- Alkaloids
- Tri-terpenes
- Pentacyclic tri-terpenes

The following chemicals with physiological importance for plants, and of potential importance for animals including humans (anti-cancer, anti-tumour properties) were identified. The assignment was based on the GC-MS library match only.

- D:A-Friedo-oleana-3,7-diene
- 5-Acetylpyrimidone
- Caffeine
- 1,1-dicyano-2-Me-3-phenylpropene
- Ergosta-4,6,22-trien-3b-ol
- 2,6-dimethyl-3-(methoxymethyl)-para-benzoquinone
- Taraxasterol
- 6a-hydroxy-14-methyl-5a-cholest-8-en-3-one

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Milkweed pyrolysis
...continued

Figure 2: Milkweed stems.

Conclusion

Dried, ground milkweed stems upon fast pyrolysis yield more fractions of char and water with lower oil yield than a typical wood pyrolysis. The minerals forming very alkaline ash, 3.7wt%, mf could be the reason for augmented dehydration/carbonization.

Milkweed stems seem to be a good starting material to consider in bio-char processing towards potential soil enhancers. Biochars production could be contemplated with expected output rich in minerals and humus-like oligomeric lignin.

By pyrolysis, a variety of phyto-chemicals were produced. The biological importance of these requires additional, in-depth knowledge.

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Contact

Jan Piskorz and Piotr Majerski
Resource Transforms International
Waterloo, Ontario
110 Baffin Pl. Unit 5
N2V – 1Z7
Canada

E: jpiskorz@rtiltd.com

Hooshang Pakdel
Pyrovac Inc
176-2, Damase-Breton Street
Saint-Lambert-de-Lauzon
Quebec
G0S – 2W0
Canada

E: hpakdel@sympatico.ca

Together the authors of this article have contributed to more than 200 publications, patents and reviews in the area of pyrolysis.

Fractional catalytic pyrolysis of biomass research at Utah State University

Foster Agblevor reviews research activities at Utah State University, USA focusing on fractional catalytic pyrolysis

Figure 1: Pyrolysis reactor at Utah State University.

Biomass pyrolysis is a complex thermal process that converts biomass into undefined slate of liquid products, gases, and solids. The liquid product (bio-oils) has been of considerable interest because of its potential as a feedstock for production of liquid transportation fuels. The biochar is also attracting attention because of its potential for soil amendment applications.

The gases for most part have been considered for combustion to fuel the pyrolysis process. Because the bio-oils are unstable, acidic and considerably difficult to process into liquid transportation fuels, a number of upgrading methods have been investigated for stabilizing the oils. These include esterification, post pyrolysis catalytic upgrading, liquid-liquid extraction and gasification. An alternative approach to addressing the bio-oil stability problem is the *in situ* and *ex situ* catalytic pyrolysis with the sole aim of producing stable pyrolysis oils that can be easily upgraded to liquid transportation fuels.

At Utah State University, we are continuing with catalytic pyrolysis research that was started at the Virginia Polytechnic Institute and State University, Blacksburg Virginia, USA. This approach, which is called *fractional catalytic pyrolysis* produces a narrow slate of compounds instead of the large number of compounds produced in the conventional pyrolysis. The catalysts are selected for specific target products. Thus, catalysts are developed to target the hemicellulose component of the biomass, the cellulose component, or the lignin component.

The undesired biopolymer is selectively gasified into non-condensable gases and the desired component is converted into liquids. This approach can generate high-value chemicals derived from lignin, cellulose, or hemicellulose. During fractional catalytic pyrolysis, which is normally carried out in a fluidized bed reactor, the catalyst serves as both heat transfer medium and catalyst and reduces the formation excessive coke compared to post-pyrolysis catalysis or *ex situ* catalysis.

However, this method normally produces large amounts of non-condensable gases and water. The oils have much lower oxygen content and are immiscible with the aqueous phase. If the condensation train is carefully designed, the pyrolysis products can be fractionated in the condensers with most of the aqueous fraction with a small amount of oil collected in the water/ethylene glycol cooled condensers while almost pure oil (<2% water) can be collected in the electrostatic precipitator.

This process enables you to characterize the properties of the bio-oil without much interference from the aqueous phase. On the other hand the aqueous phase can also be characterized without much interference from the heavy organic phase products. We have developed these processes for various products according to our needs, as well as the needs of

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Fractional catalytic pyrolysis of biomass ...continued

various sponsors. Thus we have developed processes for high phenolic oils, high sugar oils, and oils for hydrocarbon fuel production. Examples of some of the processes are highlighted below.

Production of stable biomass pyrolysis oils

One of the most important applications of fractional catalytic pyrolysis of biomass is the production of stable biomass pyrolysis oils. Conventional biomass pyrolysis oils contain heavy fractions that agglomerate with time to increase the viscosity of the bio-oils. However, by applying fractional catalytic pyrolysis, most of the heavy fraction can be broken down into low molecular weight products and the viscosity of the oil lowered considerably. The decomposition of these heavy fractions also increases the pH of the oils and reduces its density. The levoglucosan content is considerably reduced and the oils can be distilled without forming solids or chars.

Additionally, these oils also have lower oxygen content and their calorific values are about 25% higher than those of conventional bio-oils. Because of their relatively low oxygen content, they can be easily upgraded or co-processed with petroleum fluid catalytic cracking feed. These oils have been upgraded on a standalone basis to diesel and gasoline fractions.

> **‘We have developed processes for high phenolic oils, high sugar oils, and oils for hydrocarbon fuel production.’**

A major drawback of fractional catalytic pyrolysis is the production of a considerable amount of non-condensable gases that can be as high as 40 wt% yield. Although these gases are composed of mostly carbon monoxide and carbon dioxide, and low concentrations of low molecular weight hydrocarbons, which can be compressed and used to fuel the pyrolysis process, we discovered that recycling of the gases can increase the yield of the organic liquid fraction.

Thus, the recycling process is an effective means of carbon recovery and thus increasing the overall carbon efficiency of the process. These recycle gases are very effective in lowering the activation energy of the pyrolysis process and thus increasing the process efficiency.

Production of phenolic liquids for adhesives and epoxy novolac

The production of phenolic liquids from biomass pyrolysis requires several liquid-liquid extraction steps to separate the acidic products from the phenols and neutrals. This process is time consuming and the final products can be used in limited applications because of interference from the other pyrolysis compounds. We have developed new catalysts that can be used to target the carbohydrate decomposition products of the biomass and these fractions are converted into non-condensable gases and thus leaving a clean product very rich in phenols.

The liquid product can be used “as is” without any liquid extraction to replace phenol in phenol formaldehyde resins. Our tests showed that we can substitute 95% of phenol in phenol/formaldehyde resins with these pyrolysis products and obtain excellent products. These pyrolysis liquids can also be used as is to produce novolac resins and epoxidized to produce epoxy novolacs with excellent properties. Thus this one step fractional catalytic pyrolysis holds promise for the production of high value products.

Production of anhydrosugars

Instead of functionalizing the catalyst to target carbohydrate polymers and preserving the phenolic moieties, one can target the lignin fraction of the biomass. In this case, the catalyst gasifies the lignin component of the biomass leaving mostly carbohydrate decomposition products that is dominated by levoglucosan monomers and oligomers. We have used this approach to produce levoglucosan-rich pyrolysis oils for further processing to value-added products. This technique can also be used to produce bio-oils of varying viscosities and densities to study the phenomenon of viscosity related ageing of bio-oils.

Our goals now are to develop new catalysts that can be used to refine the biomass pyrolysis products in a one pot operation, and thus reducing the cost producing high value products, and to make biobased products competitive with petroleum derived products.

Contact

Foster Agblevor
USTAR Bioenergy Centre
Department of Biological Engineering, Utah State University
Logan UT 84322
USA

T: +1 435 797 1000
E: foster.agblevor@usu.edu

www.usu.edu/

UtahState University

NMR methods for product quality diagnostics in bio-oil production

Figure 1: Prototype of the 20 MHz Medium-Resolution Spectrometer (desktop device) from Bruker, Rheinstetten, Germany. It has a tempered permanent magnet with integrated electrical shimming coils, and a control unit for pulse generation and signal detection.

A summary by Klaus Raffelt of Karlsruhe Institute of Technology (KIT) in Germany

During flash pyrolysis, the polymeric structures (mainly lignin, cellulose and hemicellulose) are broken down to a complex mixture of monomeric and oligomeric organics and water. The accurate analysis of the condensate is sophisticated and time consuming; at least three laboratory methods are needed, e.g. Karl Fischer titration for water quantification, fractionated extraction for the pyrolytic lignins and GC for the organic monomers.

On the other hand, for the successful operation of the pyrolysis and gasification units the detailed knowledge of the composition is not necessary and could be constrained to key properties like heat content, viscosity and phase stability. Accomplishing this, the water content and the elemental composition of organic carbon, hydrogen and oxygen are useful parameters.

The low-field NMR approach

One possibility for a quick inline quantification of the water content is to use nuclear magnetic resonance (NMR) methods, a powerful and well known technique for structure determination of organic molecules. In the last few decades, instruments were developed with very high magnetic fields of up to 24 Tesla, which enables excellent signal resolutions and sensibility.

On the other hand high-field NMR is far too expensive for process control and the in-time adjustment of an adequate homogeneous magnetic field is problematic in multiphase pyrolysis product streams. An alternative is provided by cost-efficient low-field NMR using permanent magnets with B< 1T. The lower sensibility is no concern due to the strong water singlet in the NMR spectrum. The lower resolution can partly be balanced by a thorough calibration using multivariate mathematical analyses.

Alternatively to the spectral distinction by the chemical shift, water can be quantified by measuring the signal relaxation behaviour and referring it to the relaxation in calibration systems. The promising relaxation methods are described in detail in the scientific literature[1]. Here, we present the application of the so-called Medium Resolution NMR (MR-NMR) system. The spectrometer was developed by Bruker GmbH (Rheinstetten, Germany).

A bandwidth of 3.1 kHz was used during data acquisition of the free induction decay (FID) of one pulse sequence, which was more than enough to catch all 1H signals in the sample, making a quantitative analysis possible. The measured spectra were processed with a self-written Matlab script of the working group of Gisela Guthausen (KIT, Karlsruhe, Germany). The calibration model was obtained by partial least-squares regression (PLS-R). The results from the Karl Fischer titration were used as reference values.

Water quantification by HR-NMR is sensible to operational errors (initial weight of sample and reference, phase- and baseline correction of the NMR spectrum, broad overlapping of signals at low intensity if the magnetic field is not optimally homogenized). If the processing is done correctly, the integrals of the NMR signals are directly proportional to the molecule concentration.
But in the case of water an additional important systematic error has to be considered - the hydrogen atoms in the sample exchange quickly with hydrogen

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NMR methods for product quality diagnostics in bio-oil production*...continued*

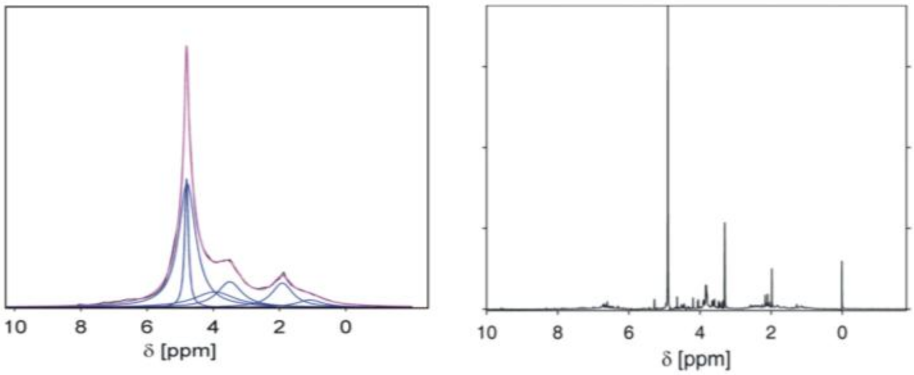

Figure 2: **Left:** Medium-resolution spectrum (20 MHz) of a pyrolysis oil of beech wood with a water content of 36.5%. Water quantification by PLS-R. **Right:** High resolution spectrum (400 MHz) of a highly organic fraction of pyrolysed eucalyptus wood with very low water content (2.7%). Water quantification by mixing a weighted sample with a known amount of reference substance (TMSP sodium salt) in an excess of deuterated methanol, and additionally comparison with a calibration curve (see the black line in Figure 3).

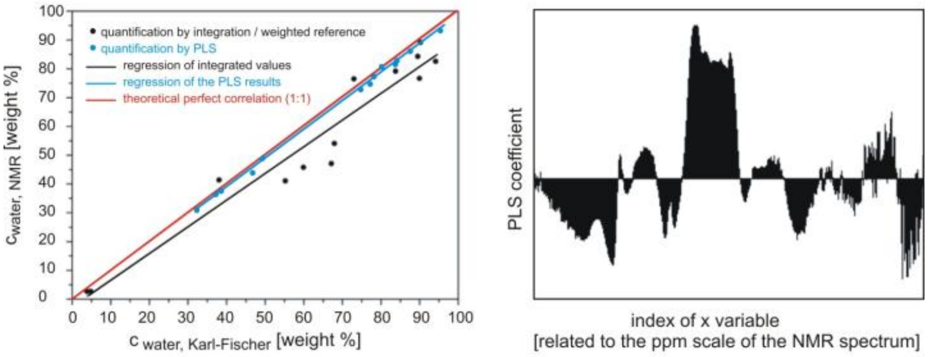

Figure 3: **Left:** Water quantification in pyrolysis oils a) by conventional NMR (HR-NMR at 400 MHz) with internal TMSP standard (black points and black regression line) and b) by MR-NMR (20 MHz) followed by PLS-R (blue points and blue regression line), compared to the water concentration obtained by Karl-Fischer titration (KF). The red line shows the theoretical perfect correlation of NMR and KF based values. **Right:** Visualization of the PLS Regression: PLS-R is an interactive mathematical algorithm for modelling hidden parameters (like the water concentration in this case) by related initial data (in this case MR-NMR spectra). Each part of the spectrum is assigned to one or more PLS coefficients (in this case 5), which result by linear combination in the key property of interest (NMR-calculated water concentration).

atoms of alcohols, carboxylic acids and other acidic species by chemical equilibrium reactions. For this reason, the water signal cannot be directly calculated by the signal integrals, but a regression line has to be calculated by preliminary calibration studies (see the black line in Figure 3). As a result of variable alcoholic and carboxylic concentrations, the error of this quantification method may be relatively high (around 5% in many of the 13 measurements shown by the black points in Figure 3).

Water quantification from the MR-NMR Spectra by direct signal integration is not possible due to signal overlapping. Therefore chemometric methods need to be used, in this case PLS-R was applied. Once the preliminary calibration has been done with appropriate reference samples, an automated water analysis can be carried out by appropriately adapted software. The addition of an accurately weighed reference is not necessary because the PLS-R compares the water-region of the proton spectra with the organic regions and relates it to the Karl-Fischer values.

To ensure reproducibility of signal intensities the receiver gain of the detector was adjusted by pure water. In the 5th order PLS-R the sample weight and the filling level of the measurement tubes were taken into account at 500 iteration steps. Validation was made by cross validation and also by a test-set, both leading to errors of less than 2% compared to the Karl-Fischer titration results. Although the information density of high field NMR is significantly higher than in the medium field NMR, the latter is superior in the case of water quantification, even if high field NMR is combined with chemometry. As the medium field method is considerably cheaper in equipment procurement and

(Continued on page 23)

NMR methods for product quality diagnostics in bio-oil production...*continued*

Table 1: Typical properties of the examined pyrolytic liquids.

	Water / wt.%	Lignin / wt.%	Viscosity / mPa·s
Condensates obtained at 20°C after separation of the higher boiling species (>100°C), diverse biomass origin.	45 - 95	0 - 5	3 - 10
Light phase after storage of beech wood tar.	30 - 45	2 - 17	10 - 80
Heavy phase after storage of beech wood tar.	3 - 12	48 - 55	4 - 50

Table 2: Comparison of the quality of water quantification by NMR at different magnetic fields (different proton frequencies). The errors of validation and prediction are lower at medium field (20 MHz) than at high field (250 and 400 MHz).

NMR-field (frequency)	Evaluation of the PLS-R model	RMS (root mean squares)		
		Deviation from regression	Error of validation	Error of prediction
400 MHz-spectrometer	Cross validation	4.007	8.838	-
250 MHz-spectrometer	Test-set validation	2.215	2.166	1.918
20 MHz- spectrometer	Test-set validation	0.990	2.817	1.507

maintenance, and also less time-intensive in sample preparation, a future development for a flow cell and automated water quantification in the condensation part of a pyrolysis plant is an interesting option. This could provide the operators of the pyrolysis facility with quick and considerably accurate data of process conditions and product quality.

As a next step it should be examined which additional information can be extracted from the MR-NMR spectra. Also, for example, the lignin content should be able to be modelled by PLS-R, but so far it is not certain if the sensitivity is enough, as the aromatic part of the spectrum (6-8 ppm in Figure 2) shows low signal intensity and the foothill of the water signal at 5 ppm still influences the aromatic region. As a potential hindrance it should also be examined to what extent solid (char) contamination lowers the quality of the spectrum interpretation bearing in mind that the separation efficiency of the hot cyclones is typically not 100%.

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Contact

Klaus Raffelt
Institute of Catalysis Research and Technology (IKFT)
Karlsruhe Institute of Technology (KIT)
Hermann-von-Helmholtz-Platz 1
D-76344 Eggenstein-Leopoldshafen
Germany

T: +49 721 6080
E: klaus.raffelt@kit.edu

www.kit.edu

Biomass to diesel through pyrolysis: an update

News from Robbie Venderbosch of BTG Biomass Technology Group in the Netherlands

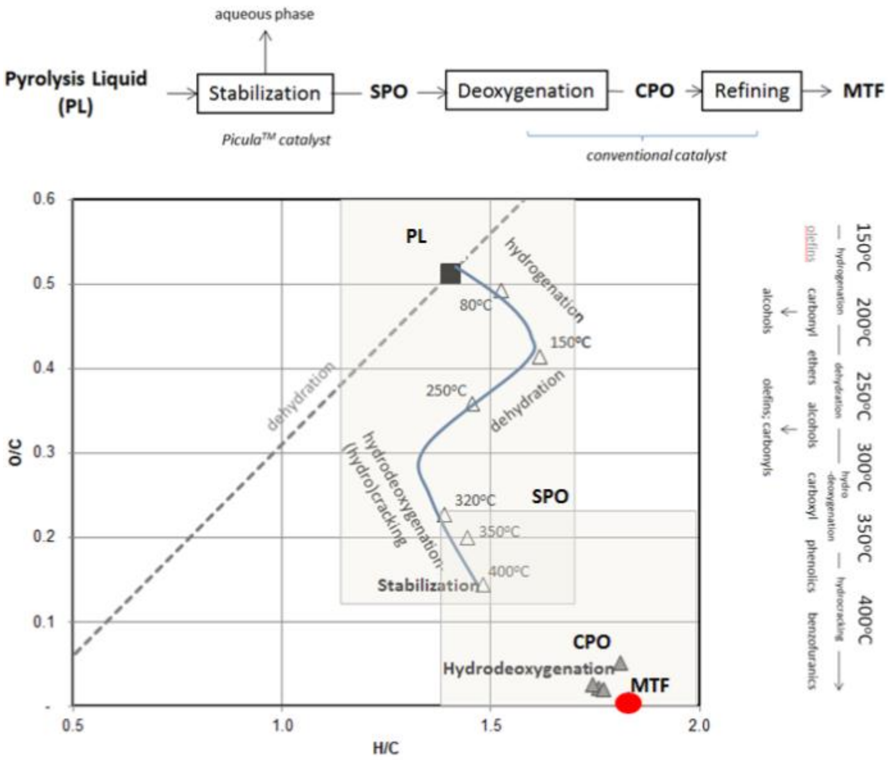

Figure 1: Van Krevelen plot for pyrolysis oil and hydrotreated products at several maximum induced bed temperatures (MIBT).
Key: PL=Pyrolysis Liquid; SPO=Stabilized Pyrolysis Oil; CPO=Cracked Pyrolysis Oil; MTF=Mixed Transportation Fuels.

Pyrolysis liquid from biomass (PL), which has approximately 70% of the carbon from the biomass going into the bio-oil, can be an interesting feedstock for petroleum refineries. The main problem related to PL however is its high coking tendency. The use of catalysts to improve the physical and chemical properties of such liquids upstraem of the refinery is an active area for RD&D.

For more than a decade and together with Groningen University (Netherlands) and Boreskov Institute of Catalysis in Novosibirsk (Russia), BTG has been developing a catalytic hydrotreating process to improve relevant properties of such pyrolysis liquids. The products are referred to as ‘Stabilized Pyrolysis Oil (SPO)’, ‘Cracked Pyrolysis Oil - CPO’ (further low-oxygen products), and oxygen-free ‘Mixed Transportation Fuels (MTF)’. Further details and results are shown in Figure 1.

PL comprises fractions from the lignins and ‘carbohydrates’ derived from the cellulosic fractions. In the approach undertaken the low-temperature induced ‘carbohydrate’ chemistry is physically separated from a high temperature lignin chemistry.

Dedicated Picula^{TM} catalysts have been developed and further optimized for this purpose. This family of these Picula^{TM} catalysts comprises high active metal loaded catalysts based on Nickel. A conventional catalyst can subsequently be applied to convert the SPO at either atmospheric FCC operations (co-feed), or at high pressures in a subsequent deoxygenation - cracking step. A general process scheme is shown in Figure 1. SPO (with oxygen content >10 wt.$_{daf}$%) is produced at reduced temperatures, which can be further converted over conventional catalysts (such as NiMo – CoMo) to CPO. This second deoxygenation step requires higher temperatures (from 325^{o}C yielding a residual oxygen content <10 wt.$_{daf}$%). If preferred the CPO can be further deoxygenated to yield a mix of hydrocarbons (MTF) at even higher temperatures.

A mechanistic view is shown in a Van Krevelen plot (Figure 1) where the molar ratio of O/C is plotted against the molar ration of H/C for the products on a dry basis. The different products derived from different process conditions are indicated. Two regions can be distinguished. The first is a stabilization regime where

(Continued on page 25)

Biomass to diesel through pyrolysis ...continued

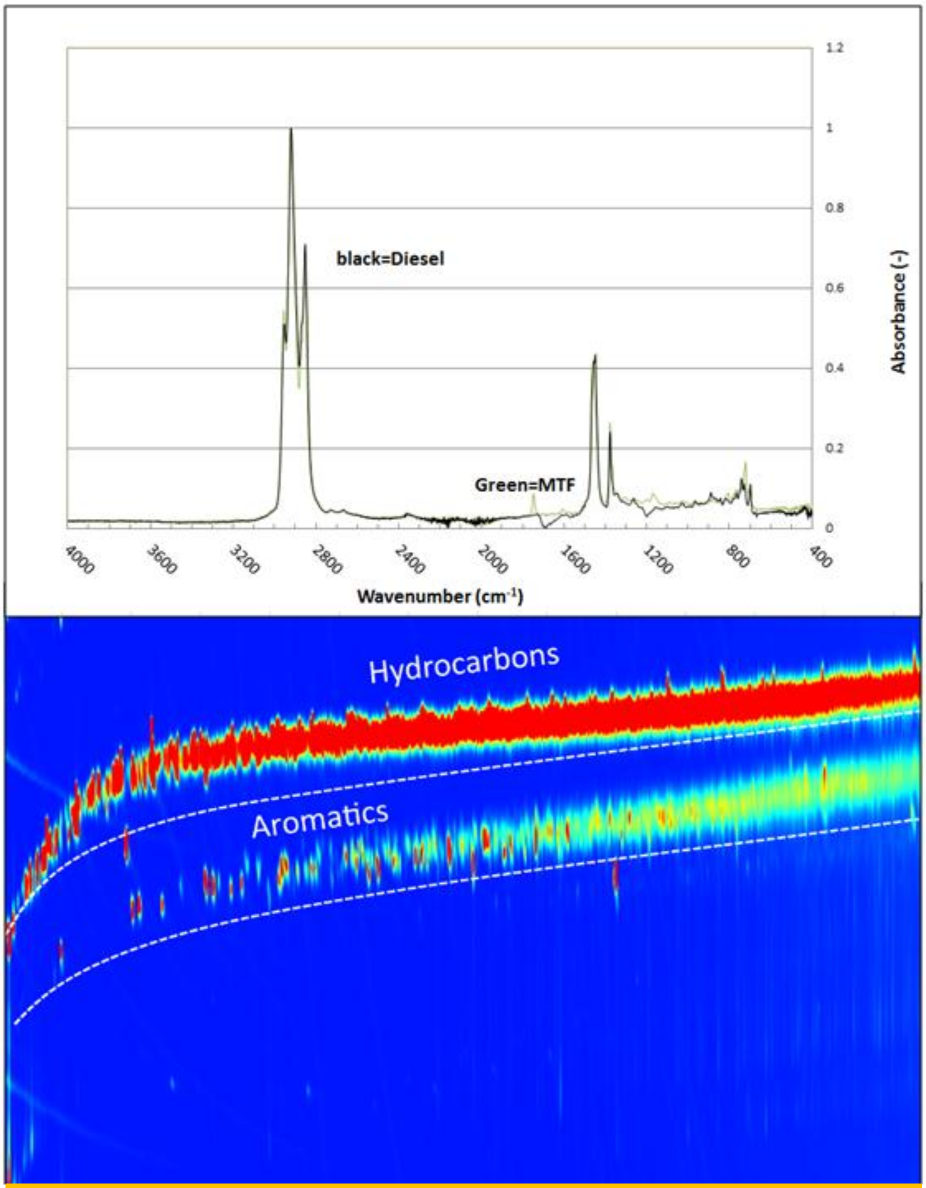

Figure 2: **Top:** FTIR spectra for the fully oxygen-free product MTF (in green) and conventional diesel (in black). **Bottom:** 2D-GC for the MTF. 2D-GC analysis carried out by Groningen University (Prof. Heeres).

pyrolysis liquids are converted into liquids with improved product properties: SPO with lower charring tendency is obtained (not shown here: at 500°C a reduction in Micro-Carbon Residue Testing (MCRT) from 18 wt.% down to 8 wt.%). The second region is the hydrodeoxygenation regime where the oxygen content is actually reduced and the oil is cracked.

The main reactions thus taking place when converting pyrolysis liquids to MTF are hydrogenation (low temperatures <200°C), dehydration of the alcohols (intermediate temperature range 200-300°C) and a further (hydro) cracking – deoxygenation of the lignitic materials at the high temperature range (>300°C). Chemically the stabilization as well as deoxygenation reactions mainly affect first the functionality of the oxygen in the pyrolysis liquid and then the oxygen content in the following sequence: (i) reactive groups (mainly aldehydes) are transformed into alcohols, followed by (ii) dehydration of the alcohols towards carbonyls and olefins and finally (iii) deoxygenation of the more stable components (such as phenols, diphenylethers and benzofuranics (see also Figure 1) to obtain the hydrocarbons.

The CPO and MTF are completely distillable below 400°C; the MTF is a product with physical (smell, colour) and chemical (SimDis, FT-IR and 2D-GC) properties similar to fossil fuels. A picture for the different samples is shown in the insert in Figure 3. The colour of the product obtained strongly depends on the severity of the process applied, providing a good indication of the residual amount of oxygen remaining in the product.

Functional groups in the pyrolysis liquids and products derived thereof can be distinguished in FTIR analysis, and going from pyrolysis liquids to stabilized oils - and finally to oxygen-free liquids - a clear transition is noted from the typical pyrolysis liquid components to alcohols and then further to aliphatic C-H groups (3000 - 2800 cm^{-1}).

The similarity between the final MTF and conventional diesel is striking (see Figure 2). A typical 2D-GC plot (prepared by the University of Groningen) for the oxygen-free MTF clearly shows a broad band of aromatics, cyclohexanes and alkanes. FTIR and 2D-GC data for the PL and intermediates SPO and CPO also show a smooth transition towards the hydrocarbons.

A further proof of principle for the proper MTF product properties is shown by demonstrating fuel mixtures (up to 75% replacement) in a commercial 5 kW$_e$ diesel aggregate (diesel electrical generator), and in a 100 km test trial in a JCB Workmax Utility

(Continued on page 26)

Biomass to diesel through pyrolysis
...continued

Figure 3: **Top left:** The JCB-Workmax UTV fuelled by a diesel–MTF mixture with Mr Kamp, Minister of Economic Affairs in the Netherlands. **Right:** Efficiency and emission levels during the 100 km trial (first 50 km 50:50; second 50 km 75:25). **Bottom left:** Products derived from pyrolysis liquids.

Terrain Vehicle (UTV); see Figure 3. Similar emissions level (CO; NO_x; O_2; CO_2 and hydrocarbons) and fuel consumptions (g/km) are reported for diesel: MTF mixtures (50:50 and 75:25).

So far hundreds of continuously operated experiments (24 h/7 d) have been carried out in 100 ml and 2 L volume packed bed systems (oil flow rates from 40 ml/h to 4 L/h), at catalyst testing stream times up to 500 h for both the stabilization and the deoxygenation step. Overall carbon yields (biomass to MTF) are in the order of 40 to 50%. Further work will be focused on an optimization of the (Picula^{TM}) catalysts for stabilization and on improving the overall carbon-to-oil yields.

More information and informative videos are provided on the BTG website www.btgworld.com.

Acknowledgement

The work described here is a summary of work carried out over a period of more than ten years in a framework programme supported by the Dutch government, European and local funds. The author would like to acknowledge the EU for partial funding of the work through the 6th Framework Programme (Contract Number: 518312), AgentschapNL (CORAF-project no. EOSLT04018, NEO-project, no. 0268-02-03-03-0001; GAP-project no. BIORF01016), the Province of Overijssel and Twente University (BE2.O project).

The author would also like to thank D. Assink, K. Lemmens, R. Groeneveld, R. Molenkamp, M. Nijland, V. Vrieswijk (BTG, NL), A. Ardiyanti, W. Yin, J. Wildschut, A. Kloekhorst and H.J. Heeres (Groningen University, NL), V. Yakovlev, M. Bykova and S. Khromova from the Boreskov Institute for Catalysis (RU).

Contact

Robbie Venderbosch
BTG Biomass Technology Group
Josink Esweg 34
7545 PN Enschede
The Netherlands

T: +31 53 486 1186
E: venderbosch@btgworld.com

www.btgworld.com

Fast pyrolysis processing of rape straw from Spain

Daniel Nowakowski and Natalia Gómez Marín.

A BRISK Project visit

Figure 1: Rape straw harvest.

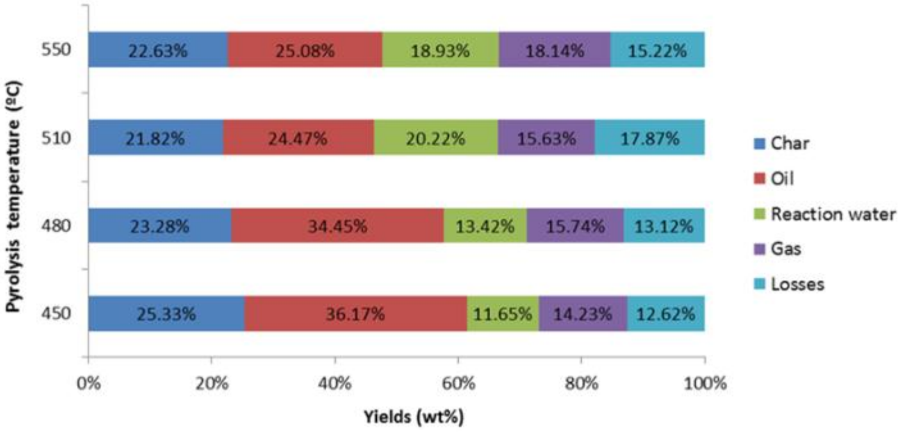

Figure 2: Mass balances (on dry basis) for rape straw pyrolised at different temperatures.

Large amounts of residual straw are generated every year and this waste can be a potential resource for chemicals production and energy generation. Thermal conversion of the straw can provide useful products and helps to reduce waste accumulation. Agricultural residues can be processed by thermochemical conversion including pyrolysis, gasification and combustion.

Aston University bioenergy researchers with the collaboration of engineers from University of Leon, Spain investigated the impact of pyrolysis temperature on the quality of rape straw fast pyrolysis derived bio-oil. The rape straw was delivered from Villaturiel, Province of Leon (Spain). Biomass was characterised using a wide range of analytical techniques including thermogravimetric analysis (TGA) and analytical pyrolysis (Py-GC-MS). Bio-oil was produced using a 1 kg/h fast pyrolysis reactor.

The experiments were carried out at four different reaction temperatures (450, 480, 510 and 550°C). Bio-oil quality was defined by its stability measured by a viscosity index, a water content index and analysis of phase separation. The normalised fast pyrolysis mass balances are shown in Figure 2. This clearly shows the differences in pyrolysis yields between different pyrolysis temperatures. The organic liquid yield was highest for rape straw processes at 450°C.

The properties of the bio-oil are affected by feedstock variation, production processes, reaction conditions, and collecting. In this study, all experiments were carried out under the similar conditions, and the only exception was the pyrolysis temperature. It was found that the bio-oil produced at 450 and 480ºC was a single-phase product. Phase separation occurred when rape straw was pyrolysed at 510 and 550°C. Figure 3 shows the percentage of each phase depending on the pyrolysis temperature.

(Continued on page 28)

Fast pyrolysis processing of rape straw from Spain...*continued*

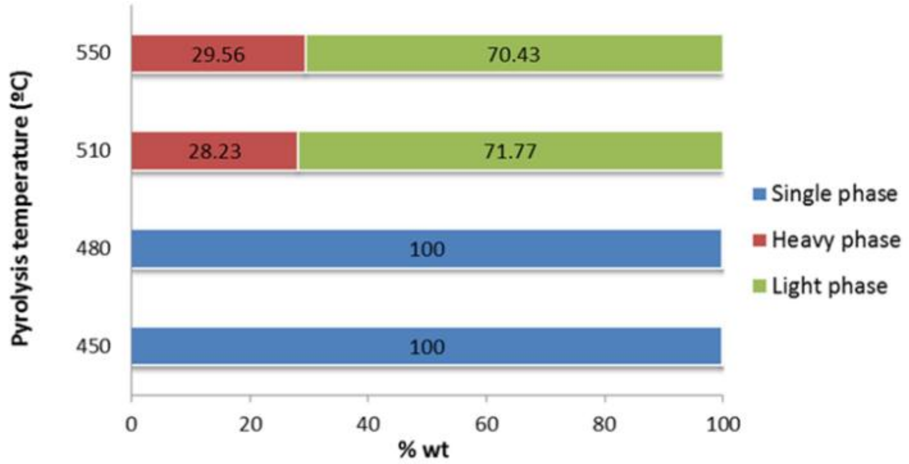

Figure 3: Bio-oil quality after the fast pyrolysis experiments.

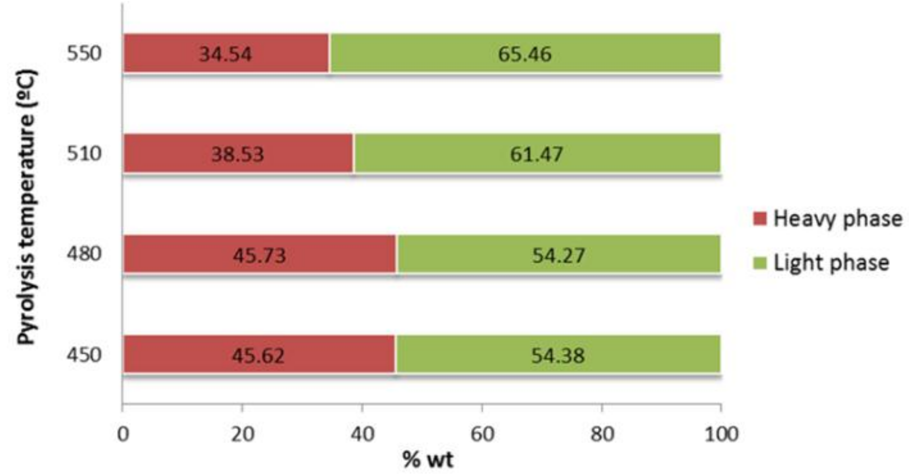

Figure 4: Percentage share (wt.%) for phase separated light and heavy bio-oil fractions after the accelerated storage experiment.

Figure 5: Natalia Gómez Marín visited Aston University through the BRISK Transnational Access initiative which provides travel grants to researchers.

For the purpose of measuring bio-oil stability, accelerated storage tests were performed at 80°C for 24 h, which is claimed to simulate degradation at ambient temperatures for one year. The whole bio-oil from the 450 and 480°C runs and the heavy fraction from the 510 and 550°C runs were assessed for stability. Figure 4 shows the results for phase separation after the accelerated storage experiment.

Conclusions

- Pyrolysis temperature impacts the bio-oil quality and stability. Fast pyrolysis processing of rape straw up to 480°C gives the highest organic yield with a single-phase bio-oil with a low water content.
- Accelerated storage experiment revealed that rape straw bio-oil undergo phase separation during long storage, thus this type of bio-liquid should be used or upgraded immediately after its production.

Natalia Gómez Marín acknowledges the financial support provided by the BRISK (Biofuels Research Infrastructure for Sharing Knowledge) project.

Contact

Daniel Nowakowski
Bioenergy Research Group
Aston University
Birmingham
B4 7ET
UK
T: +44 121 204 3417
E: d.j.nowakowski@aston.ac.uk

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International Events

JULY 2013

3rd-5th
Bioenergy China
Beijing, China

22nd-28th
Catalysis for Renewable Sources: Fuel, Energy, Chemicals
Lund, Sweden

SEPTEMBER 2013

3rd-5th
International Conference on Polygeneration Strategies
Vienna, Austria

3rd-6th
tcbiomass2013
Chicago, USA

4th-6th
Bioenergia - Bioenergy Exhibition and Conference
Jyväskylä, Finland

9th-11th
Asia Pacific Clean Energy Summit and Expo
Honolulu, Hawaii

11th-12th
Biofuels International Conference
Antwerp, Belgium

23rd-26th
EPNOE International Polysaccharide Conference
Nice, France

25th-26th
Lignofuels
London, UK

30th September - 4th October
Sardinia 2013 - 14th International Waste Management & Landfill Symposium
Cagliari, Italy

30th September - 2nd October
EFIB 2013
Brussels, Belgium

OCTOBER 2013

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ISWA World Congress 2013
Vienna, Austria

8th-10th
Biotechnica 2013 Marketplace Industrial Biotechnology
Hannover, Germany

16th-18th
International Seminar on Gasification
Göteborg, Sweden

NOVEMBER 2013

6th-7th
Gasification
London, UK

7th-9th
Wood Science and Engineering in the 3rd Millennium
Brasov, Romania

20th-21st
Bioenergy Commodity Training
Brussels, Belgium

MARCH 2014

11th-13th
International Bioenergy Conference
Manchester, UK

MAY 2014

19th-23rd
Pyro 2014
Birmingham, UK

22nd-23rd
REGATEC 2014 - Renewable Energy Gas Technology
Malmö, Sweden

JUNE 2014

3rd-5th
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Pyrolysis Research Opportunities

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Partner (Acronym)	Location	Activity
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Aston BERG	UK	Analysis, Characterisation, Fast pyrolysis, Upgrading bio-oil
BIOENERGY 2020+	Austria	Aerosols, Analysis, Combustion
Cardiff University	UK	Combustion, Spray cell, Turbine simulation
CERTH	Greece	Catalysts, Biofuel synthesis, Fast pyrolysis, FCC, FT wax cracking
CIUDEN	Spain	Gasification
TU Delft	Netherlands	Analysis, Characterisation, Combustion, Fuel cell, Gasification
ECN	Netherlands	Combustion, Gasification, Pyrolysis
ENEA	Italy	Gasification, Hydrogen
ETC Piteå	Sweden	Combustion, Gasification, Spray characterisation
TU Graz	Austria	*See BIOENERGY 2020+ for further information*
INERCO	Spain	*Transnational access through CIUDEN*
IFRF	Italy	Biomass characterisation, Gasification, Gas clean-up
NTNU	Norway	Biofuel synthesis
PALL F	Germany	*Transnational access through Delft University of Technology*
Paul Scherrer Inst.	Switzerland	Analysis, Gasification, Hydrothermal processing, Methanation
SINTEF	Norway	Catalysts, Pyrolysis, Gas conditioning, Bio-oil upgrading
TU Denmark	Denmark	Combustion, Gasification
TU Munich	Germany	Combustion, Gasification
TUBITAK	Turkey	Combustion, Gasification
UNINA Naples	Italy	Pyrolysis
TU Vienna	Austria	Gasification, Biofuel synthesis
TU Wroclaw	Poland	Analysis, Combustion
U. Zaragoza	Spain	Gasification, Hydrothermal processing

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Aston University
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Birmingham, UK, 19-23 May 2014

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Sponsors and hardware vendors are welcome and will be offered an attractive conference package. For details please enquire with:
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Important dates

Abstract submission	**01 Feb 2014**
Early bird registration	**31 March 2014**
Conference	**19-23 May 2014**

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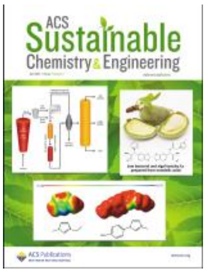
Publications

Fuel Oil Quality and Combustion of Fast pyrolysis Bio-oils
Published by VTT.
Publication date: March 2013.
Authors: Jani Lehto, Anja Oasmaa, Yrjö Solantausta, Matti Kytö, David Chiaramonti.



Sustainable Chemistry Engineering - Volume 1, Issue 4.
Published by ACS Publications.
Publication date: April 2013.

Within this journal is the following paper:
Hydroprocessing Bio-Oil and Products Separation for Coke Production.
Authors: Douglas C. Elliott, Gary G. Neuenschwander, Todd R. Hart.

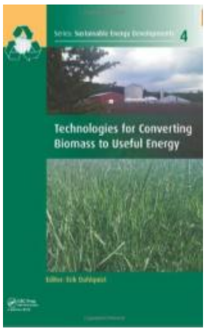
Renewable & Sustainable Energy Reviews - Volume 20.
Published by Elsevier.
Publication date: April 2013.

Within this journal is the following paper:
State-of-the-art of fast pyrolysis in IEA bioenergy member countries.
Authors: Dietrich Meier, Bert van de Beld, Anthony V. Bridgwater, Douglas C. Elliott, Anja Oasmaa, Fernando Preto.

Virtual Special Issue on Biomass, Biodiesel and Bio-Ethanol
Published by Elsevier.
This includes recent review articles published in Elsevier's key energy journals, including: Biomass and Bioenergy, Bioresource Technology, Fuel, Fuel Processing Technology, Progress in Energy and Combustion Science and Renewable Energy.

Biomass Combustion Science, Technology and Engineering
Edited by Lasse Rosendahl.
Published by Woodhead Publishing.
Publication date: April 2013.
Within this journal are the following papers:

- Fast pyrolysis of biomass for the production of liquids.
  Author: Anthony V. Bridgwater, Aston University, UK.
- Intermediate pyrolysis of biomass.
  Author: Andreas Hornung, Aston University, UK.



Technologies for Converting Biomass to Useful Energy
Combustion, Gasification, Pyrolysis, Torrefaction and Fermentation.
Edited by Erik Dahlquist.
Published by CRC Press, Taylor and Francis Group.
Publication date: April 2013.

Video links

Click on the links below to activate the relevant video clips.

90 Seconds of Discovery - Fast Pyrolysis (English)
A summary by PNNL, USA

Bioenergy in Ov (English)
This video overviews the multidisciplinary research into biomass conversion at the University of Twente in the Netherlands. It covers the development of mobile torrefaction equipment and a flash pyrolysis plant.

Diesel from Pyrolysis Oil (Dutch)
Produced by BTG (Biomass Technology Group) in the Netherlands.

BTG's Fast Pyrolysis Process (English)
Within this process solid biomass is reformed in a rotating cone in the absence of air to pyrolysis oil.

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Here is a selection:

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  (969* members)
- Biofuels
  (6,462* members)
- Biomass to Energy
  (10,344* members)
- Biomass Combustion and Co-firing GVB
  (231* members)
- Biomass, Bioenergy and Biofuels
  (1,570* members)
- World Bioenergy Association
  (522* members)
- Bioenergy, by Biofuels Digest
  (7,199* members)

* figures as at 18/06/2013

PyNe Issue 31

IEA Bioenergy
Task 34 Pyrolysis
PyNe 31
July 2012
Welcome to Task 34
By Doug Elliott, Task 34 Leader

IEA Bioenergy
Task 34 Pyrolysis
PyNe 32
December 2012
Welcome to Task 34
By Doug Elliott, Task 34 Leader

PyNe Issue 32

Further Information

If you require further information about the PyNe newsletter, or you would like to contribute to future editions, please contact the Editor:

Irene Watkinson
Bioenergy Research Group
Aston University
Aston Triangle
Birmingham, B4 7ET
UK

T: +44 121 204 3430
E: i.i.watkinson@aston.ac.uk

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IEA Bioenergy

Task 34 - Pyrolysis

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