



By Doug Elliott, Task 34 Leader

The IEA Bioenergy Task 34 for Pyrolysis is nearing completion of the current Triennium, which runs from 2013 to 2015. Participants in the Task are Finland, Germany, Netherlands, Norway, Sweden, and 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

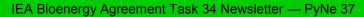
The overall objective of Task 34 is to improve the rate of implementation and success of fast pyrolysis for fuels and chemicals by contributing to the resolution of critical technical areas and disseminating relevant information, particularly to industry and policy makers. The following remain as the Priority Topics identified for the triennium by the Task:

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

Since initiation of the Task for the current Triennium the Task Members have been busy with the identified activities. The applications for bio-oil have been reviewed and new information is to be incorporated into a new IEA



Published by Aston University European Bioenergy Research Institute





PyNe 37 July 2015

ISSN 2040-2759



Visitors at the opening of the new EMPYRO BTG plant in Hengelo, Netherlands.

Bioenergy document on pyrolysis, to be released later this year. The Round Robin tests have been completed at the participating laboratories and analysis of the samples is underway at the Thünen Institute in Germany. Three feedstocks were prepared and distributed and 16 laboratories prepared fast pyrolysis bio-oils for analysis and comparison. Support to the CEN working group - which is developing standards for bio-oil for use in Europe - has been

Inside this issue

News from Around the World

Task 34 Members

ongoing, with two of the Task members actually serving as members of the working group and all Task members serving as technical consultants to the standards development effort. In recent collaborations with other IEA Bioenergy Tasks the life cycle analysis produced by two of the Members was reviewed in Task 38 and other participants in Task 34 have provided review of the bioenergy fact sheets being

(Continued on page 2)

2International Events33-363-32Publications3732Contact the Editor38

Welcome ...continued

developed as part of the Task 42 work. Finally, a new web-based interactive database of pyrolysis demonstration plants is being developed and should become an active element on the Task website by the end of the year.

In this issue of the newsletter There are several articles from the participants describing the latest developments in fast pyrolysis including exciting news of the biooil production at the newly opened EMPYRO BTG plant in Hengelo, Netherlands, as well as news from the Netherlands on the LigniFAME project. From Finland we have reports on CEN standards development; from the US we have discussion of collaborative research into lignocellulosic biomass; and from Germany a report on the IEA Bioenergy Task 34 Round Robin for pyrolysis. There is also an updated calendar of events of interest to the biomass pyrolysis community.

Please also be aware of the Country Reports located elsewhere on the <u>Task 34 website</u>. These are short introductory articles and slide sets prepared by the national team leaders from each of the participating countries summarising the particular biomass pyrolysis efforts in their countries. In addition, the latest <u>Task Meeting</u> <u>Report</u> summarises the developments within each of the Priority Topics of the Task.

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 Biologinkuja 3-5, P.O. Box 1000, Espoo, FIN02044 VTT, FINLAND T: +358 20 722 5594 E: anja.oasmaa@vtt.fi

Germany Dietrich Meier Thünen Institute of Wood Research Leuschnerstr. 91b, D-21031 Hamburg, GERMANY T: +49 40 73 962 517 E: <u>dietrich.meier@ti.bund.de</u>

Netherlands

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

Norway

Kai Toven Paper and Fibre Research Institute (PFI) Høgskoleringen 6b, NO-7491 Trondheim, NORWAY T: +47 95 21 17 04 E: <u>kai.toven@pfi.no</u>

Sweden



















Update on standardisation of fast pyrolysis bio-oils from lignocellulosic biomass











From left: Anja Oasmaa of the Technical Research Centre of Finland, Bert van de Beld of BTG in the Netherlands, Pia Saari of Fortum Power & Heat in Finland, Douglas C. Elliott of Pacific Northwest National Laboratory in the USA, and Suzan van Kruchten of NEN in the Netherlands.

Latest developments in standardisation

Availability of fast pyrolysis bio-oils (FPBO) Fast pyrolysis of woody biomass is

close to full maturity, with first-of-

their-kind commercial size installations for fuel production in operation in Finland (Fortum), in (Continued on page 4)

Table 1: Fast pyrolysis bio-oil production process in 2014 (above 100kg/h)¹.

Host organisation	Country	Technology	Capacity kg dry feed/h	Capacity kg FPBO*/h	Applications	Status				
1,000kg/h feeding capacity										
Ensyn/Fibria	Brazil	Circulating fluid bed	16,667	11,470	Fuel	In design phase				
Fortum	Finland	Fluid bed	10,000	6,313	Fuel	Operational				
BTG BioLiquids/ EMPYRO	Netherlands	Rotating cone	5,000	3,200	Fuel	Commissioning				
Ensyn Technologies	Canada	Circulating fluid bed	2,500	1,720	Fuel	Operational				
Genting	Malaysia	Rotating cone	2,000	1,200	Fuel	Dormant				
ABRI Tech.	Canada	Auger	2,000		Fuel	Dormant				
Red Arrow/Ensyn	USA	Circulating fluid bed	1,667 (3 each, 1 smaller)		Separation of chemicals & fuel	Operational				
Red Arrow/Ensyn	USA	Circulating fluid bed	1250		Separation of chemicals & fuel	Operational				
		100-1,000k	g/h feeding ca	pacity						
Ensyn Technologies	Canada	Circulating fluid bed	625		Fuel & chemicals	Operational				
Agri-Therm/Univ Western Ontario	Canada	Fluid bed (mobile)	420		Chemical feedstock	Operational				
Valmet	Finland	Fluid bed	300		Fuel	Operational				
Biomass Engineering Ltd	UK	Fluid bed	250		Fuel & chemicals	Dormant				
Pytec	Germany	Ablative	250		Fuel	Dormant				
Virginia Tech	USA	Fluid bed	250		Fuel	Dormant				
BTG	Netherlands	Rotating cone	200	150	Fuel & chemicals	Operational				
Univ. Science & Tech of China, Hefei	China	Fluid bed	120		Fuel	Operational				
Fraunhofer UMSICHT	Germany	Ablative	100		Fuel & chemicals	Commissioning				
*FPBO = Fast Pyrolysis Bio-Oil										
IFA Bioenergy Agreement Task 34 Newsletter — PyNe 37 Page 3										

IEA Bioenergy Agreement Task 34 Newsletter — PyNe 37

Update on standardisation *...continued*

Table 2: ASTM burner fuel standard D 7544 for fast pyrolysis bio-oil.

Property	Grade G	Grade D		
Gross heat of combustion, MJ/kg, min	15	15		
Water content, % mass, max	30	30		
Pyrolysis solids content, % mass, max	2.5	0.25		
Kinematic viscosity at 40°C, mm ² /s, max	125	125		
Density at 20°C, kg/dm ³	1.1-1.3	1.1-1.3		
Sulphur content, % mass, max	0.05	0.05		
Ash content, % mass, max	0.25	0.15		
рН	Report	Report		
Flash point, °C, min	45	45		
Flash point, °C, max	-9	-9		

the commissioning phase in the Netherlands (EMPYRO), and in the design phase in Brazil (Ensyn). Table 1 shows fast pyrolysis bio-oil production plants in 2014.

Standardisation of FPBO as boiler fuel

There are presently two fuel oil grades for fast pyrolysis bio-oil established by ASTM (Table 2). The differences between the two grades concern the maximum solids and ash content in the bio-oil.

Since legislation and emission limits differ from Europe to North America, EN (European) standards are needed. The need for standardisation of FPBO under CEN (the European Standardisation body) was raised in the early 2000s,¹ and in 2013 CEN received the mandate (M/525) from the European Commission to develop standards for FPBO. A Working Group (WG41) was established under TC19 (CEN Technical Committee -Gaseous and liquid fuels, lubricants and related products of petroleum, synthetic and biological origin) in early 2014. Five different qualities of FPBO were foreseen by the mandate as relevant depending on application: A European Standard for 1

FPBO replacing heavy fuel oil

- 2. A European Standard for FPBO replacing light fuel oil
- A Technical Specification for the quality for FPBO replacing fuel oils in stationary internal combustion engines
- A Technical Specification for a quality specification for FPBO suitable for gasification feedstock for production of syngas and synthetic biofuels
- 5. A Technical Specification for FPBO suitable for mineral oil refinery co-processing.

The CEN standardisation work has begun with the topics 1-3, and in due course 4-5 may follow. The focus is on boiler use because of its commercial readiness.² A European Standard is obligatory for each EU member state to implement in their respective national legislation. There is limited research on diesel-engine and gasturbine applications, with only a few available publications and so far no proven industrial-scale demonstrations. Therefore, a Technical Specification will be drawn for them. A Technical Specification is not obligatory and is prepared when insufficient information or data is available for

a full standard. The EU Norm is anticipated to be in place in 2017.

Properties and behaviour of FPBO

FPBO is completely different from mineral oils. FPBO is a mixture of many components and not uniquely defined. It is registered as CAS #1207435-39-9.3 FPBO is highly polar and hence immiscible with hydrocarbons, but miscible with alcohols. It contains roughly 25wt% water and approximately 80wt% of the FPBO is soluble in water. This means that no free water is present if the total water content is below 30wt%. FPBO contains around 5wt% acids (mainly acetic acid), which are the main reason for the low pH and high Total Acid Number.⁴ FPBO cannot be distilled, except for the lighter part including the water. As a consequence, all conclusions developed on petroleum products and based on distillation are not applicable by essence.

The same problem applies to standard test methods, which have primarily been developed for mineral oils. Once again, due to the completely different chemical and physical nature of FPBO, they are not always applicable. Some test methods were not suitable,

(Continued on page 5)

Update on standardisation *...continued*

Property	Unit	Typical range	Applicable test methods		
HHV	MJ/kg	14-19	DIN51900, ASTM D240		
LHV	MJ/kg	13-18	DIN51900, ASTM D240, ASTM D5291 for H		
Water	wt%	20-30	ASTM E203		
рН	-	2-3	ASTM E70		
TAN	mg KOH/g	70-100	ASTM D664		
Kinematic viscosity at 40°C	mm2/s	15-40	EN ISO 3104, ASTM D445		
Density at 15°C	kg/dm3	1,11-1,30	EN ISO 12185, ASTM D4052		
Pour point	°C	-9 to –36	EN ISO 3016, ASTM D97		
Carbon	wt% on d.b.	50-60	ASTM D5291		
Hydrogen	wt% on d.b.	7-8	ASTM D5291		
Nitrogen	wt% on d.b.	<0.5	ASTM D5291		
Sulphur	wt% on d.b.	<0.05	EN ISO 20846, ASTM D5453		
Oxygen	wt% on d.b.	35-40	As difference		
Solids	wt%	<1	ASTM D7579		
MCR, CCR	wt%	17-23	ASTM D4530, ASTM D189		
Ash	wt%	<0.3	EN ISO 6245		
Flash point °C		40-110	EN ISO 2719, ASTM D93B		
Sustained combustibility -		Does not sustain	EN ISO 9038		
Na, K, Ca, Mg	wt% on d.b.	<0.06	EN ISO 16476		
Chlorine	ppm	<75	Not specified		

Table 3: Properties of FPBOs and suitable test methods (d.b. refers to Dry Basis).

some methods had to be modified, and some new methods have been developed.⁵ FPBO is not as stable as conventional petroleum fuels and a stability test based on viscosity change has been developed. The modified methods were validated by international Round Robins. The method for flash point (ASTM D 93) has not been proven to be suitable for FPBO. An alternative method to determine the flammability of FPBOs is the sustained combustibility test. Various FPBOs were tested via this method, and none of the oils sustained combustion either at the test temperature (60°C) or at the elevated temperature (75°C). For lubricity no suitable test method has yet been validated. The current list of properties (as opposed to the

draft standard quality parameters) and recommended analysis methods are summarised in Table 3. Cetane number methods are not well suited to FPBO and correlative methods such as Cetane Index ASTM D4737 are infeasible as they are based on distillation.

CEN Round robin

Part of the mandate (M/525) given to CEN on pyrolysis oil aims at executing a test programme. The Mandate is executed by the Working Group (WG) CEN/TC 19/ WG 41/TF, whereas NEN (The Netherlands Standardisation Institute) is the organisation responsible for all test method assessment. This process involves a Round Robin in order to determine the right quality parameters, choose the proper test methods, and determine the applicability and precision of the required test methods for the development of the future pyrolysis bio-oil specifications.

The pyrolysis oils Round Robin consists in general of two parts. The test organisation, which consists of the sample preparation and distribution as well as results gathering from a pre-selected set of labs, is the first part of the work. The second part is the statistics: establishing for each of the assessed properties the precision of the standard procedures used and advising on the validity of each of the test results.

The WG 41 and its taskforce has been preparing the Round Robin (Continued on page 6)

Update on standardisation *...continued*

by defining a property list for testing, finding testing labs and suppliers of pyrolysis fuels (available for testing), establishing test method descriptions and setting up a tender for the test organisation.

Nine pyrolysis oils have been sourced for the Round Robin work. They are as-marketed fuels and give a good spread in feedstock used for production of the pyrolysis oil. All oils will be used as straight base fuels for the Round Robin. In order to come to the same spread with blending, a total of 13 base blends are available for the sampling. A total of eight sets of samples (in duplo) will be bottled and used by eight labs for different sets of test methods.

The tests are planned to be executed by the testing labs in the late summer (2015) and the first (statistical) results will be available later this year.

Handling, storage, transportation

FPBO has to be mixed properly before immediate sampling. A Safety Data Sheet (SDS) and other health and safety instructions should be followed. Alcohols can be used for clean-up. The recommended industrial storage conditions for FPBO are between 15 and 20°C. FPBO has to maintain adequate fluidity, and must not be allowed to polymerise as this causes the viscosity to increase due to high temperatures in long-term storage. By shortduration preheating of the fuel below 80°C, the viscosity can be lowered to the desired value. The FPBO must be pumped satisfactorily from the storage tank to the preheater and further to the burner and must provide good atomisation. Storage containers should be made of corrosion resistant steel and materials such as AISI 304, AISI 316, PTFE (polytetrafluoroethylene), HDPE (high density polyethylene) and



Figure 1: Fast pyrolysis bio-oil.

PVC (polyvinylchloride). For FPBOs, there is no UN number assigned at the moment.⁷

A more detailed version of this article can be found in the American Chemical Society journal Energy & Fuels.³

Contact

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

W: www.vttresearch.com



References

- Meier, D., van de Beld, B., Bridgwater, A.V., Elliott, D.C., Oasmaa, Anja, Preto, F. 2013. State-of-the-art of fast pyrolysis in IEA bioenergy member countries: Elsevier. Renewable and Sustainable Energy Reviews, Vol. 20, pp. 619 – 641.
- Lehto, J.; Oasmaa, A.; Solantausta, Y.; Kytö, M.; Chiaramonti, D. Fuel oil quality and combustion of fast pyrolysis biooils. VTT Technology 87, VTT, Espoo, Finland, 2013. http://www.vtt.fi/inf/pdf/ technology/2013/T87.pdf.
- Oasmaa, Anja, Bert van de Beld, Pia Saari, Douglas C. Elliott, Yrjö Solantausta. Norms, Standards & Legislation for Fast Pyrolysis Bio-Oils. Energy & Fuels 2015, 29, 2471-2484.
- Christensen, E.D.; Chupka, G.; Luecke, J.; Smurthwaite, T.; Alleman, T. L.; Iisa, K.; Franz, J. A.; Elliott, D. C.; McCormick, R. L. Energy Fuels 2011, 25, 5462–5471.
- Oasmaa, A.; Peacocke, C. A guide to physical property characterisation of biomass-derived fast pyrolysis liquids. A guide. VTT, Espoo, 2010; 79 p. + app. 46 p. (VTT Publications 731) ISBN 978-951-38-7384-4 http://www.vtt.fi/inf/pdf/ publications/2010/P731.pdf.
- Diebold, J.P.A Review of the Chemical and Physical Mechanisms of the Storage Stability of Fast Pyrolysis Biooils. In Fast Pyrolysis of Biomass: A Handbook; Bridgwater, A.V., Ed.; CPL Press: Newbury, U.K., 2002; Vol. 2. http://gisceu.net/PDF/U918.pdf.
- Oasmaa, A.; Källi, A.; Lindfors, C.; Elliott, D.C.; Springer, D.; Peacocke, C.; Chiaramonti, D. Guidelines for transportation, handling, and use of fast pyrolysis bio-oil. 1. Flammability and toxicity. Energy & Fuels 2012, 26(6), 3864–3873.

Field to fuel performance testing of lignocellulosic feedstocks







From top: Daniel Howe, Tyler Westover, and Daniel Carpenter

Not all biomass is created equal. Lignocellulosic feedstocks can show highly variable bio-oil yields during fast pyrolysis, ranging from 36 to 62% on a dry basis.¹⁻⁴ The yield of upgraded fuel blendstocks from these bio-oils can also show variable yields and is being studied extensively.^{5, 6} The wide range of reported yields coupled with Daniel Howe of Pacific Northwest National Laboratory, Tyler Westover of Idaho National Laboratory, and Daniel Carpenter of the National Renewable Energy Laboratory, all USA, discuss the advantages of lignocellulosic biomass

unknown upgrading performance presents a challenge for the bioenergy industry in successfully designing and operating a fast pyrolysis biorefinery. In addition, the Billion Tonne Study⁷ and Billion Tonne Update⁸ have shown that no single feedstock will be able to meet the demands of the emerging biofuels industry, and multiple sources of biomass will be required. Understanding the overall conversion performance as a function of feedstock properties is a critical element of reducing these risks for the emerging industry. In addition, this understanding would allow for commoditisation of biomass. allowing producers to optimise quality vs. quantity tradeoffs for specific feedstocks.

In order to address these challenges, researchers at the Pacific Northwest National Laboratory (PNNL), Idaho National Laboratory (INL), and National Renewable Energy Laboratory (NREL) have begun a detailed performance study dubbed "Field to Fuel" to integrate and examine feedstock conversion from harvest through hydrocarbon blendstock production. The work is part of the Feedstock Interface project funded by the Bioenergy Technology Office (BETO) of the US Department of Energy. This study relies on the specific skills available at each national laboratory and is utilising the feedstock handling and preparation expertise at INL, the pyrolysis oil generation and characterisation knowledge at NREL, and the

hydrotreating proficiency at PNNL. In this joint study, eight different feedstocks-including six pure feedstocks and two blends-were prepared and characterised at INL. The feedstocks then were processed via fast pyrolysis at NREL to generate bio-oils that were subsequently characterised. The bio-oils were then hydrotreated at PNNL to generate an upgraded hydrocarbon fuel blendstock. This blendstock was characterised and analysed to determine overall yields from feedstock to upgraded fuel, as well as potential fuel product distributions (gasoline, diesel, jet fuel). Results have been published in Energy and Fuels.9

The biomass varieties chosen for this study include specific types identified by the Billion Tonne Update⁸ as being available in large quantities (>50 million tonnes/year combined) that could be potentially blended and delivered at a cost approaching \$80/dry tonne. They include clean (i.e. with all bark removed) pine (pinus taeda), whole -tree (i.e. with bark remaining) pine (pinus taeda), hybrid poplar (populous x euramericana), tulip poplar (L. tulipifera), corn stover (zea mays), and switchgrass (panicum virgatum). The clean pine and whole-tree pine were selected because these materials are generally expected to have important and perhaps dominant roles in biofuels production via thermochemical conversion pathways. Switchgrass was selected because it is expected to

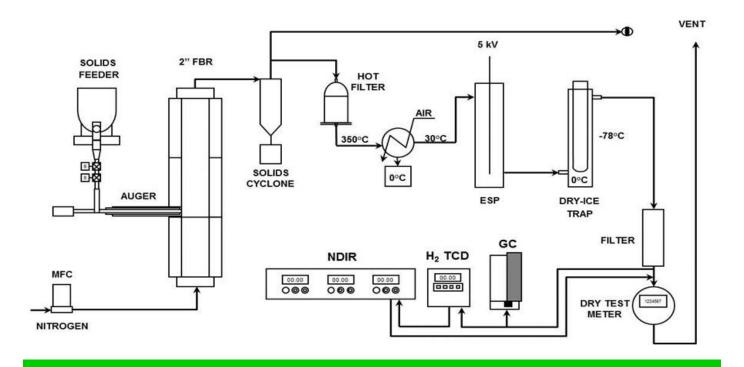


Figure 1: Process flow diagram of 2FBR system used for generating fast pyrolysis bio-oil.

be important in order for thermochemical conversion processes to achieve volume targets set by congressional mandates in the United States.¹⁰ Corn stover was selected as a second widely available herbaceous material. Hybrid poplar and tulip poplar were selected as representative hardwoods with very different syringal/guaiacol (S/ G) ratios in lignin. Two blends were also prepared. Blend 1 consisted of equal weight proportions of the whole-tree pine, tulip poplar, and switchgrass mentioned above. Blend 2 consisted of equal weight proportions of the whole-tree pine, clean pine, and hybrid poplar mentioned above. The blends were selected to test a relatively clean all-wood blend and a very different blend containing an herbaceous material with high inorganic content.

The fast pyrolysis bio-oils were produced at NREL in a 5cm fluidised bed reactor system (2FBR). A schematic of this system is shown in Figure 1. Biomass was pyrolysed in a bed of silica sand heated to 500°C, and the oils were condensed in a three stage condensation train. The oils were then sent to PNNL, where they were upgraded in a bench-scale two-stage hydrotreater to produce a refinery-ready fuel. A schematic of this system is shown in Figure 2. This system used a Ru catalyst on a C support in the first stage, and a Co/Mo catalyst on an alumina support in the second.

As expected, the herbaceous materials contained much higher concentrations of inorganics and structural proteins and lower levels of lignin than the woody materials. Other results of interest are that the ash and fixed carbon contents of the tulip poplar were lower than those of the other feedstocks, and the S/G ratios of the tulip and hybrid poplars were significantly higher than those of the other feedstocks. Relative to the other woody materials, the hybrid poplar had high Ca and K contents. During fast pyrolysis, the herbaceous materials exhibited lower CO and higher CO₂ generation compared to the woody materials. Corn stover and tulip poplar had the highest (22.3wt%) and lowest (13.5wt%) total gas vields, respectively. The char from the herbaceous materials contained lower carbon concentrations and higher ash concentrations than the woody materials. The carbon content of the pyrolysis oils from the herbaceous materials was also lower than those of the woody feedstocks, while the nitrogen and oxygen contents from the herbaceous materials were higher than those of the woody feedstocks. The switchgrass and the blend containing switchgrass exhibited the highest total acid numbers (TANs), followed by the hybrid poplar and tulip poplar. The tulip poplar exhibited significantly higher oil yield at 73.9 wt% than the other materials. Herbaceous materials resulted in the lowest oil (Continued on page 9)

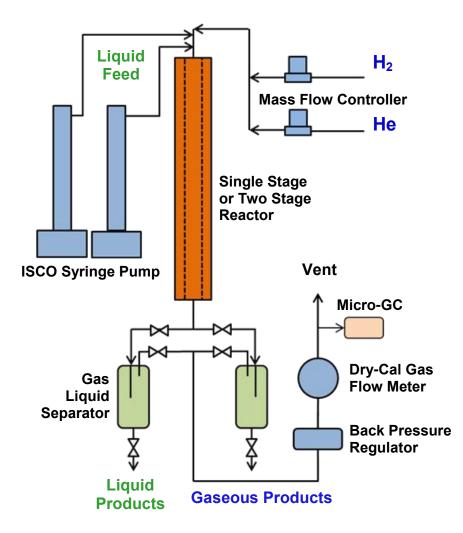


Figure 2: Process flow diagram of the two-stage hydrotreater used to upgrade the fast pyrolysis bio-oils. Prior to each run the catalysts are sulfided by feeding Di-tert-butyl-disulfide to the reactor via the ISCO syringe pumps.

yields at 56.2 wt% for the corn stover and 62.1 wt% for the switchgrass. Product yields and characterisation are shown in Table 1.

Results from the hydrotreater showed that the upgraded oil yield varied significantly, ranging from 40 to 57% (g fuel/g dry feed). The tulip poplar was the worst performing feedstock in terms of conversion to fuel at 40.1%, while the corn stover performed best at 56.8%. The blended materials showed comparable performance to the clean and whole pine materials. The field-to-fuel yield

was then calculated by multiplying the fast pyrolysis oil yield by the upgraded oil yield. This allows for an even comparison across feedstocks, given that some materials may have a high fast pyrolysis oil yield but a low upgraded oil yield. Results are shown graphically in Figure 3. The field-to-fuel yield ranges from 17 to 27% on an organic matter basis and from 30 to 48% on a carbon throughput basis. The clean woody materials have the highest yields, while the grass and corn stover have the lowest yields.

The blended feedstocks exhibit a

field-to-fuel yield that is lower than that of the clean pine but approximately equal to the whole pine and poplars. Expected values for the blends are shown as Xs in Figure 3. Overall, Blend 1 exhibited a total process C yield that was 4% higher than expected while Blend 2 exhibited a total process C yield that was 3% lower than expected. Interestingly, these results indicate that blending may reduce the impact of operating conditions on specific components in blends because the performance of Blend 1 in fast pyrolysis was higher than expected. These results also indicate that the effects of minerals in the feedstock do not linearly affect total process vields. For example, the mineral contents of the tulip poplar, the hybrid poplar, the whole-tree pine, and the blends were all quite different, yet their total process yields were similar. The fact that the clean pine exhibited a better total process yield than any of the other materials indicates that small perturbations in properties may have profound implications in conversion performance. A final consideration in comparing the conversion performance of the different materials is that all materials were subjected to fast pyrolysis at a reactor temperature of 500°C. Previous tests indicate that this temperature optimises the liquid bio-oil yield from pine materials; however, other materials may have higher yields at higher or lower reactor temperatures, so the yield results presented in Figure 3 are not necessarily optimised for all feedstocks.

This study has shown that the compositional parameters of the biomass feedstock will affect both the bio-oil generated by fast pyrolysis as well as the final quantity and quality of the upgraded fuel blendstock. Although some feedstocks, such as tulip poplar, generate a high yield of biooil, the bio-oil does not necessarily *(Continued on page 13)*

	Clean	Whole	Hybrid	Tulip	Corn	Switch	Blend 1	Blend 2	
	Pine	Pine	Poplar	Poplar	Stover	Grass			
Liquid Fraction									
C (wt%)	45.0	45.3	45.9	44.8	37.2	35.1	40.1	43.0	
H (wt%)	7.8	8.1	8.1	7.7	9.1	9.0	8.5	8.4	
N (wt%)	0.08	0.09	0.08	0.08	0.7	0.36	0.19	0.09	
O (wt% calc.)	47.1	46.5	45.9	47.4	52.9	55.4	50.3	48.4	
S (wt%)	0	0	0	0	0	0	0	0	
Water (wt%)	21.1	22.5	20.7	18.8	40.0	37.0	27.1	25.9	
TAN (mg/g KOH)	39.6	37.9	65.5	70.8	43.8	104.3	71.5	47.3	
Viscosity (cP, 25°C)	83.4	92.2	59.5	101	400.2	16.6	38.7	44.4	
Tot. Carbon (wt% biomass C)	60.7	57.9	62.1	67.3	46.9	46.2	54.4	53.5	
Tot. Liquid Yield (wt% dry biomass)	66.9	64.2	67.5	73.9	56.2	62.1	66.9	62.7	
Al (ppm)	1.2	1.4	2.4	1.9	1.6	1.8	1.1	3.2	
Ca (ppm)	4.5	4.7	7.6	41.0	29.2	48.6	48.2	43.1	
Fe (ppm)	BDL	2.5	BDL	BDL	1.2	0.5	0.6	0.6	
K (ppm)	BDL	BDL	BDL	BDL	14.8	BDL	BDL	27.2	
Mg (ppm)	0.9	0.8	1.2	7.7	5.1	8.7	8.8	7.9	
Na (ppm)	BDL	BDL	BDL	7.2	5.5	7.9	8.4	10	
P (ppm)	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	
S (ppm)	37.2	41.1	56.3	48.3	486.9	239.7	112.1	49.8	
		Char	Fraction						
C (wt%)	75.8	80.9	77.8	74.6	54.7	61.9	72.6	80.1	
H (wt%)	5.0	4.2	4.2	4.1	2.6	3.6	4.8	5.3	
N (wt%)	0.2	0.2	0.3	BDL	BDL	BDL	0.5	0.3	
O (wt% by difference)	13.6	8.9	10.1	13.6	24.8	14.5	10.4	10.3	
S (wt%)	0.04	0.06	0.05	0.06	0.07	0.15	0.08	0.04	
Ash (wt% dry)	5.37	5.76	6.05	7.53	17.85	19.69	11.74	3.99	
% Tot. Carbon (wt% biomass C)	24.2	13.9	14.2	11.6	21.4	21.4	11.8	23.7	
% Char Yield (wt%)	12.0	15.0	8.9	7.6	19.1	10.8	7.3	13.3	
Nitrogen-Free Gas Fraction									
CO (%)	40	40	34	42	27	31	36	39	
CO ₂ (%)	46	46	55	45	62	58	52	47	
CH4 (%)	8	8	6	7	6	6	7	8	
C2+ (%)	5	5	4	5	4	4	4	4	
% Tot. Carbon (wt% biomass C)	11.9	12.4	12.4	9.3	14.2	12.2	13.8	14.8	
% Gas Yield (wt%)	17.9	18.9	19.2	13.5	22.3	18.1	19.2	20.4	
BDL = Below Detection Limit							(Continued	on Page 14)	

Table 1: Pyrolysis product characterisation including liquid, solid, and gas fractions.

IEA Bioenergy Agreement Task 34 Newsletter - PyNe 37

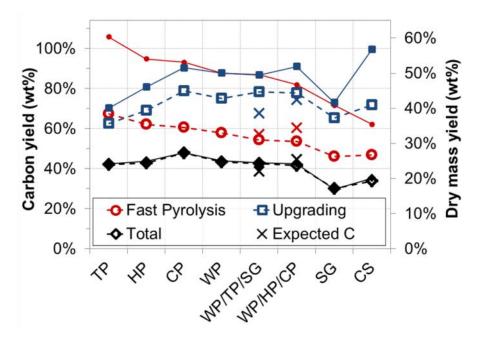


Figure 3: Yields of feedstocks for the fast pyrolysis, hydrotreating (upgrading), and combined fast pyrolysis and hydrotreating processes (total) as a ratio of total product carbon to total input carbon (hollow markers, left axis) and as a ratio of dry oil product to dry ash free infeed material (solid markers, right axis). Xs represent expected values on a carbon basis for the blends based on the sum of the constituents.

exhibit a high yield in the hydrotreater; therefore, the product yields and qualities of both fast pyrolysis and hydrotreating must be considered in comparing the conversion performance of different biofuel feedstock materials, including blends. Another important consideration is that nonlinearities in conversion and upgrading processes may cause blended materials to perform better or worse than separated feed streams. Specifically, results obtained from clean pine, wholetree pine, and other samples in this work indicate that the effects of small changes in key properties, such as mineral content, may have profound effects on conversion performance. However, larger changes in key properties do not have correspondingly larger effects on conversion, indicating that the relationship between feedstock attributes and conversion properties is nonlinear.

Contact

Daniel Howe Pacific Northwest National Laboratory (PNNL) 902 Battelle Boulevard P.O. Box 999 Richland Washington, 99352 USA

T: +1 (509) 372 4355

E: daniel.howe@pnnl.gov

W: www.pnnl.gov







References

- Di Blasi, C.; Signorelli, G.; Di Russo, C.; Rea, G., Product distribution from pyrolysis of wood and agricultural residues. Industrial & Engineering Chemistry Research 1999, 38, (6), 2216 -2224.
- Di Blasi, C.; Branca, C.; Santoro, A.; Gonzalez Hernandez, E., Pyrolytic behaviour and products of some wood varieties. Combustion and Flame 2001, 124, (1), 165-177.
- Agblevor, F.; Besler, S.; Wiselogel, A., Production of oxygenated fuels from biomass: impact of feedstock storage. Fuel science & technology international 1996, 14, (4), 589-612.
- Oasmaa, A.; Solantausta, Y.; Arpiainen, V.; Kuoppala, E.; Sipilä, K., Fast pyrolysis bio-oils from wood and agricultural residues. Energy & Fuels 2009, 24, (2), 1380-1388.
- Zacher, A. H.; Olarte, M. V.; Santosa, D. M.; Elliott, D. C.; Jones, S. B., A review and perspective of recent bio-oil hydrotreating research. Green Chemistry 2014, 16, (2), 491-515.
- Grange, P.; Laurent, E.; Maggi, R.; Centeno, A.; Delmon, B., Hydrotreatment of pyrolysis oils from biomass: reactivity of the various categories of oxygenated compounds and preliminary techno-economical study. Catalysis today 1996, 29, (1), 297 -301.
- Perlack, R. D.; Wright, L. L.; Turhollow, A. F.; Graham, R. L.; Stokes, B. J.; Erbach, D. C. Biomass as feedstock for a bioenergy and bioproducts industry: the technical feasibility of a billion-ton annual supply; DTIC Document: 2005.
- Perlack, R. D.; Eaton, L. M.; Turhollow Jr, A. F.; Langholtz, M. H.; Brandt, C. C.; Downing, M. E.; Graham, R. L.; Wright, L. L.; Kavkewitz, J. M.; Shamey, A. M., US billion-ton update: biomass supply for a bioenergy and bioproducts industry. 2011.
- Howe, D. T.; Westover, T.; Carpenter, D. L.; Santosa, D.; Emerson, R.; Deutch, S.; Starace, A.; Kutnyakov, I.; Lukins, C., Field-to-Fuel Performance Testing of Lignocellulosic Feedstocks: An Integrated Study of the Fast Pyrolysis/Hydrotreating Pathway. Energy & Fuels 2015.
- 10. INL The Feedstock Logistics Design Case for Multiple Conversion Pathways; Idaho National Laboratory Bioenergy Programme: 2014.

NWO: CatchBio



Sascha Kersten of the University of **Twente in the** Netherlands discusses developments in the field of catalytic pyrolysis

After pyrolysis comes catalytic pyrolysis

Production of pyrolysis oil is at the brink of commercial exploitation in Twente in the Netherlands. In the meantime, research within the framework of the CatchBio research programme goes on to establish catalytic pyrolysis as an integrated, one step process for 'green crude oil'. This research comprises the entire production chain and is carried out on a scale that makes it relatively easy for industry to continue development towards practical application.

Chemical companies are well aware that their feedstock supply should be affordable, reliable and clean in the long run. Given these demands, there is only one alternative to fossil fuel energy sources as feedstock in the future bio-based economy: biomass. In 2009 the Dutch CatchBio consortium initiated an ambitious eight year research programme in the field of catalytic biomass conversion. Approximately half of the 29 million euro budget is financed by the Dutch Ministries of Economic Affairs and Education, Culture and Science. The other half is financed by all industrial and academic partners involved in CatchBio.

CatchBio

CatchBio stands for Catalysis for Sustainable Chemicals from Biomass. The consortium's aim is to process the various components in biomass such as cellulose, hemicellulose, lignin, proteins and oils. CatchBio has a diversified approach and aims at the conversion of raw materials into low cost and sustainable fuels, bulk chemical and fine chemicals, as well as pharmaceuticals.

This perspective inspired the 21 public and private partners in the consortium, which unites the complete value chain of the chemical industry, and includes a number of leading names in Dutch chemistry. However, CatchBio isn't an entirely Dutch venture; there is close collaboration with the RWTH Aachen University in Germany and the University of St Andrews in Scotland. At this point the third and last phase of the programme has started, with focus on 'step-by-step valorisation' of competitive catalytic technology for biomass conversion. The CatchBio partners aim to deliver products and processes to industrial R&D labs by the end of 2016.

Pyrolysis

The Twente region in the Netherlands has a long tradition of research and pioneering work on pyrolysis. Pyrolysis is an anaerobic cracking process which can convert wood into pyrolysis-oil in only two seconds, as shown via CatchBio research at Twente. Biomass is thus cracked into 'oil gas', which condensates into an oil. This process was originally conceived at the University of Twente (UT) and during the last two decades was optimised by BTG in Enschede. These activities are now entering the operational phase.

On the site of Akzo Nobel in Hengelo rises EMPYRO, the first Dutch pyrolysis plant to produce oil from wood and the realisation of which will have taken more than 19 million Euros. The plant officially opened in May 2015. BTG Bioliquids BV (technology supplier) and Tree Power (sustainable longterm investor) founded EMPYRO BV to apply pyrolysis technology on a commercial scale. The EMPYRO plant in Hengelo will convert 5 tonnes of biomass into nearly 3.5 tonnes of pyrolysis oil every hour, and at full capacity the plant will produce a total of 20 million litres of pyrolysis oil annually, equivalent to 12 million cubic meters of gas. This corresponds to the annual gas consumption of 8,000 households and equals an annual CO₂ saving of 20,000 tonnes. The plant will produce enough electricity for its own use and will also supply steam to the adjacent Akzo Nobel salt plant.

Catalytic pyrolysis

Alongside this progress towards commercial operation, research continues to further improve the pyrolysis process. The pyrolysis oil currently produced can be used for heating and electricity production. However, further treatment via the additional step of stabilising/hydrotreatment is needed to make pyrolysis oil

(Continued on page 13)

NWO: CatchBio ...continued



Figure 1: Test unit for catalytic fast pyrolysis at the University of Twente in the Netherlands.

suitable for use as transport fuel. After this step, up to 20% of the resultant oil can be mixed with crude oil for use in the existing refinery process. By making smart use of catalysts, researchers are now working on enhancing the pyrolysis oil quality, with the goal of catalytic pyrolysis being to create an integrated, one step production process to create 'green crude oil'.

Catalytic pyrolysis is an important line of research within CatchBio and is probably the closest to industrial application. The second phase of the research consisted of catalyst screening and optimisation, among other activities, and has led to the selection of some very promising catalysts. During the second phase it was also established at which step in the process it would be best to apply catalysis. It was concluded that integrating catalysis into the liquid collection system was not viable, but that applying the process during feedstock pretreatment or adding the catalyst into the reactor were both options to consider during the third phase of valorisation. The choice depends, among other things, on the intended use of the produced pyrolysis oil. For co-refining, integration of catalysis in the reaction process would be the preferred option. When the oil production is aimed at specific end products, however, pre-treatment would be the better route.

Demand driven

The research to make better pyrolysis oil by applying catalysis is tuned in to industrial demand. Unlike 95% of research in this field, which is done on a laboratory micro-scale, tests are carried out on a kilogramme per hour scale which is suitable for industrial process development. Furthermore, the entire production chain is included in the research process, considered by separate groups within the project. The group of Seshan and Lefferts (UT) works at catalyst optimisation and catalyst regeneration – very rare in published research but vital for industrial application. The groups of Kersten (UT), Heeres (University of Groningen) and De Wild (Energy research Centre of the Netherlands) study various reactor concepts, such as fluidised bed and auger reactors, with focus on typical operational biomass conversion challenges, such as ash on the catalyst. Finally, the group of Makkee (Delft University of Technology) uses the pyrolysis oil batches produced by Kersten, Heeres and De Wild to establish whether these products qualify for co-refining in existing gasoline production processes.

By the end of 2016 the aim is to have performed a series of experiments in order to provide the necessary insight into the entire process and thereby enable the corefining of pyrolysis oil after a single step catalytic conversion process. The resulting dataset should be sufficient for the industry to take the next step of upscaling towards commercial exploitation. The technology seems to be moving in the right direction, but it is too early to suggest that the current goals can definitely be achieved.

Contact

Sascha Kersten University of Twente P.O. Box 217 7500 AE Enschede The Netherlands

T: +31 53 489 9111 E: <u>s.r.a.kersten@utwente.nl</u>

W: www.utwente.nl

UNIVERSITY OF TWENTE.

Transportable fast pyrolysis process for distributed conversion of waste biomass to bio-oil



Paul Yelvington of Mainstream Engineering Corporation, USA, takes us through progress in their pyrolysis reactor development

Mainstream Engineering Corporation (MEC) is developing a transportable, small-scale pyrolysis reactor for the conversion of lignocellulosic waste biomass and mixed waste to pyrolysis bio-oil. The company operates a 1 tonne/ day (tpd) pilot reactor at its Rockledge, Florida facility. Funding for the work has come primarily from the US Air Force with additional funds provided internally and from the US Office of the Secretary of Defence. The Air Force's interest arose from a desire to extend the lives of landfills at Air Force installations by diverting some of the incoming organic waste material.¹ In addition, expanded on-site generation of renewable energy was seen as a way to improve energy security and help mitigate the risk of power outages, supporting the Air Force's goal of



Figure 1: Mainstream Engineering Corporation's pyrolysis project team (left to right: Nich Schwartz, Paul Yelvington, and Ted Amundsen) pictured with the 1 tonne/day pilot reactor at the company's Rockledge, Florida facility.

producing 25% of on-base power from renewable sources by 2025.¹ MEC is also targeting commercial applications—as MEC is a Florida company, initial waste biomass feedstocks of interest include logging residues, yard waste, storm debris, and sugarcane bagasse.

While MEC's implementation of fast pyrolysis includes new features geared to address several key roadblocks, the underlying fast pyrolysis technology benefits from at least 25 years of development and refinement by the global scientific and engineering community. The focus has been on circumventing technical and cost barriers that have prevented smallscale pyrolysis from taking hold commercially, namely keeping unit production costs low while avoiding shrinking process capacity (i.e., overcoming the "six-tenths" rule), as well as finding a viable nearterm offtake route for raw or mildy upgraded bio-oil. The current pilot process uses a bubbling fluidised bed reactor (41cm ID) with a patent -pending quench stage designed to minimise secondary cracking reactions.

The company's biomass programme began in 2008 and has progressed from analytical pyrolysis kinetics measurements to bench-scale testing (1kg/hr), and now to pilot-scale testing (45kg/hr). The 100-person firm specialises in providing solutions to energy

(Continued on page 15)

Transportable fast pyrolysis *...continued*

conversion and thermal control problems, so thermochemical biomass conversion was a natural extension of previous work at the company. Pyrolysis kinetic data along with yield data (bench scale) and product quality data (benchscale and pilot-scale) were reported in 2013.² The bench-scale reactor has been run with pine sawdust and the pilot reactor has been run with pine sawdust as well as a mixed-waste surrogate feedstock. The mixed-waste feedstock contained granulated paper, corrugated cardboard, and several plastics (polystyrene, PET, and HDPE).

The pine bio-oil from the benchscale reactor was fully characterised and found to meet all ASTM D7544 requirements with the exception of ash content, which was slightly higher than the acceptable value. The high ash content may have been due to entrainment of solid ash/char particles in the bio-oil. The pine bio -oil collected from the pilot-scale reactor was slightly higher in moisture content and lower in heating value compared to the bench-scale reactor. These differences in product quality are believed to be due to differences in bio-oil collection efficiency between the pilot and bench reactors.

The water content was lower for the mixed-waste bio-oil compared to the pine bio-oil and the heating value was considerably higher. The oxygen content of the bio-oil produced from mixed waste was also considerably lower than the pine bio-oil. The lower oxygen content of the oil derived from mixed waste is due to lower oxygen content in the feedstock which included some oxygen-free plastics. The lower oxygen content lends itself to better bio-oil stability (less ageing) and improved upgrading potential (lower hydrogen requirement for deoxygenation). Although not measured, the mixed-waste bio-oil



Figure 2: Pilot-scale fast pyrolysis process during laboratory testing (bubbling fluidised bed reactor shown in inset).

was observed to have a considerably higher viscosity than the pine bio-oil.

Recently, the team's efforts have focused on making improvements to the solids conveyance and product separation portions of the process. Under a recently announced grant from the US Department of Energy set to begin this month, a new feedstock preprocessing and conveyance unit will also be developed with the aim to reduce capital and operating costs. This technology is particularly well-suited to smallscale operations where operator costs have a huge impact on the bottom line.

The long-term vision of the company is to commercialise small -scale pyrolysis reactors at the 1tpd scale for military applications and the 10tpd scale for commercial applications. It is envisioned that the 1tpd unit would be packaged in a standard Tricon shipping container, and the 10tpd unit in a standard semi-trailer. MEC is also interested in partnering with other researchers to evaluate innovative fast pyrolysis techniques in our well equipped pilot facility.

Contact

Paul Yelvington Mainstream Engineering Corporation 200 Yellow Place Rockledge, FL 32955 USA

T: +1 321 631 3550 E: <u>pyelvington@mainstream-</u> <u>engr.com</u>

www.mainstream-engr.com/ research/energyconversion/



References

- "Renewable Fuel from Transportable Waste Converter," Air Force SBIR/STTR Innovation Story, Nov. 2013, available from www.afsbirsttr.com/Publications/ SBIRImpactStory.aspx.
- Yelvington, P.E., N.R. Schwartz, D.J. Zastrow and T.J. Amundsen, "Transportable Fast-Pyrolysis Process for Distributed Conversion of Waste Biomass to Renewable Liquid Fuels," paper presented at the 2013 AIChE Annual Meeting, San Francisco, CA, Paper No. 324743.

Easy molecular characterisation of bio-oil via the Polyarc[™] reactor





Andrew J. Jones (top) and Paul J. Dauenhauer (bottom).

High-temperature pyrolysis of lignocellulosic biomass produces gases, solid residue and condensable vapours which can be converted to biofuels and biochemicals.¹ The vapours, referred to as 'bio-oil,' are comprised of a large number of highly oxygenated chemical species, some of which have

e larc

Andrew J. Jones of Activated Research Company and Paul J. Dauenhauer of the Catalysis Centre for Energy Innovation, both USA, discuss the advantages of the Polyarc[™] reactor

multiple functional groups and are extremely reactive.

Commercialisation of the thermochemical biorefinery concept necessitates the production of bio-oil in sufficient quantity and quality to meet the requirements for commodity chemicals on the open market. The biorefinery concept bifurcates a processing plant into upstream pyrolysis and downstream refining processes, where the latter is accomplished with an approach similar to today's centralised petroleum refineries. High energy density and thermal stability are also required for the economical distribution of bio-oils through the existing pipeline infrastructure. In spite of the need for higher quality bio-oils, processing technology controlling the production of biooils is not well developed, especially processes pertaining to controlling pyrolysis chemistry² and rapidly quantifying molecular distributions of bio-oil and upgraded fuel mixtures.

We introduce a new technology, referred to as the Polyarc™ reactor,^{3,4} to quantify the molecular distribution of complex mixtures such as bio-oil without the need for the identification or calibration of individual organic chemical species. As depicted in Figure 1, the Polyarc[™] reactor is comprised of a small 3D-printed microreactor which is integrated within existing gas chromatography flame ionisation detector (FID) analysis systems. The microreactor utilises cascade catalytic channels to convert all potential analytes (e.g. levoglucosan, HMF, glycolaldehyde) to methane, thus allowing for identical detector response factors. In other words, the resulting flame ionisation detector response is always proportional to the quantity of carbon in the eluent. Thus, separation of bio-oil mixtures using a Polyarc[™] reactor within a GC-FID will result in chromatographic separation of 50-200 compounds, which can be integrated individually or in groups (i.e.

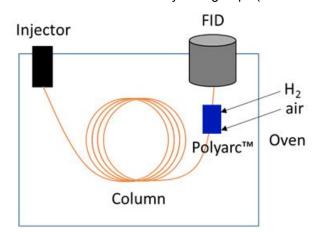


Figure 1. Polyarc[™] reactor system.⁴ Left: 3D-Printed Reactor. Right: Schematic of Integrated Polyarc[™] reactor.³

IEA Bioenergy Agreement Task 34 Newsletter - PyNe 37

Easy molecular characterisation of bio-oil *...continued*

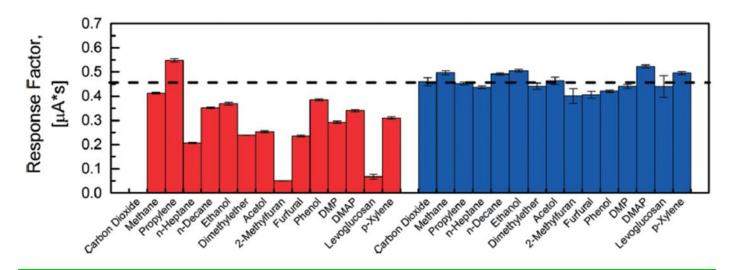


Figure 2: Relative response factors (normalised to a methane internal standard) of molecules in a GC-FID (red; left) and in a GC-FID with the PolyarcTM reactor (blue; right).³ The GC-FID response varies over an order of magnitude depending on the identity of the molecule (CO₂ is not detected), while response factors with the PolyarcTM reactor are similar.

clustered compounds) to determine their carbon content.

The optimal design of the Polyarc[™] reactor ensures accurate quantification of pyrolysis oils and subsequent hydrotreated/upgraded mixtures. The 3D-printed reactor includes micro-channels that maintain chromatographic resolution. The Polyarc[™] reactor can be directly inserted into existing GC systems designed to separate bio-oil and fuel mixtures without altering the separation quality. The microreactor system was also designed using thermodynamic calculations of converted bio-oil compounds to ensure >99.9% conversion to methane,³ thus ensuring the accurate quantification of carboncontaining compounds in all possible bio-oil and fuel compounds.

Figure 2 shows detector response data for several bio-oil compounds using conventional detection (FID – flame ionisation detection) versus the detection with an integrated microreactor (as discussed previously³). Conventional methods result in a detector response that can vary by as much as an order of magnitude, with highly oxygenated

or hydrogen-deficient compounds common to bio-oil providing only negligible response. In comparison, the same compounds provide nearly identical response via the new method of an integrated microreactor.

The microreactor technology has been commercialised via Activated Research Company (Minneapolis, MN, USA) which provides the Polyarc™ reactor in a small device (Figure 1) which can be incorporated into existing GC-FID and GC-FID/MS systems. The PolyarcTM reactor is designed to integrate with existing GC-FID software, hardware and gases. Complete details of the device are available via the company's website including device cost and installation information.⁴

Support

Development of the Quantitative Carbon Detector (now called the Polyarc[™] reactor for commercial purposes) was sponsored by the US Department of Energy, Basic Energy Sciences as part of the Catalysis Center for Energy Innovation, a US Energy Frontier Research Center (www.efrc.udel.edu).

Contact

Andrew Jones Activated Research Company 7561 Corporate Way Eden Prairie, MN 55344 USA

E: contact@activatedresearch.com

W: www.activatedresearch.com



References

- 1. Di Blasi, C., Progress in Energy and Combustion Science 2008, 34, 47-90.
- Mettler, M.S., Paulsen, A.D., Vlachos, D.G., Dauenhauer, P.J., Catalysis Science and Technology 2014, DOI: 10.1039/c4cy00676c.
- Maduskar, S., Teixeira, A.R., Paulsen, A.D., Krumm, C., Mountziaris, T.J., Fan, W., Dauenhauer, P.J., Lab on a Chip 2015, 15, 440-447.
- 4. Activated Research Corporation. <u>http://</u><u>www.activatedresearch.com/</u>.

IEA Round Robin on pyrolysis oil production and analysis in progress



Dietrich Meier of Thünen Institute of Wood Research in Germany, updates readers on the IEA Round Robin

In Spring 2014 the IEA Bioenergy Task 34 members agreed on the execution of a Round Robin aimed at enhancing the pyrolysis community's understanding of the production of fast pyrolysis bio-oil by providing three common feedstocks for bio-oil preparation: hybrid poplar, wheat straw, and a blend of 70wt% hybrid poplar, 15wt% wheat straw, and 15wt% thinning residues. The biomass samples were prepared, conditioned, and distributed to the participants by Idaho National Laboratory, USA. Samples were sent out in summer 2014. The participants were required to produce a minimum of 500ml biooil from each feedstock and return the samples to a central analytical laboratory (Thünen Institute of Wood Research, Hamburg, Germany) for property



Figure 1: Bio-oil samples received at Thünen Institute of Wood Research.

determination. Participants were also asked to provide a description of the reactor system used, yields of bio-oil, char and gases as well as operating conditions such as reactor temperature, residence time, condensation temperature etc. Table 1 gives an overview of the sample characteristics.

The following 19 laboratories from the six member countries agreed to participate: USA

- PNNL
- NREL
- Michigan State University
- University of Maine
- Georgia Tech
- Iowa State
- University of Minnesota
- University of Washington

UK

- Aston University
- Future Blends
- Leeds University

Germany

- TI
- KIT
- Fraunhofer UMSICHT

Netherlands

- University of Groningen
- ECN

Sweden

- ETC
- KTH
- Finland
 - VTT

The following list shows the analytical methods applied at Thünen Institute of Wood Research:

- 1. Water content (Karl-Fischer titration)
- 2. Elemental analysis, CHNS (complete oxidation)
- Quantitative determination of volatiles (GC/MS/FID)
- Pyrolytic lignin content (precipitation in water)
- 5. Molecular weight of pyrolytic lignin (SEC)
- 6. Density (pygnometer)
- 7. Kinematic viscosity (Ubbelohde U-tube viscometer)
- 8. Total acid number, TAN (titration)
- 9. Solids (filtration)
- 10. Ash composition (ICP)
- 11. Ash (combustion)

To date bio-oils from 14 laboratories have been received.

(Continued on page 19)

S (%)

0.02

ge 18

Table 1: Proximate and ultimate analysis of feedstocks.									
Сгор Туре	State	County	Volatiles (%)	Ash (%)	C fix (%)	H (%)	C (%)	N (%)	O (%)
Wheat straw	Idaho	Jefferson	72.4	12.8	14.7	5.3	43.8	0.6	50.2
Thinning residues			73.1	1.4	19.9	6.3	49.7	0.3	43.8
Hybrid poplar	Oregon	Morrow	84.9	0.9	14.2	5.8	49.9	0.2	44.1
IEA Bioenergy A	IEA Bioenergy Agreement Task 34 Newsletter — PyNe 37 Pag								

IEA Round Robin *...continued*

Pictures were taken of all packages, as well as of the unpacking procedure and the biooil bottles. Sometimes videos were taken to demonstrate different viscosities and phase separation.

The first interesting observation was that none of the laboratories were able to produce a single phase bio-oil from wheat straw; all wheat straw bio-oil samples were phase separated into an aqueous and a heavy tarry phase. The phase separation of the pyrolysis liquids from the blend was less pronounced. All bio-oils from hybrid poplar arrived as a single phase liquid.

Following completion of the bio-oil production, analysis, and evaluation of results, the results of the round robin will be published by the end of 2015 in a technical journal under the authorship of the IEA Task members. Participating laboratories and operating personnel will be acknowledged by name, but results will be presented in a blind format without direct attribution to specific participants. Participants are free to publish their own results separately, but are requested to acknowledge the IEA supplied feedstocks.

Contact

Dietrich Meier Thünen Institute of Wood Research Leuschnerstr. 91b D-21031 Hamburg Germany

T: +49 40 73 962 517 E: <u>dietrich.meier@ti.bund.de</u>

W: www.ti.bund.de



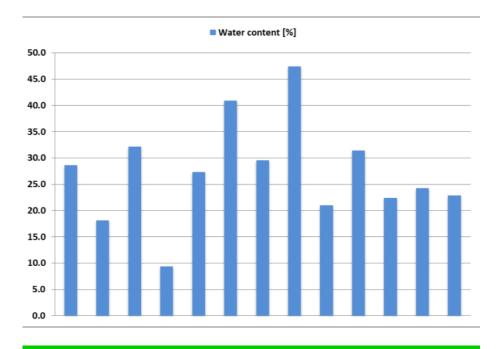


Figure 3: Water content of bio-oils from hybrid poplar.

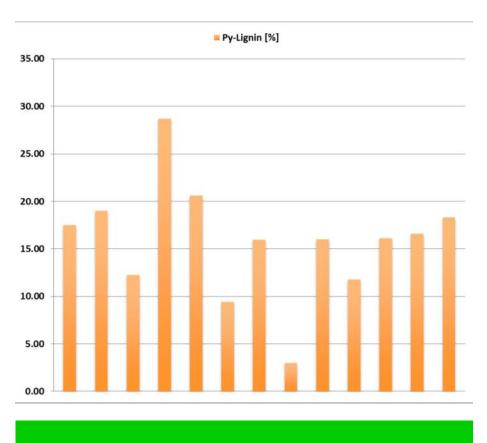


Figure 3: Pyrolytic lignin content of bio-oils from hybrid poplar.

Ablative pyrolysis surfaces for suppression of the reactive Leidenfrost effect



Paul J. Dauenhauer of the University of Minnesota, USA, takes us through recent breakthroughs in the optimisation of ablative pyrolysis

Pyrolysis of lignocellulosic biomass occurs via high temperature conversion of biopolymers to gases, solid residue, and condensable vapours which are subsequently converted to biofuels and biochemicals.¹ Conversion of woody particles (and biomass particles/fibres in general) occurs via rapid heating within an array of reactor types which vary in heating method between convective. radiative, and direct ablation. While the most common reactor types, including circulating fluid beds for fast pyrolysis, provide high yields of bio-oil, their throughput is ultimately limited by their internal heating rates. Design of the next generation of mobile pyrolysis reactors will require order-ofmagnitude enhancement in

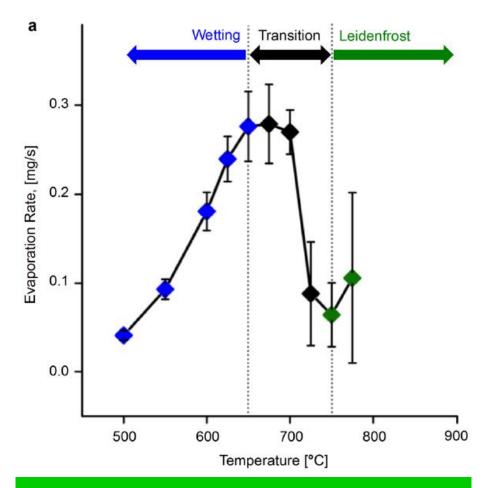


Figure 1: Reactive Leidenfrost effect cellulose on polished silicon.⁴ The evaporation rate of molten cellulose increases with increasing surface temperature before dramatically reducing at the film-boiling transition temperature. Complete particle lift-off occurs in the reactive Leidenfrost regime.

throughput, which will require substantially improved biomass particle heating rates.

Ablative (direct contact) reactor designs will be required for dramatic enhancement in fast pyrolysis throughput. While it is difficult to substantially increase gas-to-particle heat transfer by convection within a fluid/fixed bed, direct contact provides numerous tunable design parameters which can be utilised for increasing heat transfer to organic particles, including: (a) application pressure, (b) surface roughness, and (c) surface polarity. However, optimisation of surface design will first require insight into the behavior of molten cellulose

liquids. Biomass, including cellulose and lignin biopolymers, is known to form liquid intermediates which can wet surfaces, eject aerosols, coalesce as droplets, and serve as a lubricant for ablating particles.²⁻³ However, only estimates exist of the intermediate liquid viscosity and surface tension, and the behaviour of the reacting bubbling fluid(s) interacting with complex surfaces remains almost completely unknown.

In a recent publication in Nature Scientific Reports,⁴ we show for the first time that reacting intermediate liquids of cellulose exhibit complex heat transfer behaviour on heated surfaces. On polished silicon

(Continued on page 21)

Ablative pyrolysis surfaces *...continued*

surfaces (smooth), the heating rate to poly-crystalline cellulose particles increases with surface temperature, as shown in Figure 1. However, particle conversion between 650-750°C exhibits a dramatic reduction in rate as the molten cellulose droplet proceeds to generate vapours and vigorously bubble. Above 750°C, the emission rate of vapours is sufficiently high that molten cellulose droplets are physically lifted above the surface and float on the off-gas vapour. This sees the molten cellulose droplet exhibit 'reactive Leidenfrost' behaviour, whereby the vapours generated via pyrolysis flow below the droplet and lift it above the surface. Under these conditions, the particle is unstable and skitters violently about the surface. More importantly, the vapour barrier layer between the surface and molten cellulose droplet serves to dramatically reduce the overall heat transfer rate and slow droplet conversion. Visualisation of the droplet in Figure 2a reveals the extent of droplet lift-off.

Evaluation of droplet conversion on porous (pressed alumina) surfaces reveals dramatically different particle conversion behaviour. In contrast to the smooth surface, the porous surface does not exhibit transition boiling or the reactive Leidenfrost effect. As temperature increases to 750°C, the rate of heat transfer to the molten cellulose droplet increases proportionally, with no observable change in heat transfer mechanism. Additionally, the molten cellulose droplet remains stationary, as depicted via high speed photography in Figure 2b. Suppression of the reactive Leidenfrost effect was proposed to occur via vapour flow through the surface macropores, as depicted in Figure 2c.

Support

Discovery of the reactive Leidenfrost effect was sponsored by the U.S. Department of Energy,

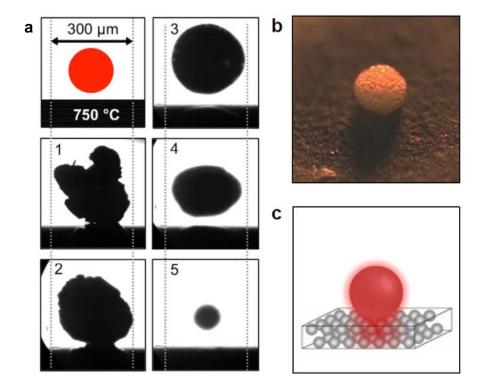


Figure 2: High-Speed Imaging of the molten cellulose reactive Leidenfrost effect. (a) Droplet liftoff on polished silica forms a suspended cellulose droplet. (b-c) Molten cellulose on a hot porous surface inhibits the reactive Leidenfrost effect and enhances heat transfer.⁴

Basic Energy Sciences as part of the Catalysis Center for Energy Innovation, a USA Energy Frontier Research Centre (www.efrc.udel.edu).

Contact

Paul J. Dauenhauer University of Minnesota Department of Chemical Engineering and Materials Science 421 Washington Ave. SE Minneapolis Minnesota 55455 USA

E: hauer@umn.edu

W: www.cems.umn.edu



References

- Mettler, M.S., Vlachos, D.G., Dauenhauer, P.J., "Top ten fundamental challenges of biomass pyrolysis," Energy & Environmental Science 2012, 5, 7797-7809.
- Lede, J., Li, H.Z., Villermaux, J., "Fusion -Like Behaviour of Wood Pyrolysis," J. Anal. Appl. Pyrolysis, 1987, 10, 291– 308.
- Teixeira, A.R., Mooney, K.G., Kruger, J.S., Williams, C.L., Suszynski, W.J., Schmidt, L.D., Schmidt, D.P., Dauenhauer, P.J., "Aerosol Generation by Reactive Boiling Ejection of Molten Cellulose," Energy and Environmental Science 2011, 4, 4306.
- Teixeira, A.R, Krumm, C., Vinter, K.P., Paulsen, A.D., Zhu, C., Maduskar, S., Joseph, K.E., Greco, K., Stelatto, M., Davis, E., Vincent, B., Hermann, R., Suszynski, W., Schmidt, L.D., Fan, W., Rothstein, J., Dauenhauer, P.J., "Reactive Liftoff of Crystalline Cellulose Particles," Nature Scientific Reports. 2015.

Ensyn bio-oil powering New Hampshire hospital



Tom Butcher of Brookhaven National Laboratory, USA, describes his experience of visiting Memorial Hospital in New Hampshire to see their bio-oil fired Ensyn boiler at work

This site visit was made as part of the Technical Information Exchange on Pyrolysis Oil Combustion meeting March 30-31, 2015. This meeting was held as part of the US-Canada Clean Energy Dialogue Programme.

Memorial Hospital is a 115,000ft² regional facility heated with two oilfired, Cleaver-Brooks, 150HP firetube boilers. In 2014 a conversion was implemented on one of the boilers to enable firing of 100% bio-oil (pyrolysis oil – wood derived). This fuel contains a high amount of water, is acidic, and is not miscible with petroleum fuels. The fuel supplier, Ensyn, took all technical responsibility for the



Figure 1: The new bio-oil tank.

conversion which included:

- Installation of a new, 15,000 gallon, stainless steel, unheated, outdoor storage tank;
- A modification of the burner by Cleaver-Brooks
- Stainless steel piping and two recirculation pumps;
- A new boiler automated control system;
- Addition of a heat exchanger soot blower system.

Fuel is delivered by stainless steel tanker trucks from the Ensyn plant in Canada. Because of the "hours of service" rules, this is a two day trip. However, during the peak heating season, several deliveries per week can be made. The site used 140,000 gallons per year of No. 4 oil prior to the conversion. Roughly twice the volume of bio-oil is needed to replace this.

Upon reaching the facility, fuel is offloaded by a pump system. During loading, the tank vents back to the truck to reduce odour potential. The atmospheric vents on the tank have charcoal filters. Standing at the base of the tank the distinct odour of the bio-oil is clear but not at all strong, and hospital staff have reported no concern with the fuel odour.

From the tank, the fuel is circulated to the boiler face where it is heated to around 160°F. Fuel pressure is ~50psi and it is air atomised. The burner is nearly "stock". Some of the fuel is returned back to the tank and 4-oil firing capability has been retained. The burner is ignited with a propane pilot which is shut off after a "brief period". During warmer weather, the unit serves only domestic hot water load and cycles without difficulty. The sootblowers involve compressed air and "blast" every 15 minutes, although the process is very short and apparently mild. Soot blowers were installed at Cleaver Brooks' request.

PM emission measurements have been made; results were not made (Continued on page 23)

Ensyn bio-oil ...continued



Figure 2: Front boiler face.

public but were stated to be only half of the emission limit. The insurance company and the Fire Marshall have visited the site and approved the conversion. The burner is UL listed for #6 oil and lighter grades but clearly not this fuel. The fuel meets the ASTM standard for pyrolysis oil. All parties consider this a very successful conversion, with start up commencing only 9 months after the hospital agreed to the project. The system operated well throughout the winter, even at -30°F outdoor temperatures.

Going forward there are plans to convert the adjacent boiler at this site. For this unit the plan is to run for one month without the soot blowers to see if they are necessary. Ensyn believe the boiler will need to be cleaned three times per year as opposed to once per year with the #4 oil. A similar conversion at another regional hospital is planned also.

Before deciding to make this conversion, hospital staff considered other alternatives including CNG, LNG, and wood chips. Economic analysis of the wood chip option vs the bio-oil option showed that the wood chips would require a much higher capital investment and 15 years to "catch up" to the pyrolysis oil, although after those 15 years the chips would transition to being the better option. However, a second significant factor in the decision was the loss of parking lot space with the wood chips.

Going forward, Ensyn realises that truck shipments from Canada are

not practical. Production expansion will involve regional pyrolysis plants.

Contact

Dr. Thomas Butcher Brookhaven National Laboratory Building 815 Rutherford Drive Upton New York 11973 USA

E: <u>butcher@bnl.gov</u>

W: www.bnl.gov/world



Opening of the EMPYRO fast pyrolysis plant

Bert van de Beld of BTG Biomass Technology Group BV and Ruud Meulenbroek of BTG Bioliquids BV in the Netherlands discuss the new EMPRYO plant and EMPYRO symposium



Bert van de Beld (above) and Ruud Meulenbroek (below)



In previous newsletters the EMPYRO demonstration project has been introduced (see PyNe Newsletters 35 & 27). The objective is to demonstrate fast pyrolysis technology at a biomass capacity of 5t/hr (~25MWth) and to simultaneously produce process steam, electricity and pyrolysis oil. The pyrolysis oil will be transported to FrieslandCampina and used on their site to replace natural gas as fuel for a steam boiler.

A national symposium was organised to take place commencing May 21 2015, parallel to the IEA Bioenergy Task 34 meeting. The symposium included 75 participants from 15 different countries and included the official opening of the EMPYRO plant. In the morning session of the first day Kyriakos Maniatis – Principal Administrator in the Directorate General for Energy of the European Commission - informed the audience of the latest developments around the Renewable Energy Directive and the Fuel Quality Directive, and also addressed new developments related to the 2030 Roadmap and the Energy Union. Doug Elliott



Figure 1: A two day symposium was organised around the opening of the EMPYRO plant.

introduced IEA Bioenergy Task 34 and the role of the Task in supporting the further development of fast pyrolysis technology and products. A number of presentations followed on the development and implementation of the EMPYRO project, and subsequently at midday delegates were able to visit the EMPYRO plant for its opening ceremony and a tour. The opening ceremony was conducted by Eddy van Hijum, governor of the Province of Overijssel, who pushed the button to start the filling of a tank truck with freshly produced fast pyrolysis oil. Some 80 participants attended the first day of the symposium and presentations were given on national policies, realisation of the plant and the use of pyrolysis oil. FrieslandCampina provided an insight into the reasoning behind their choice to use pyrolysis oil to further develop their green operations.

In the afternoon session the focus of the presentations shifted to the main product of the process, fast pyrolysis liquid/pyrolysis oil (or "bio -oil"). Martijn Vis (BTG) discussed the sustainability and certification of fast pyrolysis oil, and Pia Saari (Fortum) provided an update on ongoing European standardisation work. Next, three (potentially) nearterm applications of pyrolysis oil were presented. Marco Beune (Stork) delivered a presentation on the design, construction and implementation of the new steam boiler for FrieslandCampina, which has seen the boiler system modified so that it is suitable to cofire pyrolysis oil with natural gas and will be where the majority of the EMPYRO oil will be utilised. Lars-Uno Axelsson - chief engineer at Opra Turbines -

(Continued on page 25)

Opening of the EMPYRO fast pyrolysis plant *...continued*



Figure 2: The EMPYRO production facility.

discussed the successful modification of their OP16 turbine to enable the use of low caloric fuels including pyrolysis oil. Marlon Almeida presented the work of Petrobras on co-feeding fast pyrolysis oil with vacuum gas oil (VGO) in their large fluid catalytic cracking (FCC) demonstration plant. It appears that 5 to 10wt% of untreated pyrolysis oil can be cofed without operational problems to produce renewable diesel and gasoline. The formal programme was concluded by a short introduction from Patrick Reumerman (BTG) on the development of the fast pyrolysis platform called PyroKnown (www.PyroKnown.eu). This platform was set-up within the framework of the European EMPYRO project.

Contact

Bert van de Beld BTG Biomass Technology Group BV PO Box 835 7500AV Enschede The Netherlands

E: vandebeld@btgworld.com

W: www.btgworld.com



Figure 3: Tours of the EMPYRO plant were included in the symposium.

Ruud Meulenbroek BTG Bioliquids BV PO Box 835 7500AV Enschede The Netherlands

E: ruud.meulenbroek@btg-btl.com

W: www.btg-btl.com



biomass-to-liquid

NEWSFLASH: Ensyn and Youngstown Thermal sign RFO[™] biofuel supply agreement

An Ensyn Press Release 3rd June 2015

YOUNGSTOWN, OHIO, - Ensyn Fuels Inc. ("Ensyn Fuels"), a wholly -owned subsidiary of Ensyn Corporation ("Ensyn"), has signed a contract with Youngstown Thermal LLC ("Youngstown Thermal") for the supply of RFO™, Ensyn's advanced cellulosic biofuel. Ensyn Fuels is to provide Youngstown Thermal up to 2,500,000 gallons of Renewable Fuel Oil or RFO per year, with deliveries to begin as soon as the fourth quarter of 2015, in time for the 2015-2016 winter season. Youngstown Thermal will use the RFO to displace up to 50% of its fuel needs in their natural gas fuelled boiler. This five-year contract follows a series of successful RFO combustion demonstrations carried out at Youngstown Thermal in 2014.

Youngstown Thermal is the owner and operator of the steam distribution system in Youngstown, Ohio. Youngstown Thermal provides steam for heat and hot water for the central business district of Youngstown including the Youngstown State University. Youngstown Thermal owns and operates four boilers at the site.

Ensyn Fuels' initial deliveries of RFO are expected to be produced at Ensyn's three million gallon/year facility in Ontario, with eventual supply from the Ontario facility and/ or one of several new projects Ensyn and its partners are developing in Eastern Canada/ Eastern US. Ensyn's Ontario facility has been qualified by the **US Environmental Protection** Agency (EPA) under the US Renewable Fuel Standards (RFS2) program. Ensyn expects that sales of RFO to Youngstown Thermal will qualify for Renewable Identification Numbers (RINs) under the RFS2 program.

This initiative represents the first commercial use of Ensyn's RFO in a district heating system and demonstrates Youngstown Thermal's leadership in innovative district heating solutions. This



Ensyn's Ontario facility

contract will anchor Youngstown Thermal's commitment to transition its fuel requirements from fossil fuels to renewable energy sources. The RFO supply contract will allow the company to reduce greenhouse gas emissions and produce and sell heating services with enhanced sustainability characteristics. Youngstown Thermal will be able to achieve all of this this while also generating cash savings.

Ensyn Fuels will provide Youngstown Thermal with dedicated on-site storage for the RFO and an RFO delivery system, including a new burner.

New pyrolysis knowledge platform: www.pyroknown.eu

PyroKnown, get to know everything about fast pyrolysis!

The <u>Pyroknown</u> website is dedicated to sharing knowledge and learning about biomass fast pyrolysis. In this process biomass is converted by thermochemical treatment into a versatile liquid fast pyrolysis liquid. This liquid can be used for the production of energy, chemicals and biobased materials.

On this pyrolysis platform, knowledge is shared in four ways: <u>PyroWiki</u>: all relevant information about pyrolysis is shared in this wiki. PyroWebinar: webinars about pyrolysis and related projects. PyroMovies: movies about all aspects of pyrolysis such as production, use, and application. PyroLearn: In this section, courses about pyrolysis can be followed.

If you have any further questions or if you want to contribute to the website, please send an email to info@pyroknown.eu.

The website was founded as part of the EU FP7 funded project EMPYRO.



www.pyroknown.eu

Bamboo pyrolysis for fuels, chemicals and energy









From top: Paul de Wild, Ron van der Laan, Jan Hanse and Raghu Sumbharaju

Paul de Wild, Ron van der Laan, Jan Hanse and Raghu Sumbharaju of ECN in the Netherlands offer an insight into ECN's work on the Dutch national project, LigniFAME

Within the Dutch national project "LigniFAME" (Lignin for Fuel Additives, Materials and Energy), ECN explores the valorisation potential of lignin and lignin-rich biomass types via pyrolysis. Among the feedstock addresssed are cornstover lignin, spruce bark and bamboo.

Bamboo vulgaris, or common bamboo, is a globally abundant and fast growing herbaceous type of biomass that demands little and offers much. It is a common plant species in the (sub) tropics in Asia, Africa and South America, and has a wide variety of uses, especially as a construction material. Its use as a feedstock for value-added fuels, chemicals and/or energy is relatively underexploited. Bamboo grows fast and has – in general – a high tolerance to various environmental conditions. It does not compete with food and/or feed crops and its high content of lignin makes it an interesting feedstock for the production of aromatic chemicals, e.g. by pyrolysis.

Within the LigniFAME project, a specific type of continuous pyrolysis technology is being developed and deployed to convert bamboo into (precursors for) liquid fuels, chemicals and performance materials. Using a continuous (Continued on page 28)



Figure 1: Paul de Wild holding a freshly recovered bamboo pyrolysis liquid sample.

Bamboo pyrolysis ...continued

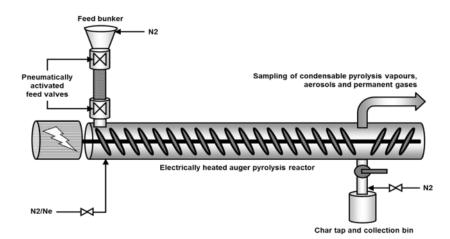








Figure 2: Intermediate pyrolysis of bamboo in a fully automated single screw auger reactor.

auger (screw) reactor with staged condensation of the pyrolysis vapours, bamboo was pyrolysed at 450°C into bio-oil, biochar and combustible gas. Figure 2 presents a schematic overview of the auger reactor.

The bio-oil was collected in two fractions: an organic phase, containing a high concentration of phenolic compounds, and an aqueous fraction predominantly containing acetic acid, furfural and other sugar-derived degradation fragments. Figure 3 gives an overview of the main pyrolysis products that were recovered and analysed.

Most phenols are found in the organic phases (KO-drum organic + ESP) while the aqueous fractions

are substantially higher in acids, carbonyls and methanol compared to the organic fractions. Levoglucosan predominantly shows up in the ESP fraction. 75 -85wt% is water plus unidentified organics (unknown GC-detectables and unidentified/non-detectable organics that likely consist of larger bamboo degradation fragments of various natures). Aside from a higher content of poly-aromatic hydrocarbons, which is possibly due to condensation of hot pyrolysis vapours on the char, the bamboo char qualifies as "premium quality biochar" for soil improving. Pyrolysis tar condensation has been verified via SEM analysis on a representative biochar piece. This condensation can be prevented by proper flow conditions of the carrier gas.

The organic phase can be exploited as a liquid fuel for both stationary boilers and mobile applications (e.g. shipping fuel), as feedstock for extraction of highvalue chemicals and possibly as a renewable alternative for petrochemical phenol in applications such as phenolformaldehyde resins and similar. The aqueous phase may be used as a cheap and bio-alternative to synthetic pesticides. In addition, its high content of acetic acid may render it a potential feedstock for the production of calcium magnesium acetate as an environmentally friendly de-icer (when compared to the corrosive rock salt). Depending on the content of sugar-derived degradation fragments, specific

(Continued on page 29)

Bamboo pyrolysis ...continued

biochemical routes (fermentations) could be considered as well. Finally, the char is useful in fertiliser/soil improving applications. Char combustion in co-firing applications may also be an option; feasibility will depend on type and amount of inorganic material with regard to possible slagging and fouling of boilers and downstream equipment.

The results so far indicate the valorisation possibilities of bamboo via pyrolysis. Techno-economic assessments, scale-up and end-use trials of the pyrolysis products are necessary to provide further insight into the near-future-potential of thermochemical exploitation of this versatile material for fuels, chemicals and energy.

The presented work has been conducted with financial support from the Dutch Ministry of Economic Affairs in the framework of the "LigniFAME" project, part of the national programme TKI-BBEI (Biobased Economy, Innovation projects).

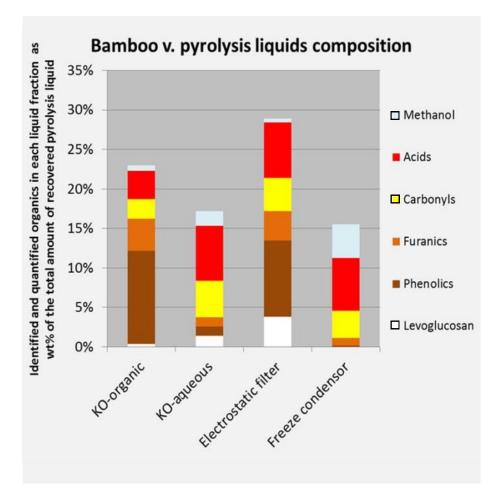
Contact

Paul de Wild ECN Westerduinweg 3 NL-1755 LE Petten Netherlands

T: +31 88 515 4270 E: <u>dewild@ecn.nl</u>

W: www.ecn.nl





Bamboo v. pyrolysis product recovery as wt% of the total feedstock intake

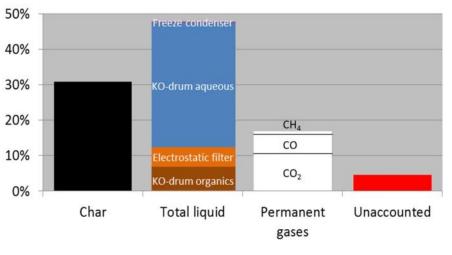


Figure 3: Data on bamboo pyrolysis products.

In situ catalytic pyrolysis of biomass and upgrading the bio-oil to liquid hydrocarbons



From left: Doug Elliott, Daniel M. Santosa, Yrjö Solantausta, Ville Paasikallio, and Foster Agblevor.

Doug Elliott and Daniel M. Santosa of Pacific Northwest National Laboratory, USA, Yrjö Solantausta and Ville Paasikallio of VTT, Finland, and Foster Agblevor of Utah State University, USA, offer an insight into catalytic pyrolysis research

Fast pyrolysis is a direct route to liquid bio-oil from solid biomass. However, the quality of the bio-oil is such that further processing is made more difficult by the thermal instability of the mix of components. Catalytic hydroprocessing has been applied to bio-oil in order to produce infrastructure-compatible liquid hydrocarbon fuels but difficulties have led to multi-step processing in order to avoid bio-oil decomposition and fouling of the catalyst bed.¹ The alternative of catalytic pyrolysis has been suggested as a route to lead to a

more stable and therefore more easily upgradeable bio-oil. Catalytic pyrolysis bio-oil can be produced in circulating fluidisedbed reactors akin to the catalytic crackers used in petroleum processing. Through careful selection of the catalyst and operating parameters, a bio-oil with improved properties can be produced, as reported at tcbiomass 2014.² The resulting product has a reduced oxygen content, lower water content and modified component composition and therefore can be more readily hydroprocessed than raw bio-oil



Figure 1: 3D model image of the fast pyrolysis pilot plant at VTT in Espoo, Finland.

from fast pyrolysis.

A collaborative research and development project involving a partnership between Pacific Northwest National Laboratory (PNNL), VTT Technical Research Centre of Finland (VTT) and Utah State University (USU) has been implemented to validate an integrated conversion process for biomass to liquid hydrocarbon fuel by in situ catalytic pyrolysis and catalytic hydrotreating. This new effort is geared towards developing (at bench scale) and demonstrating (at pilot scale) the hydrotreating technology for in situ catalytic pyrolysis bio-oil. In situ catalytic pyrolysis in a circulating fluidised bed reactor was demonstrated at VTT and the proof of principle of hydrotreating that product bio-oil in a single step hydrotreater was first shown at PNNL.

Initial tests with *in situ* catalytic pyrolysis in the VTT process development unit (PDU) produced sufficient product oil for initial tests in the mini-hydrotreater reactor (nominal 30mL catalyst bed) at PNNL. The tests provided initial data input, which was provided to NREL/PNNL for process analysis.

Using only a single-stage, fixedbed catalytic system at higher space velocities, the catalytic

Page 30

In situ catalytic pyrolysis *...continued*

pyrolysis bio-oil can be hydrotreated to a liquid hydrocarbon product with low oxygen content, <1wt%, in a continuous-flow reactor system. Catalysts used included promoted molybdenum sulfide catalysts. The results show that the aluminasupported catalyst was physically degraded during the test, which has led to formulating a new catalyst on an alternative catalyst support. The new catalyst was tested in the mini-hydrotreater and was successfully operated for 57 hours. This test validated the stability of the new formulation and the possibility of operating with a single stage hydrotreater for catalytic pyrolysis bio-oil. This catalyst formulation has now been tested with a different catalytic pyrolysis bio-oil from USU using a red mud catalyst. The hydrotreating test proceeded for over 300 hours before being terminated when the feedstock was consumed. Stability of the catalyst was good throughout and the product quality and yield was high.

These initial tests and the resulting analysis suggested that additional effort should be undertaken to further develop catalysts and to validate the hydrotreating results. This project will have significant impact in 2015 as it will demonstrate production of liquid hydrocarbon fuels in litre quantities through collaboration with in situ catalytic pyrolysis process development at VTT in their new half tonne per day fast pyrolysis pilot plant and bench-scale hydrotreating at PNNL. In the subsequent years of 2016 and 2017 the technology will be transitioned to larger scale production, if the initial assessment is positive. A 2017 demonstration of the two technologies, in situ catalytic pyrolysis and catalytic hydrotreating of the product bio-oil, will be undertaken.

The future

VTT has been operating a fast

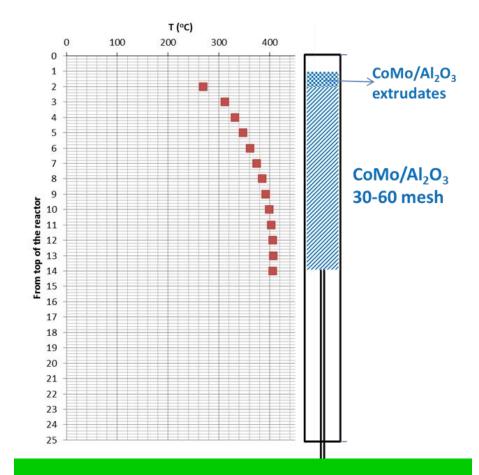


Figure 2: Mini-hydrotreater bed schematic with temperature profile from PNNL in Richland, Washington, USA.

pyrolysis PDU for the past 20 years in Espoo. Finland. At the end of 2014, VTT started to build a new pilot unit in their new experimental facilities, which are located in the district of Kiviruukki in Espoo, approximately 10km west of the old laboratories in Otaniemi. The new Bioruukki facility includes all of the large scale VTT pyrolysis and gasification units. The main components of VTT's new fast pyrolysis pilot unit were delivered to the premises and mechanically installed during the first quarter of 2015. This includes the biomass feeding system, reactor and cyclones, combustor, liquid recovery system, and a wide array of other components associated with the aforementioned key items. Both thermal and catalytic pyrolysis developments will continue, with operations expected to resume over the summer of 2015.

We look forward to presenting the research details in the coming months at the US Department of Energy's Bioenergy2015 conference in Washington, DC, in June and the tcbiomass2015 conference in Chicago in November.

Contact

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
- W: www.pnnl.gov

(Continued on page 32)

In situ catalytic pyrolysis *...continued*



Figure 3: Fast pyrolysis pilot plant at Utah State University in Logan, Utah, USA.



References

- Zacher, A.H., Olarte, M.V., Santosa, D.M., Elliott, D.C., Jones, S.B., A Review and Perspective of Recent Biooil Hydrotreating Research. Green Chemistry, DOI: 10.1039/c3gc41382a.
- Paasikallio, V., Lindfors, C., Kuoppala, E., Solantausta, Y., Oasmaa, A., Lehto, J., Lehtonen, J., Product quality and catalyst deactivation in a four day catalytic fast pyrolysis production run. Green Chemistry, DOI: 10.1039/ C4GC00571F.

Dr Donald Scott

Tony Bridgwater of Aston University, UK, remembers his friend and colleague, Dr Donald Scott, who passed away in April this year



Donald Scott (left) receiving an award from Tony Bridgwater for his contribution to the field of fast pyrolysis.

Dr Donald Scott died peacefully on April 7th, 2015, in his 93rd year. His academic career started with a Master's degree from the University of Alberta and he studied Chemical Engineering at the University of Illinois where he received his PhD In 1949 he was appointed as an Assistant Professor in the Department of Chemical Engineering at the University of British Columbia, where he remained for the next 15 years.

After a year as a visiting Professor at Cambridge University (UK), he was appointed in 1964 as a Professor and Chairman of the Chemical Engineering Department at the newly established University of Waterloo, in Ontario. He remained at the University until his retirement in 1989, although he continued as a Research Professor with a major research programme in energy until 2004. He is notable for his contributions to the development of fast pyrolysis in fluidised beds for production of liquids from biomass. He published extensively and established himself and his team at Waterloo as leaders in fast pyrolysis, attracting world-wide interest and resulting in the establishment of semicommercial demonstration plants in Canada and Spain.

He leaves a wide international circle of fellow researchers and colleagues in his field who were privileged both to work alongside him and to count him as a friend.

International Events

July 2015

9th-10th <u>Canada - EU Workshop on: Renewable Carbon</u> <u>Sources Processing to Fuels and Chemicals</u> Brussels, Belgium

19th-22nd <u>World Congress on Industrial Biotechnology</u> Montreal, Canada

20th-22nd <u>1st Chemistry in Energy Conference (CEC)</u> Edinburgh, UK

August 2015

10th-12th Industrial Biotechnology Congress Birmingham, UK

17th-19th <u>RISI Latin American Conference</u> Sao Paulo, Brazil

21st-23rd <u>World Renewable Energy Technology Congress &</u> <u>Expo-2015</u> Delhi, India

26th-28th Biofuels-2015 Valencia, Spain

September 2015

2nd-4th BIOENERGY 2015 Jyväskylä, Finland

7th-9th ISWA 2015 Antwerp, Belgium

16th-17th European Biomass to Power Berlin, Germany

22nd-24th Biofuels International Conference & Expo Porto, Portugal 24th-26th WCBE-2015 Xi'an, China

26th September-1st October <u>ECCE10</u> Nice, France

27th September-2nd October <u>Biorefinery I: Chemicals and Materials from</u> <u>Thermo-Chemical Biomass Conversion and Related</u> <u>Processes</u> Chania, Greece

29th-30th <u>4th Conference on Carbon Dioxide as Feedstock</u> <u>for Chemistry and Polymers</u> Essen, Germany

October 2015

19th-22nd BioCycle REFOR15 Boston, USA

21st-23rd International Bioenergy (Shanghai) Exhibition and Asian Bioenergy Conference 2015 Shanghai, China

27th-29th IEA Bioenergy Conference 2015 Berlin, Germany

November 2015

2nd-5th tcbiomass2015 Chicago, USA

18th-20th <u>RENEXPO® SOUTH-EAST EUROPE</u> Bucharest, Romania

23rd-25th <u>4th Latin American Congress BIOREFINERIES</u> Concepción, Chile

For the latest news on events visit WWW.DVNE.CO.UK

International events

IEA Bioenergy

The upcoming conference will provide stakeholders from industry, academia and policy with an insight into recent research and market developments in bioenergy. All topics covered by IEA Bioenergy and by partner organisations like FAO, GBEP and UNDP will be addressed. A special section is dedicated to industrial developments and applications.

Presentations will respond to challenges in all steps in bioenergy value chains from biomass production and conversion to energy carriers to different end uses. Crosscutting topics like sustainability (GHG emissions), socio-economic issues and trade will also be discussed. Policy makers will benefit from the latest recommendations by a global scientific energy technology network.

Participants will also receive the latest information on promising bioenergy technologies and learn about bioenergy applications with a special insight into German developments. Outstanding achievements and results in the bioenergy sector will be shown through over 50 visual presentations. The conference takes place in the stimulating surroundings of Berlin and Brandenburg.

Registration is open until 29 September 2015 through

Facilities for B2B meetings will be provided. The social programme also offers opportunities for networking.



Realising the world's sustainable bioenergy potential

Berlin | Germany | 27 - 29 October 2015

With support from







by decision of the German Bundestag

ieabioenergy2015.org



and technology.

21st International Symposium on Analytical and Applied Pyrolysis

Nancy, France, 9-12 May 2016



Work related to the following topics will be especially welcome:

- Fundamental mechanisms and reactor developments for biomass, coal, petroleum and waste pyrolysis
- Pyrolysis in organic geochemistry, art and forensic, etc.
- 🝉 Catalytic pyrolysis
- Technical-economical and environmental assessment of pyrolysis processes
- Novel sampling and analytical methods for the analysis of solid, liquid or vapour pyrolysis products
- Reactive pyrolysis (such as hydro-pyrolysis)
- Synthetic polymer degradation and stability

Contact

pyro2016@progepi.fr +33 3 83 17 53 93

www.pyro2016.com

IEA Bioenergy Agreement Task 34 Newsletter - PyNe 37

Pyro2016 will offer a platform where scientists,

from academia as well as industry, can meet to discuss the recent advances in pyrolysis science

We intend to propose a scientific program with

applied work in various fields (biomass, organic

geochemistry, wastes, coal, polymers, art and forensic, etc.). Studies dealing with a multi-scale

approach to bridge the gap between molecular mechanism and reactor development will be

especially welcome. The scientific program will

follow the tradition of the previous PYRO

symposia with only one session (no parallel sessions) including invited key notes and talks.

a good balance between fundamentals and

International events



International Congress and Expo on **Biofuels & Bioenergy**

August 25-27, 2015 Valencia, Spain

OMICS Group invites you to attend the International Congress and Expo on Biofuels & Bioenergy which will be held on August 25-27, 2015 at Valencia, Spain. The theme of the conference is "Accelerating Advancements and Frontiers in Biofuels & Bioenergy"

QUICK LINKS

Abstract Submission

Registration

Scientific Programme Day 1 - August 25 Day 2 - August 26 Day 3 - August 27

Organising Committee

Call for Abstracts

Brochure & Contact Details

Biofuels-2015 is an extraordinary event designed for the international professionals to facilitate the dissemination and application of research findings related to Biofuels and Bioenergy as replacement fuels. The conference invites participants from all leading universities, research institutions and leading companies to share their research experiences on all aspects of this rapidly expanding field. The conference focuses on the production, industrial implementation strategies and economic growth from biofuels. It is a scientific platform to meet fellow key decision makers all-around the Biotech organisations, Academic Institutions, Industries, & Environment Related Institutes etc., and making the congress a perfect platform to share and gain the knowledge in the field of bioenergy and biofuels.

biofuels-bioenergy.conferenceseries.com

BIOENERGY 2015

JYVÄSKYLÄ, FINLAND 2.-4.9.2015

Registration is open

Link to registration page [here]

Call for Paper for Poster Session is still open

Submit your abstract for poster session [here] or email it to: bioenergy@benet.fi

The 2015 conference will focus on the factors affecting the future of bioenergy and biobased modern technologies and business solutions. This will include logistic systems, management, total procurement chains, the effects of the energy markets, the influence of green marketing and other trends affecting forestry, agriculture, industry and climate.

For more information about conference topics [click here]

Get together and registration: 1st September, 2015

Conference: From 2nd to 3rd September, 2015

B2B meetings: From 2nd to 3rd September, 2015

Tours: 4th September, 2015

Call for papers flyer pdf-format [here] Conference Venue: Conference and Fair Centre Paviljonki, Jyväskylä, Finland.

www.bioenergyevents.fi

International events



tcbiomass2015 The International Conference on Thermochemical Conversion Science

The Gas Technology Institute (GTI) is pleased to
announce tobiomass2015, the International
Conference on Thermochemical BiomassSave the Date
November 2-5, 2015
Westin River NorthConversion Science, to be held 2-5 November 2015
in downtown Chicago, IL USA.

A Mark your calendars and plan to connect with many of the world's leading researchers, scientists, and engineers. The scientific forum will focus on putting research into action as emerging integrated biorefineries

are being built across the globe. Be at the centre of dramatic change to discuss, learn, and assess the progress and promise of this exciting area of bioenergy. <u>Contact</u> to receive more information on tcbiomass2015 as it becomes available

3rd Iberoamerican Congress 4th Latin American Congress 2nd International Symposium on Lignocellulosic Materials Biorefinere

Science, Technology and Innovation for the Bioeconomy November 23 to 25, 2015, Concepción-Chile

www.biorrefinerias.cl

We are pleased to announce the following joint events:

3rd Iberoamerican Congress on Biorefineries (CIAB), 4th Latin American Congress on Biorefineries, and 2nd International Symposium on Lignocellulosic Materials from November 23 to 25, 2015, in the city of Concepción, Chile.

This will be the most important event in the Americas on the new uses of biomass derived from forest, agricultural and algal resources. It will bring together regional and world experts from academia, industry and government. The oral and poster presentations, and their discussion, will provide an accurate snapshot of the state of knowledge in this field, with emphasis on challenges and opportunities in Central and South America.

The Congress will include specific courses and seminars, as well as visits to companies and demonstrationscale plants, together with social and recreational activities.

Thematic areas

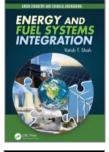
Chicago, IL USA

- Thermochemical conversion
- Biological and chemical conversion
- Economic, environmental and social sustainability
- Biomaterials and bioproducts
- Bioenergy

Important dates

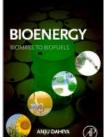
- Submission of Abstracts: March 1-July 15
- Submission of Full Papers (for oral presentations only): August 25
- Programme Announcement: September 1
- Online Registration: August 1-November 23
- IEA Bioenergy Agreement Task 34 Newsletter PyNe 37

Publications



Energy and Fuel Systems Integration (Green Chemistry and Chemical Engineering)

Published by CRC Press Publication date: September 2015 Authors: Yatish T. Shah

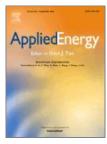


Bioenergy: Biomass to Biofuels Published by Academic Press, Elsevier Publication date: November 2014 Editor: Anju Dahiya



Biomass Power for the World

Published by Pan Stanford Publication date: April 2015 Editors: Wim van Swaaij, Sascha Kersten, Wolfgang Palz



<u>Applied Energy</u> - Volume 155 Published by Elsevier Publication date: October 2015 (in progress)

Within this journal is the following paper: <u>A new concept for enhancing energy recovery from agricultural residues by coupling</u> <u>anaerobic digestion and pyrolysis process</u> Authors: F Monlau, C Sambusiti, N Antoniou, A Barakat, A Zabaniotou



ExCo

IEA Bioenergy News - February 2015 The newsletter of the International Energy Agency (IEA)



BRISK Newsletter - Issue 7 Biofuels Research Infrastructure for Sharing Knowledge Published by Aston University Publication date: June 2015



PyNe 35



PyNe 36

Further Information

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

Kerri Lyon

European Bioenergy Research Institute School of Engineering and Applied Sciences Aston University Aston Triangle Birmingham, B4 7ET UK

T: +44 121 204 3416 E: k.lyon@aston.ac.uk

Past editions of PyNe newsletters are available on the website.



www.pyne.co.uk



Task 34 - Pyrolysis



Disclaimer: The PyNe newsletter is edited and produced by the European Bioenergy Research Institute, Aston University, UK on behalf of IEA Bioenergy Task 34 Pyrolysis. Any opinions or material contained within are those of the contributors and do not necessarily reflect any views or policies of the International Energy Agency, Aston University or any other organisation.

IEA Bioenergy Agreement Task 34 Newsletter — PyNe 37