IEA Bioenergy

Task 34
Direct Thermochemical Liquefaction
PyNe 40

40th Issue - Celebrating 21 Years of Thermochemical Liquefaction

Task 34 Meeting: Rotorua, New Zealand

Recognizing 21 years of PyNe history and the people who brought it to you!
Page 21

Task members met in Rotorua, New Zealand on November 7th and 8th to discuss recent results, plans, and strategy, graciously hosted by Ferran de Miguel Mercader who represents New Zealand at Task 34. The meeting was adjacent to the IEA Bioenergy ExCo78 so that task members were able to give talks and participate at the

ExCo workshop on Marine and Aviation fuels in addition to presenting at the Advanced Biofuels Research Network symposium held every year in New Zealand. Ferran also hosted a tour of Scion.

The ABRN conference was an excellent opportunity to experience the

Inside this Issue:

Task 34 members visiting Rotorua, New Zealand

Task 34 Meeting in Rotorua, New Zealand...continued

mixture of the dynamic interactions of the New Zealand community in the context of a country that takes a very thoughtful and long term strategic approach to managing biomass resources.

The Marine and Aviation fuels workshop was also an important forum to discuss the opportunities and challenges for thermally liquefied biomass as well as listen to the needs and challenges faced by industries that are considering renewable fuels.

Attending were Fernando Preto, Christian Lindfors, Nicholaus Dahmen, Bert van de Beld, Ferran de

Task 34 team at the Scion Nursery

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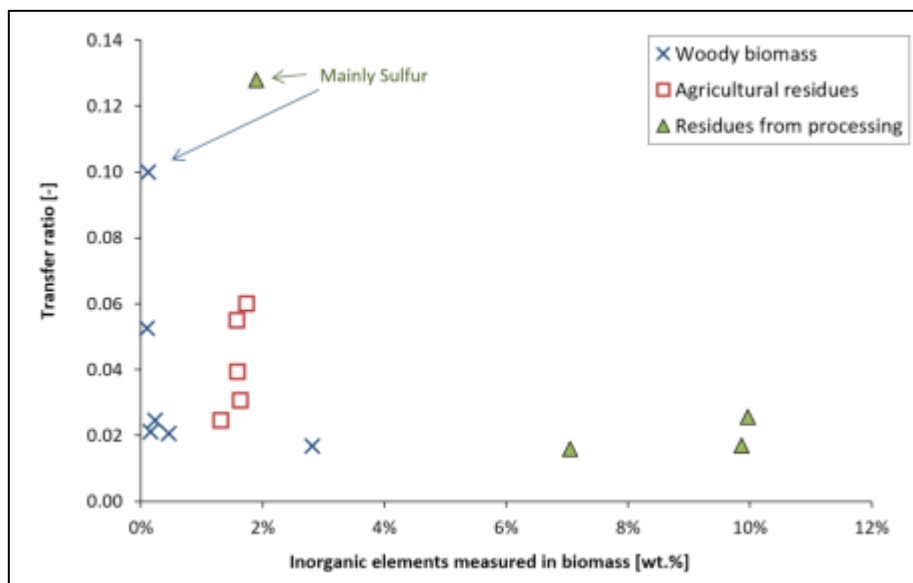# Inorganic element transfer from biomass to pyrolysis oil

Evert Leijenhorst
Process Engineer
BTG biomass technology group

The presence of inorganic elements in biomass materials can cause serious operational difficulties in high-temperature (thermochemical) conversion processes. Particularly biomass materials with relatively low ash melting temperatures are difficult to convert for example by gasification. Fast pyrolysis might be a way to avoid the difficulties caused by the inorganic elements. Most of the inorganic elements from the biomass are assumed to be retained in the solid (char) product upon pyrolysis. When the char is combusted, which is the common approach in large scale fast pyrolysis plants, the residual ash can be separated from the process. Combustion of the char can be performed at relatively low temperatures (< 600 °C), which allows the use of most biomass materials.

A detailed study has been performed on the gasification of biomass via fast pyrolysis, aiming to develop feedstock flexible processes. This work has been part of a collaboration between BTG Biomass Technology Group BV (NL) and the University of Ghent (B). In a joint PhD project, BTG's employee Evert Leijenhorst worked as part-time PhD student under the supervision of Prof. Wolter Prins and Dr. Bert van de Beld. Three different routes were investigated in which biomass is gasified via fast pyrolysis. In previous publications, the gasification of pyrolysis oil in an autothermal catalytic reformer (PyNe 31, p. 15-17) and an entrained flow gasifier (PyNe 32, p. 4-6) have been discussed. The third system is a directly coupled system producing clean fuel gas from biomass via fast pyrolysis. The assumption that most of the inorganic elements can be separated from the gaseous stream in the fast pyrolysis process has been investigated as well, and is the topic for the current contribution. Further details on the three gasification processes can be found in the various papers [1-4] or the PhD thesis [6].

From a careful literature review, the major pathways for the transfer of inorganic elements from biomass to pyrolysis oil were determined. Transfer of inorganic elements to the pyrolysis oil can occur as a result of physical processes such as the entrainment of solid particles to the gas stream, or by evaporation/sublimation of molecules containing inorganic elements. Inorganic elements can also be transferred as a result of chemical reactions between the inorganic elements and the organic volatiles produced in the pyrolysis process.

Experimental work has been performed using 16 different biomass materials, in three different pyrolysis systems (screw reactor, bench- and pilot scale modified rotating cone

Fig. 1: Transfer ratio of the sum of all inorganic elements to the pyrolysis oil as a function of the concentration in the biomass feedstock for three biomass groups.

Inorganic element transfer from biomass to pyrolysis oil ...continued

reactor). The concentration of inorganic elements in the biomass feedstock and pyrolysis oil product(s) were measured by external laboratories, and the transfer of inorganic elements from biomass to pyrolysis oil has been calculated. Results were compared with data from literature, in order to determine the dominating pathways for the transfer of the individual elements. Fig. 1 shows the experimental results on the transfer ratio of all inorganic elements (the sum) from the biomass to the pyrolysis oil. In Table 1, the averaged and median transfer for the various groups of inorganic elements to the pyrolysis oil, along with the most important pathways are presented.

The most important conclusions from the work are:

- Fast pyrolysis is an adequate technique to separate most (> 95 %) of the inorganic elements present in the biomass from the liquid product. Production of pyrolysis oil which is completely free of inorganic elements however seems unlikely, due to the wide variety and forms of inorganic elements present in the biomass.

- The separation of solid particles from either the gas and/or the liquid is the most effective way to decrease the concentration of inorganic elements in the pyrolysis oil for all elements but sulfur.

- Inorganic elements can be transferred to the pyrolysis oil by reacting with organic volatiles. This is particularly relevant for sulfur, and to a lesser degree for sodium and potassium.

Table 1: Transfer degree and the important pathways for inorganic contaminations to pyrolysis oil

Group	Transfer (average)	Transfer (median)	Important pathways to pyrolysis oil
Alkali metals (Na, K)	8.2 wt.%	2.0 wt.%	Primary: entrainment of solid particles Secondary: interaction with volatiles
Alkali earth metals (Mg, Ca)	1.8 wt.%	1.2 wt.%	Entrainment of solid particles containi
Construction metals (Fe, Ni, Cr, Mn, Zn)	20.6 wt.%	4.9 wt.%	Entrainment of solid particles containi
Non-construction metals (Pb, Co, Cd, Cu, Al)	40.7 wt.%	3.8 wt.%	Entrainment of solid particles containi Optionally: elements with low vapor p gas phase
Non-metals (S, P)	S= 47.6 wt.% P= 1.7 wt.%	S = 36.4 wt.% P = 1.1 wt.%	Sulfur: interaction with volatiles Phosphorus: entrainment of solid part

For more information, the reader is referred to the full publication [5].

References:

1. E.J. Leijenhorst, W. Wolters, L. van de Beld, W. Prins. Autothermal catalytic reforming of pine wood derived fast pyrolysis-oil in a 1.5kg/h pilot installation: Aspects of adiabatic operation. Fuel Process Technol. 2013;115:164-73.

2. E.J. Leijenhorst, W. Wolters, L. van de Beld, W. Prins. Autothermal Catalytic Reforming of Pine-Wood-Derived Fast Pyrolysis Oil in a 1.5 kg/h Pilot Installation: Performance of Monolithic Catalysts. Energ Fuel. 2014;28(8):5212-21.

3. E.J. Leijenhorst, D. Assink, L. van de Beld, F. Weiland, H. Wiinikka, P. Carlsson, O.G.W. Öhrman. Entrained flow gasification of straw- and wood- derived pyrolysis oil in a pressurized oxygen blown gasifier. Biomass and Bioenergy. 2015;79:166-76.

4. E.J. Leijenhorst, W. Wolters, L. van de Beld, W. Prins. Staged Biomass Gasification by Autothermal Catalytic Reforming of Fast Pyrolysis Vapors. Energ Fuel. 2015;29(11):7395-407.

5. E.J. Leijenhorst, W. Wolters, L. van de Beld, W. Prins. Inorganic element transfer from biomass to fast pyrolysis oil: review and experiments. Fuel Proces Technol. 2016;149:96-111.

6. E.J. Leijenhorst, Biomass gasification via fast pyrolysis. PhD thesis, University of Ghent, ISBN 978-90-5989-894-3.

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PHASR Reactor for Intrinsic Kinetics and Energetics of Biomass Pyrolysis

Figure 1. PHASR Pyrolysis Method (Pulse-Heated Analysis of Solid Reactions)[2]. Thin films of biomass (<70 μm) are exposed to a thermal pulse varying in length from 20 milliseconds to 2.0 seconds, followed by rapid quench. The resulting quenched intermediate and vapors are then analyzed by chromatography.

Paul J. Dauenhauer - University of Minnesota, Department of Chemical Engineering & Materials Science

Pyrolysis of lignocellulosic biomass occurs via high temperature conversion of biopolymers to gases, solid residue, and condensable vapors which are subsequently converted to biofuels and biochemicals[1]. Conversion of woody particles (and biomass particles/fibers in general) occurs via rapid heating within an array of reactor types which vary heating method between convective, radiative, and direct ablation. Rapid heating of lignocellulosic biopolymers initiates a complex network of spontaneous reactions that proceed to fragment the chain; subsequent rapid quenching halts the decomposition to optimize the range of condensable volatile organic compounds. Design of the next generation pyrolysis reactors will require detailed design based on molecular-level kinetic models, which are tuned for desirable distribution of bio-oil product composition.

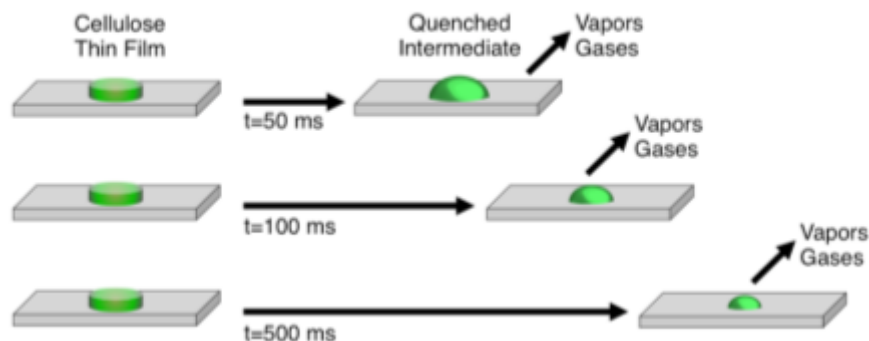Elucidating the pathways, mechanisms, and kinetics of cellulose, hemicellulose and lignin has remained a major research problem through the course of thermochemical process development. Characterizing the time-resolved evolution of decomposing biopolymers is challenging due to the mismatch of time scales between biopolymer decomposition, which occurs in milliseconds, and product analysis, which requires minutes or even hours by conventional analysis methods such as liquid/gas chromatography. Moreover, conventional thermogravimetric analysis is slow (100 °C / min) relative to high temperature pyrolysis rates; by the time a TGA temperature ramp achieves the pyrolysis temperature range, the biopolymer has significantly decomposed and is not reflective of pyrolysis conditions.

The alternative to matching reaction and analysis time scales is experimental decoupling, whereby pyrolysis reactions and product analysis occur separately. In a recent publication in Chemistry of Materials[2], we introduce a new method of studying high temperature (250 – 800 °C) solid reactions called PHASR (Pulsed-Heated Analysis of Solid Reactions) whereby thin film samples of biomass (<70 μm) are exposed to a short duration (e.g. 20 ms) thermal pulse and then rapidly quenched.

Following the thermal pulse and quench, the produced vapors and resulting biomass residue can be evaluated by slow analytical methods such as gas chromatography, liquid chromatography, NMR, or electron microscopy. This approach, depicted in Figure 1, enables temporal control of reactions and the capability of resolving compositional changes based on reaction temperature and reaction time (i.e. extent of conversion).

Temporal analysis of reacting biomass enables intrinsic measurements of reaction rates of individual molecules at pyrolysis conditions. A set of thermal pulses of biomass films by the PHASR technique produces a pyrolysis vapor mixture of 100s of compounds for every combination of reaction temperature (400, 450, and 500 C) and reaction time scale (20 – 2000 milliseconds). As pictured in Figure 2A, the yield of each individual pyrolysis product molecule is tracked with time and temperature; in this case, the yield of furan is depicted. From this analysis, it is clear that cellulose pyrolysis occurs in only a small fraction of a second above 400°C.

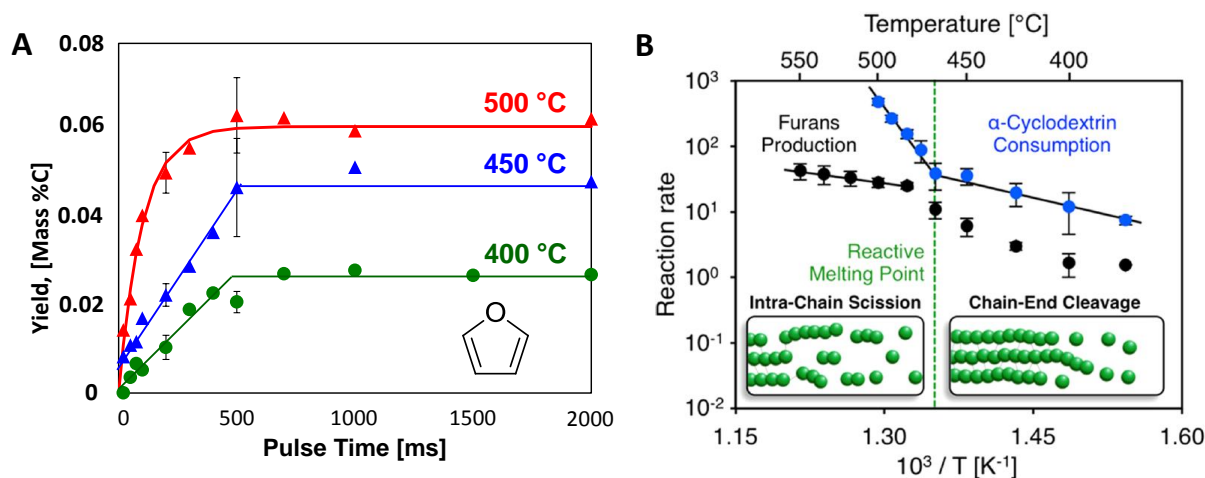# PHASR Reactor for Intrinsic Kinetics and Energetics ...continued

Figure 2. PHASR Kinetics of Cellulose Films. (A) Time-resolved yield of furan from cellulose at 400, 450 and 500 °C. (B) The differential rates of cellulose conversion (using surrogate cyclodextrin) and furans production on an Arrhenius plot reveals a kinetic transition at 467 °C consistent with a "reactive melting point" of cellulose.

By the method of quenching, it is also possible to characterize the rate of biopolymer conversion for varying reaction temperature. As depicted in Figure 1, the biopolymer residue remaining after quench can be analyzed to evaluate the extent of reaction. In this work[2], the cellulose surrogate, α-cyclodextrin, was reacted at varying temperatures (400 – 500 °C), and the initial reaction rate was measured under differential conditions (X<20%). These initial reaction rates, when plotted in Arrhenius form (Figure 2B), allow for the first measurement of cellulose conversion under transport-free conditions and reveal a distinct transition near the optimum.

Time-resolved evolution of cellulose also reveals a distinct kinetic transition at 467 °C. As shown in Figure 2B, the rate of cellulose conversion and product formation are matched (e.g. parallel lines) when correcting for product yield below 467 °C. However, higher temperatures result in a divergence of initial and product-forming rates, resulting in the formation of a kinetic intermediate identified visually as liquid intermediate cellulose. By this interpretation, cellulose exhibits a 'reactive melting point' of ~467 °C, above which processes such as pyrolysis and gasification are more favorable.

Support

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References

[1] M.S. Mettler, D.G. Vlachos, P.J. Dauenhauer, "Top ten fundamental challenges of biomass pyrolysis," Energy & Environmental Science 2012, 5, 7797-7809.
[
2] C.Krumm, J. Pfaendtner, P.J. Dauenhauer, "Millisecond Pulsed Films Unify the Mechanisms of Cellulose Fragmentation," Chemistry of Materials 2016, DOI: 10.1021/acs.chemmater.6b00580

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Hydrothermal liquefaction of microalgae

Diego López Barreiro

Wolter Prins

Fig. 1 - Biocrude oil yield for different algae species at 375 ºC and 5 min.

Microalgae are regarded as a promising feedstock for biofuel production, based on their high photosynthetic efficiency, fast growth rates and high area-specific yields. Various (hydro)thermal conversion techniques are available for converting microalgal biomass into biofuels. In this sense, hydrothermal liquefaction (HTL) appears as a highly interesting technology, as it avoids the energy penalty of drying the microalgae feedstock by processing the whole wet microalgal biomass in hot compressed water. HTL is able to deliver higher biocrude oil yields than other conversion techniques, such as lipid transesterification for biodiesel production, because it converts all the biochemical constituents of microalgae. Near-critical temperatures
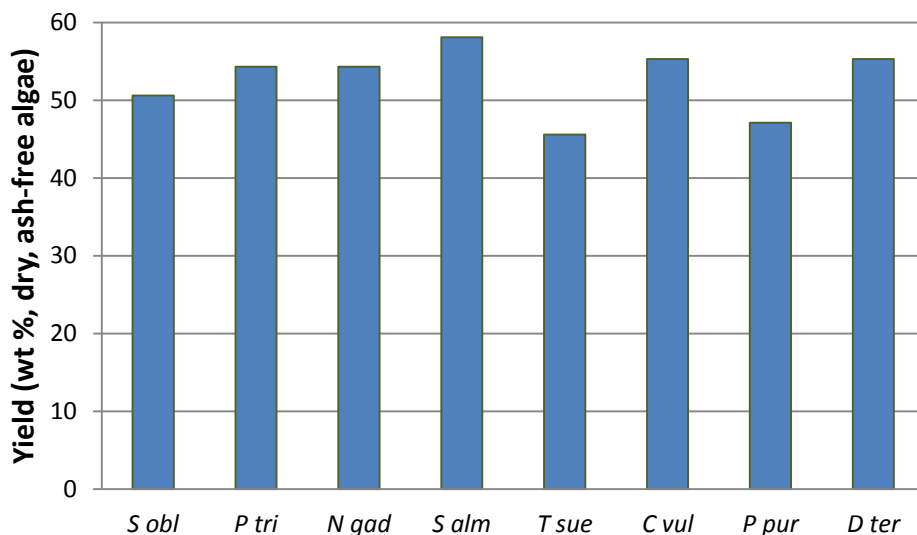
and short holding times (5 min) are optimal conditions to maximize the conversion of microalgae to biocrude oil.

Our research group on thermochemical conversion of biomass at Ghent University (Belgium), led by Prof. Wolter Prins, has become active in hydrothermal techniques since 2011. A co-operation on this field with the group from Prof. Andrea Kruse at the Karlsruhe Institute of Technology (Germany) and Dr. Wim Brilman at the University of Twente (The Netherlands) has provided plenty of new data for the development of the field of microalgae HTL. We intend to summarize in this article the main outcomes that our joint research has produced.

Species selection for the HTL process
A series of screening experiments were performed to study the effect of different species on the biocrude oil production via HTL. For that reason, microalgae slurries from eight different species were liquefied at 250 and 375 ºC in batch microautoclaves during 5 minutes [1] (Figure 1). These eight species covered a wide range of species-specific parameters (cell structure, biochemical composition and growth environment). Species-

specific parameters (especially the presence or absence of cell wall material) appeared to impact the biocrude oil yields at 250 ºC.

Conversely, the species used had no relevant influence on the results of HTL processing at 375 ºC: the biocrude oil yield and elemental composition appeared to be largely unaffected by the type of microalgae used.

Some additional screening experiments were carried out with three macroalgae species (Laminaria saccharina, Fucus vesiculosus and Alaria esculenta) [2]. The results showed that the highest biocrude yield was obtained for Alaria esculenta (29.4±1.1 wt %) at 360 ºC and 15 min of holding time. However, macroalgae produced less biocrude oil than microalgae under similar HTL conditions. Factors like the higher content of carbohydrates in macroalgae or their more complex structure (compared to the unicellular nature of microalgae) were likely the reason for this different behavior.

Influence of the biochemical constituents on microalgae HTL

Hydrothermal liquefaction of microalgae...continued

Our groups have also investigated how the biochemical constituents of microalgae affect the oil yield and quality [3]. Nannochloropsis gaditana and Scenedesmus almeriensis were subjected to HTL as raw biomass, and also after removing the lipids and proteins. Lipids were removed by solvent extraction, while proteins were enzymatically hydrolysed. The hydrolysis of proteins seemed promising, because it led to the obtainment of a valuable co-product (amino acids concentrates) while reducing the nitrogen content of HTL oil.

Separation of the HTL products

We assessed as well the influence on the HTL product yields of the use of an organic solvent (dichloromethane) to separate the aqueous phase from the biocrude oil and solid products [4]. It was shown that mixing together dichloromethane with the biocrude oil and aqueous phases to separate the two product phases increased the biocrude oil yield because organic molecules originally present in the aqueous phase were transferred to the oil phase. The biocrude oil yield appeared to increase by ca. 12 % compared to the separation without a solvent. This increase was accompanied by a higher nitrogen and oxygen content in the biocrude, showing that the use of an organic solvent transfers molecules to the biocrude oil that reduce its quality, despite increasing its yield. These results discourage the use of organic solvents for separating the HTL products, and call for the development of systems that separate them by gravity.

Continuous HTL

The vast majority of the studies on microalgae HTL reported in the literature have been done in batch reactors. For that reason, we developed a HTL operation in a continuous stirred-tank reactor (CSTR) [5]. Algae loadings in the feed slurry up to 18.2 wt % could be processed without noticeable problems for at least 3 h. Biocrude yields in the range of those from batch experiments were obtained, reaching a maximum of 54.8 wt %. However, some differences were noticed between batch and continuous results. In general, the use of batch systems stimulated the production of biocrude oil, compared to a CSTR, when similar reaction conditions are applied. This is most likely caused by the fact that biocrude oil is formed through repolymeryzation reactions that have reaction orders higher than 1. This kind of reactions are enhanced in batch or tubular reactors, as the average concentration of reactants is higher than in a CSTR. Repolymerization seems to be driven by the reaction of molecules from the protein fraction of microalgae, as higher loadings result in a higher nitrogen content for the biocrude oil.

Nutrient recycling in an HTL-based microalgae refinery

The analysis of the aqueous product obtained from HTL (HTL-AP) shows that it is highly loaded with nutrients that were originally present in the biomass feed. Recycling these nutrients back to cultivation would steer the algae biorefinery in the direction of a cheaper and more nutrient-neutral process. For this reason, we assessed the cultivation of microalgae with nutrients recovered from the HTL step [6]. The use of the HTL aqueous phase (HTL-AP) to cultivate microalgae proved

Fig. 2 - Algae slurry (left) and HTL products (right) obtained though continuous HTL.

to be a successful way to recycle nutrients, while providing a way to handle the wastewater generated during the production of biofuel. The tolerance of algae to nutrients recovered in HTL-AP proved to be species-dependent. Scenedesmus almeriensis and Phaeodactylum tricornutum could not grow when HTL-AP was used in a cultivation medium. Conversely, Chlorella vulgaris and Nannochloropsis gaditana grew equally well (compared to a standard medium) when 75% of the nutrients from the standard medium were substituted by nutrients recovered through HTL-AP.

Hydrothermal liquefaction of microalgae...continued

Biocrude oil upgrading

The elemental and molecular composition of biocrude oil indicate that it cannot be used directly for transportation. Other physicochemical properties (e.g., viscosity, acidity) hinder its utilization as well. This calls for the development of upgrading techniques to remove the heteroatoms (nitrogen,
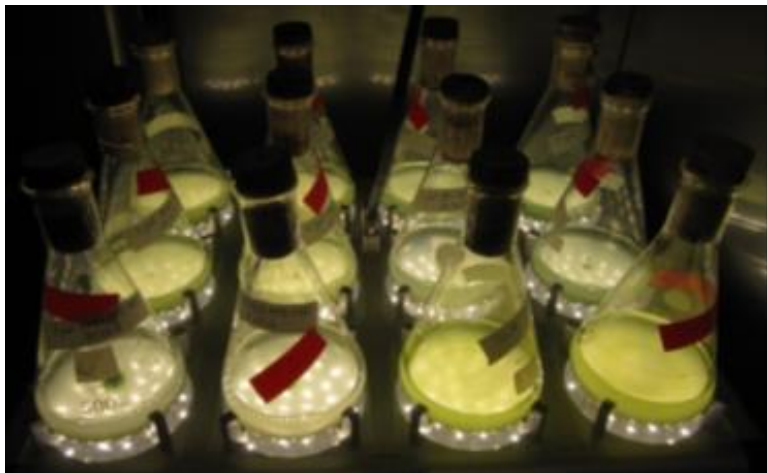

Fig. 3 - Algae cultivation with nutrients recovered from HTL

oxygen, sulphur) and crack the high molecular weight compounds in biocrude oil, in order to increase its quality as transportation fuel. This is typically done by catalytic hydrotreatment. By scouting the literature available, a lack of experiments with continuous equipment can be identified. Using batch reactors hinders the obtainment of significant data, and so far only one study reports on upgrading of microalgal biocrude oil by using a trickle-bed reactor [7].

Techno-economic analyses

The experimental data collected during the research developed in these last years was used to carry out a techno-economic analysis of an algae biorefinery with HTL as core conversion technique. The plant was designed for an output of 0.5 MW in the form of biocrude oil. The selected size was matching a production surface area of 7.1 ha by using flat panel airlift (FPA) reactors. The outcomes identify algae cultivation as the most expensive step of an algae biorefinery. It is also shown that the simultaneous production of valuable co-products together with biocrude oil is needed to achieve an economic operation. Only when a fractionation step was included to obtain a valuable co-product (protein hydrolysates) together with a biofuel the economics of the process were positive.

References:

1. López Barreiro, D., Zamalloa, C., Boon, N., Vyverman, W., Ronsse, F., Brilman, W., Prins, W. Influence of strain-specific parameters on hydrothermal liquefaction of microalgae, Bioresource Technology, 146:463-471, 2013

2. López Barreiro, D., Beck, M., Hornung, U., Ronsse, F., Kruse, A., Prins, W. Suitability of hydrothermal liquefaction as a conversion route to produce biofuels from macroalgae, Algal Research, 11:234-214, 2015.

3. López Barreiro, D., Samorì, C., Terranella, G., Hornung, U., Kruse, A., Prins, W. Assessing microalgae biorefinery routes for the production of biofuels via hydrothermal liquefaction, Bioresource Technology, 174:256-265, 2014.

4. López Barreiro, D., Riede, S., Hornung, U., Kruse, A., Prins, W., Hydrothermal liquefaction of microalgae: overestimation of the biocrude oil yields caused by the use of an organic solvent to separate the aqueous phase, Algal Res, 12:206-212, 2015.

5. López Barreiro, D., Ríos Gómez, B., Hornung, U., Kruse, A., Prins, W., Hydrothermal liquefaction of microalgae in a continuous stirred-tank reactor, Energy Fuel, 29:6422–6432, 2015.

6. López Barreiro, D., Bauer, M., Hornung, U., Posten, C., Kruse, A., Prins, W. Cultivation of microalgae with recovered nutrients after hydrothermal liquefaction, Algal Research, 9:99-106, 2015.

7. Elliott, D. C., Hart, T. R., Schmidt, A. J., Neuenschwander, G. G., Rotness, L. J., Olarte, M. V., Zacher, A. H., Albrecht, K. O., Hallen, R. T., Holladay, J. E. Process development for hydrothermal liquefaction of algae feedstocks in a continuous-flow reactor, Algal Res. 2:445–454, 2013.

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Catalytic fast pyrolysis of biomass

Guray Yildiz

Wolter Prins

Frederik Ronsse

The presence of oxygen in bio-oils (ca. 35–40 wt.%) is commonly believed to be the origin of problems caused by its high water content (15–30 %), corrosiveness (pH of 2–3), relatively low heating value compared to fossil fuels (ca. 17 MJ/kg), poor volatility, and high viscosity (35–1000 cP at 40 °C). However, not only the level of oxygen in the bio-oil is too high, but also the way it exists (functionality) is a part of the problem. Improving the quality of the bio-oils, whether or not in combination with a certain degree of oxygen removal, would include a selective transformation of certain oxygen functionalities such as acids and aldehydes into 'desired' or acceptable ones like alcohols, phenols, and ethers.

urgent need for the translation of laboratory results to viable process concepts and bench/pilot plant trials. Together with the development of efficient catalysts, the design and the intensification of the process with efficient heat integration are of significant importance in the catalytic conversion of lignocellulosic biomass to the targeted liquid product.

Our research group on thermochemical conversion of biomass at Ghent University (Belgium), led by Prof. Wolter Prins, has become active in the area of thermochemical conversion of biomass (e.g. slow, intermediate, fast, and catalytic fast pyrolysis, torrefaction)

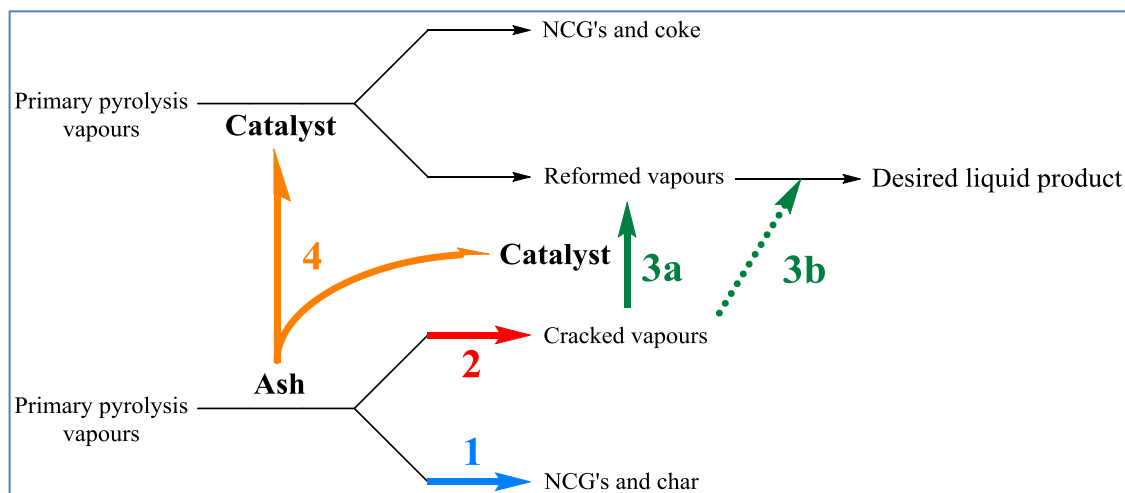Fig. 1. Possible impact of ash on the catalyst and on the products in catalytic fast pyrolysis of biomass.

Application of heterogeneous catalysis in fast pyrolysis (i.e. catalytic fast pyrolysis; CFP) may lead to a liquid product (i.e. catalytic fast pyrolysis oil, CFP-oil) with an improved quality compared to that of crude bio-oil. Here, the improvement in bio-oil quality refers to the production of either high yields of transportation fuel compounds (e.g. aromatics, olefins) and specialty chemicals (e.g. phenolics), or just a drop-in refinery feedstock to be blended with the feed streams of existing petroleum refineries. While the literature on catalytic fast pyrolysis of biomass ☐mainly focused on catalyst screening☐ is rapidly expanding, there is an

since 2010. In this article, we intend to summarize the main outcomes that our research has produced.

The final goal of this work was to come up with recommendations and suggestions on how to realize this technique at a commercial/industrial scale. That requires a better understanding of the precise effects of the essential process parameters (e.g. processing mode; in- or ex situ) and design elements (e.g. reactor type, catalyst type) on the one hand, and definitions and outcomes of possible obstacles (e.g. successive regeneration

Catalytic fast pyrolysis of biomass...continued

of the catalyst, effect of biomass ash) on the other.

The effect of the processing mode (i.e. in situ vs. ex situ) and the screening of metal doped zeolite catalysts
In this work, two types of continuously operated (catalytic) fast pyrolysis reactors were used, viz. an auger reactor and a mechanically stirred bed reactor. In all experiments performed in both setups, pine wood with a particle size range of 1 to 2 mm was pyrolyzed at a constant reactor temperature of 500 °C. In the auger reactor, first the effect

situ catalysis; more aromatics and phenols were produced in the case of in situ operation. That may be caused by different vapour residence times and vapour-catalyst contact times. Among all eight catalysts tested, the acidic catalyst containing some redox active metal, the basic catalyst with a mixture of two metal oxides (calcined), and a metal oxide doped gamma-alumina catalyst (calcined) were found to be the best performing ones, based on both the deoxygenation requirements and the production of desirable compounds in high yields.
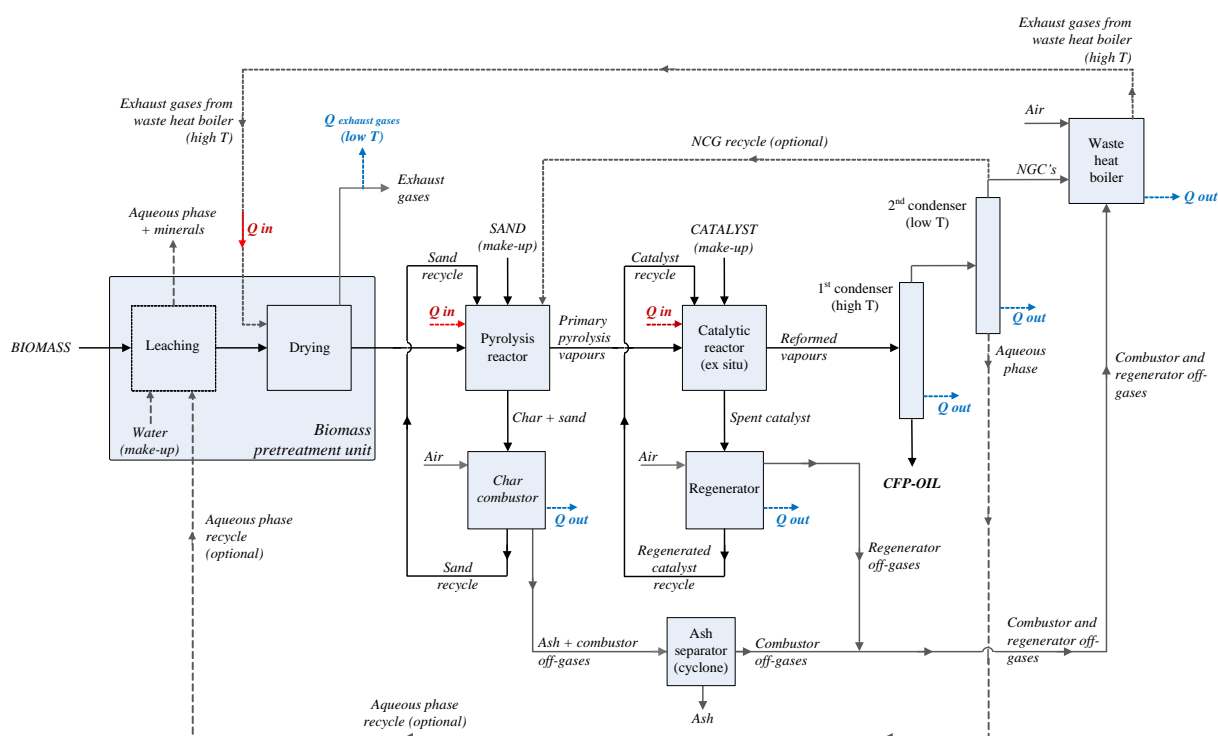

Fig. 2. Proposed scheme of a CFP process for low-ash (<1 wt.%) containing woody biomass.

of the operation mode on the product yields and compositions has been investigated while using a single type of heterogeneous ZSM-5 based acidic catalyst [1].

Two operation modes were tested. In situ operation includes the mixing of biomass and catalyst inside a single reactor, while ex situ refers to catalytic treatment of the pyrolysis vapours in a secondary reactor. A second study was concerned with the screening of various heterogeneous catalysts (and their metal doped counterparts) in in situ operation [2]. In all experiments, the presence of catalysts led to the production of additional water, coke and gases at the expense of the liquid organics and char. The overall performance of in situ catalysis in terms of oil quality was considerably better than that of ex

Effect of successive catalyst regeneration and the presence of biomass ash in catalytic pyrolysis

In the mechanically stirred bed reactor, we studied i) the effect of a repeated catalyst regeneration (eight cycles in total) [3], and ii) the effects of the pine wood ash on the yields and composition of the products [4]. In all catalytic experiments, a single type of a ZSM-5 based catalyst was used in situ. Along the reaction/regeneration cycles, trends in pyrolysis product yields converging to that of non-catalytic levels were observed. This revealed that the activity, and thus the influence of the catalyst slowly declined, which was confirmed by a BET surface area reduction of 63 %. Ash concentrations as low as ca. 3 wt.% relative to the amount of pine wood fed, and ca. 0.002 wt.%

Catalytic fast pyrolysis of biomass...continued

relative to the amount of bed material, were found sufficient to affect the yield and composition of the CFP products unfavorably.

Challenges in the design and operation of processes for catalytic fast pyrolysis of biomass

In order to obtain the target products in CFP of biomass with desired yields and compositions, the process conditions such as the processing mode (e.g. in situ, ex situ), the reaction temperature, heating rate and the residence time of the biomass feedstock, catalyst-to-biomass ratio, and the vapour residence time need to be optimized precisely. Moreover, a careful selection of the biomass feedstock (including its particle size, moisture and ash contents), and the type of the catalyst (e.g. resistance to deactivation) is essential. In this work, the technical and operational barriers for the implementation of catalytic fast pyrolysis technology are discussed while focusing on the process modes and parameters, economical use of the primary and secondary products, and heat integration. Some process alternatives for an efficient CFP operation are suggested as well [5].

Overview

Research has, until now, been focused mainly on screening and small-scale testing of various catalysts. One challenge in developing CFP of biomass is the design and large scale production of such catalysts to enable testing in continuously operated, bench and pilot scale installations. FCC types of catalysts are the only suitable ones commercially available. But they are developed especially for use in a riser reactor and short contact times (differing significantly from typical biomass devolatilization times). The main problem in CFP of biomass was found to be the presence of the biomass originated alkaline ash which eventually poisons any catalyst in case of direct contact. In a commercial process, a solution may be to separate the biomass fast pyrolysis from the catalytic treatment of the vapours (i.e. ex situ processing mode) where the physical contact between the biomass minerals and the catalyst is excluded. Even though this requires significant process adjustments, ex-situ processing allows the catalyst to be re-used in a much larger number of reaction/regeneration cycles than in case of in situ operation.

References

[1]   Yildiz, G., Pronk, M., Djokic, M., van Geem, K. M., Ronsse, F., van Duren, R., & Prins, W. (2013). Validation of a new set-up for continuous catalytic fast pyrolysis of biomass coupled with vapour phase upgrading. Journal of Analytical and Applied Pyrolysis, 103, 343–351.

[2]   Yildiz, G., Ronsse, F., Vercruysse, J., Daels, J., Toraman, H. E., van Geem, K. M., Marin, G. B., van Duren, R., & Prins, W. (2016). In situ performance of various metal doped catalysts in micropyrolysis and continuous fast pyrolysis. Fuel Processing Technology, 144, 312–322.

[3]   Yildiz, G., Lathouwers, T., Toraman, H. E., van Geem, K. M., Marin, G. B., Ronsse, F., van Duren, R., Kersten, S. R. A., & Prins, W. (2014). Catalytic fast pyrolysis of pine wood: effect of successive catalyst regeneration. Energy&Fuels, 28, 4560–4572.

[4]   Yildiz, G., Ronsse, F., Venderbosch, R., van Duren, R., Kersten, S. R. A., & Prins, W. (2015). Effect of biomass ash in catalytic fast pyrolysis of pine wood. Applied Catalysis B: Environmental, 168, 203–211.

[5]   Yildiz, G., Ronsse, F., van Duren, R., & Prins, W. (2016). Challenges in the design and operation of processes for catalytic fast pyrolysis of woody biomass. Renewable & Sustainable Energy Reviews, 57, 1596–1610.

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Hydrothermal Liquefaction of Black Liquor and Lignin

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Alexi Välimäki

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Background

Black liquor is an attractive feedstock for biofuel production because it is available in huge amounts, globally 170 million tons or 2 EJ or typically 250 -500 MW per mill [1]. A modern Kraft pulp mill have a surplus of energy because of improved energy efficiency and the steam and power consuming paper mill might also be nowadays far away from the pulp mill. Therefore a significant fraction of black liquor can be directed for hydrothermal liquefaction (HTL) or extracted as lignin (e.g. Lignoboost) and remaining black liquor still have enough energy content needed for proper combustion in the recovery boiler.

Fig. 1. Black liquor and processing equipment

At VTT biofuel production from black liquor by HTL has been demonstrated in 90s at temperatures of 300 -350°C with sodium hydroxide and nitrogen, carbon monoxide or hydrogen addition to the reactor. After washing with a dilute acid solution the HTL product with a low sodium content of 0.02 wt. - % was obtained. Subsequently after two-stage hydrotreating with sulphided NiMO catalyst at 280 or 390 °C a high bio oil yield of 88 wt.-% was obtained [2].

Presently the HTL process is studied in the LignoHTL project (Figure 1) as a part of the Wood Wisdom network to demonstrate the transportation fuels production from black liquor in laboratory scale [3]. In this project,

no reducing gas, but additives such as glycerol and NaOH are used in the hydrothermal liquefaction step and the other project partners are in charge of studying subsequent bio-oil upgrading by the hydrodeoxygenation and co-refining by catalytic cracking after the HTL step.

Methods

Experiments were performed at VTT in 1 l, 10 l and 30 ml reactors. In the latter one fast cooling and heating rates was provided. Experiments were done mostly applying reaction time of 45 min in temperatures ranging from 330°C to 370 °C and concentrations of solids ranging from 17 wt.-% up to 54 wt.-%. Different amounts of base catalyst (10 wt.-% and 25 wt. - % sodium hydroxide) of the black liquor solid content and an additive (25-50 wt.%)were used. The effect of different hydrogen donor additives such as glycerol, ethanol and sodium formate was also tested. In addition the effect of additional industrial lignin and substitution of sodium hydroxide with sodium carbonate was investigated.

After the reaction the reactor was cooled down and the reaction mixture was taken out at room temperature. Next, the aqueous phase and oil phase was allowed to settle for 1 hour before they were

separated. The yield of oil, aqueous phase and gas were calculated and the molecular mass distribution of black liquor and the final oil were measured. Next, the oil sodium content was reduced by washing oils from selected runs several times with 2M sulfuric acid solution at 80 °C and the washed products were analysed for water content, elemental analysis (CHN), heating value, sodium and sulphur content.

Next steps

The further work include experiments to determine reaction kinetics, testing of wheat straw lignin with black liquor and finding possibilities to perform HTL experiments with a continuous reactor applying black liquor and lignin as feedstocks.
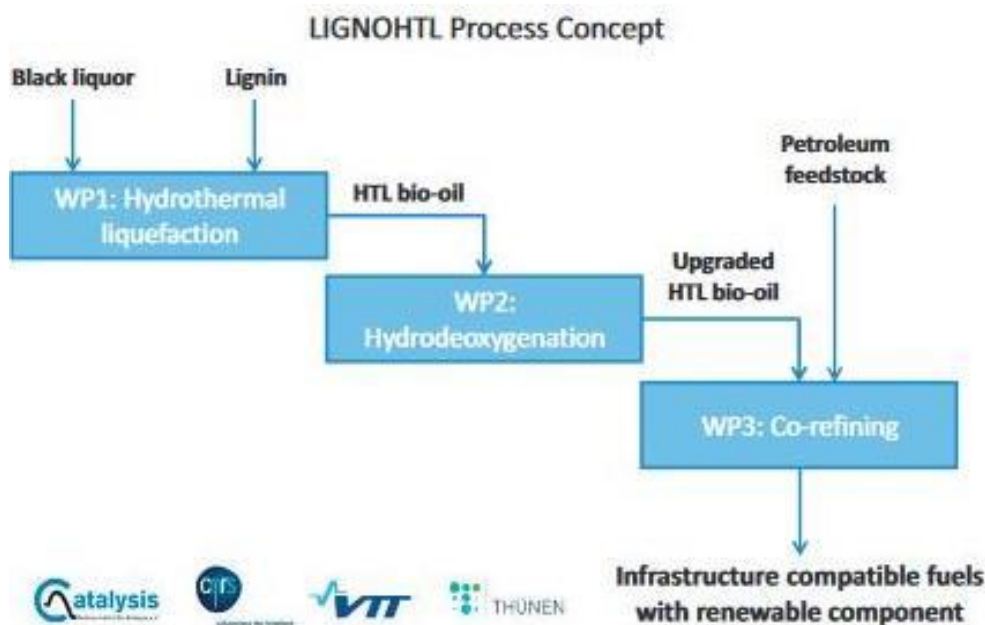

Figure 2. Process concept in LignoHTL project

Results

• The results indicate so far that with the initial black liquor solid concentration of approximately 30 wt.-% the reaction product separates into oil and aqueous phase after cooling without acidification (pH 10). Typically the oil yields were approximately 30wt.-% of black liquor dry matter and up to 75 % on energy basis.

• Interestingly with glycerol no visible solid char residue was obtained, contradictory to many HTL experiments with other feedstock according to literature. Compared to other additives glycerol gave the best results: HTL product separated easily after cooling and 1 hour settling time at room temperature. The product also had the lowest average molecular mass.

• The weight based average molecular mass decreased from 2300 g/mol in the initial black liquor to 680-920 g/mol, in the reaction products. Higher temperature resulted in lower molar mass as expected. In addition, higher glycerol amount and lower concentration of solids slightly lowered the molar mass. The average molecular mass might affect the solubility of the HTL product so that the lower molecular mass product is more soluble in the aqueous phase.

References

1. http://www.ieabioenergy.com/wp-content/uploads/2013/10/Black-Liquor-Gasification-summary-and-conclusions1.pdf, accessed 25.1,2017

2. Oasmaa, Anja. 1991. Thermochemical conversion of black liquor organics into fuels. Licenciate Thesis. Espoo, VTT, 0 p.
http://www.vtt.fi/inf/julkaisut/muut/1991/1950_001.pdf

3. http://www.woodwisdom.net/wp-content/uploads/2014/09/summary_lignohtl.pdf , accessed 25.1, 2017

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VTT Technical Research Centre of Finland

Fractional condensation of pyrolysis vapors produced in cyclone pyrolysis

Linda Sandström

Ann-Christine Johansson

Figure 1. Schematic view of the fractional condensation system

Pyrolysis oil is a complex mixture of different types of chemical compounds with a wide range of molecular weights and boiling points. Fractionation of the oil may facilitate efficient use of the oil. In a recent paper [1], we describe a fractional condensation system attached to a cyclone pyrolysis pilot plant, in which five different oil fractions are obtained. The fractions are thoroughly characterized and possible applications are suggested.

Fractional condensation system

The fractional condensation system was connected to a 20 kg h^{-1} cyclone pyrolysis plant earlier described by Wiinikka et al. [2]. A small part of the gases and vapours exiting the cycl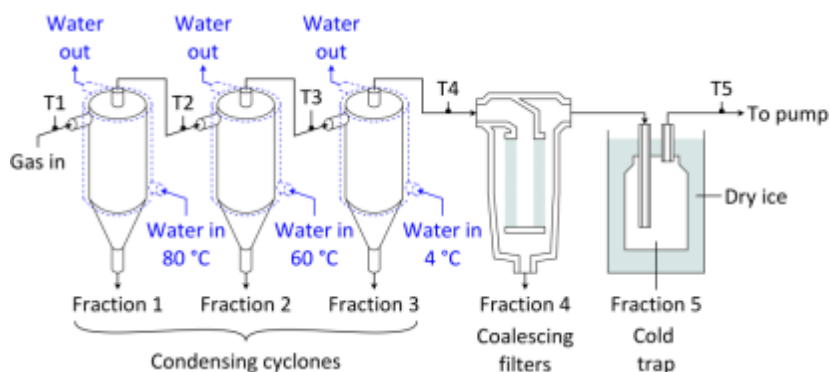one reactor were withdrawn to the fractional condensation system, in which five fractions of oil were condensed and collected as shown in Figure 1. Three condensing cyclones at gradually decreasing temperatures were followed by coalescing filters for the collection of aerosols. Finally, light components were recovered in a cold trap cooled by carbon dioxide ice and ethanol. Three types of feedstock were studied in this work: stem wood (a mixture of pine and spruce), forest residue and short rotation willow (Salix).

Mass distribution

The total mass distribution of the five oil fractions collected during pyrolysis of stem wood is shown in Figure 2. The largest mass is collected in the coalescing filters, Fraction 4. Figure 2 also shows the mass distribution of chemical component groups. This was assessed by analyzing the oil fractions according to the solvent fractionation scheme developed at VTT [3]. Water is mainly collected in Fractions 3 and 5,
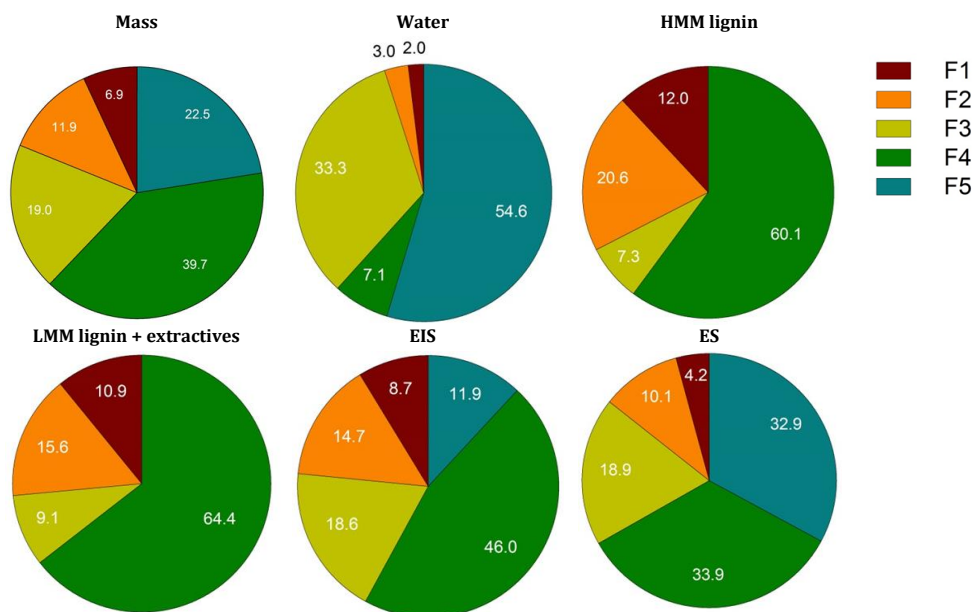
Figure 2. Distribution of total mass and of chemical component groups, expressed in mass percent. The feedstock is stem wood. Fractionation is performed according to [3]. HMM lignin: high molecular mass lignin, insoluble in dichloromethane; LMM lignin: low molecular mass lignin, dichloromethane soluble; EIS: water soluble but ether insoluble compounds, e.g. anhydrosugars, hydroxy acids; ES: water soluble and ether soluble compounds, e.g. aldehydes, ketones, lignin monomers

Fractional condensation of pyrolysis vapors...continued

i.e. in the coldest of the three condensing cyclones and in the carbon dioxide cold trap. Lignin, on the other hand, is primarily collected in the coalescing filters, Fraction 4.

Properties of the oil fractions

Figure 3 shows a so-called Van Krevelen plot, which illustrates the molar ratios H/C and O/C (on dry basis), for
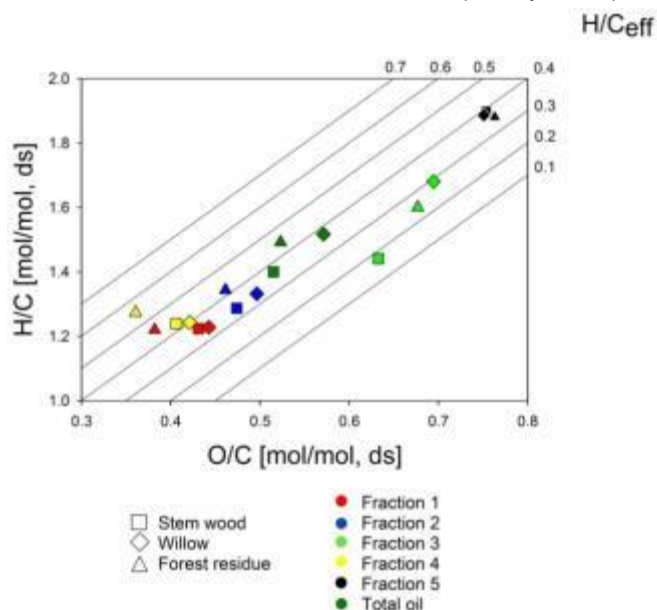

Figure 3. Van Krevelen plot for the oil fractions and total calculated oil produced from stem wood, willow and forest residue.

all produced oil fractions. Fractions 1, 2 and 4 all have lower H/C ratios than the total oil, likely due to the higher concentrations of pyrolytic lignin in these fractions. Diagonal lines in Figure 3 represent the hydrogen to carbon atomic effective ratio, $\left(\frac{H}{C}\right)_{eff} = \frac{H-2O}{C}$, which can be used as an index to evaluate the liquid quality for further upgrading processes. The (H/C)$_{eff}$ ratios of the oil fractions are similar, and the fractioning does not seem to affect the effective H/C ratio to a high extent.

The oil fractions were also investigated by ^{13}C NMR analyses, summarized in Figure 4. The most abundant single carbon type in all oils is aliphatic C-O carbons, which is especially dominant in Fractions 3 and 5. These bonds include carbons in anhydrosugars, alcohols and hydroxycarbonyls, and originate mainly from the carbohydrate fraction of the biomass. The aromatic content is on the contrary higher in Fractions 1, 2 and 4 and lower in Fractions 3 and 5. This is consistent with the results of the solvent fractionation analysis, where fractions 1, 2 and 4 were found to have high lignin content.

Discussion

Fractional condensation is a way to produce oil fractions with different chemical and physical properties. Possible applications of the fractions include combustion, catalytic upgrading to transportation fuels and chemicals, and extraction of valuable chemicals such as pyrolytic lignin, sugars, acids and aldehydes.
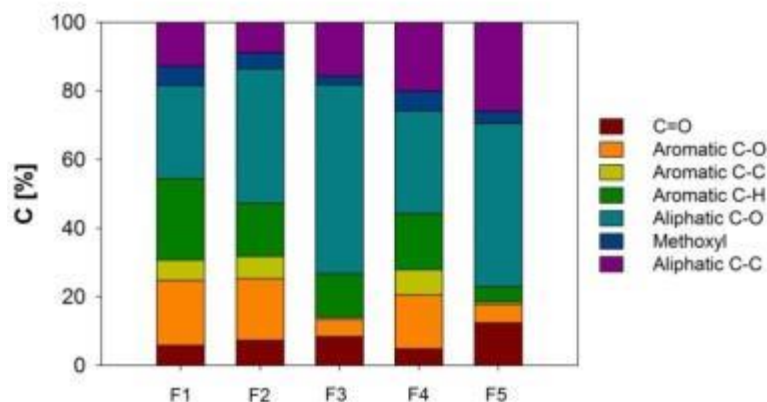

Figure 4. 13C NMR analysis of the five oil fractions produced from stem wood.

References

[1] Johansson, A.-C., Iisa K., Sandström, L., Haoxi, B., Pilath, H., Wiinikka, H., Öhrman, O.G.W., Fractional condensation of pyrolysis vapors produced from Nordic feedstocks in cyclone pyrolysis, Accepted for publication in Journal of Analytical and Applied Pyrolysis
[2] Wiinikka, H., Carlsson, P., Johansson, A.-C., Gullberg, M., Ylipää, C., Lundgren, M., Sandström, L., Fast pyrolysis of stem wood in a pilot-scale cyclone reactor, Energy and Fuels, 29 (2015) 3158-3167
[3] A. Oasmaa, C. Peacocke, Properties and Fuel Use of Biomass-derived Fast Pyrolysis Liquids, VTT Publications, VTT (2010)
http://www.vtt.fi/Documents/P731.pdf

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Scale-up Of Catalytic Hydrotreating of Biomass Liquefaction Products

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Figure 1. Distillation Tower (left) and Hydrotreater (right)

The Pacific Northwest National Laboratory has been involved in the development of catalytic hydroprocessing for biomass liquefaction products for over 30 years. Throughout that period experimental testing for process optimization and catalyst development has been underway in several laboratory-scale continuous-flow reactor systems. These reactors have typically been operated as trickle-bed (down-flow) fixed-bed catalytic reactors. Operating scales have ranged from mL to hundreds of mL per h of fast pyrolysis bio-oil feedstock, derived from a range of biomass types. The same reactors have been operated similarly for the catalytic hydroprocessing of catalytic pyrolysis bio-oil product and biocrudes from hydrothermal liquefaction. Typical operations have been for tens of hours on line and more extensive tests involving hundreds of hours on-line have also been recorded.

Based on the design of the laboratory reactors, a scale-up was attempted to achieve a scale of operation to produce multiple gallons of product and including a distillation column unit to allow fractionation for fuel testing and validation. The construction of the unit was contracted to Zeton in Burlington, Ontario, Canada, who

delivered the unit to PNNL in 2013. Following extensive review and operational system development, the unit has been started up this year and has now produced liquid hydrocarbon products from bio-oil acquired from the National Renewable Energy Laboratory (NREL) in Colorado, USA.

The unit is designed at a scale of 2.5 L/h of bio-oil with a LHSV of 0.15 (17 L of catalyst bed). The unit shown in Figure 1 has a feeding system, reactor system, product recovery system, and offgas treatment (which can be modified to include gas recycle in the future). On a separate skid is found the distillation tower in which fuel fractions can be recovered from the liquid hydrocarbon products. The reactor is heated in an 8 zones and can be operated over a temperature range from 150°C to 400°C to allow initial stabilization of the bio-oil and to complete the hydroprocessing to a product with near 0 residual oxygen content. The operating pressure is nominally 100 to 135 atm with a high flow of hydrogen gas to maintain a high partial pressure of hydrogen (typically 90% or higher). The products are

Scale-up Of Catalytic Hydrotreating...continued

separated into liquid and gaseous streams after cooling. Liquid products are captured in product receiver tanks and the offgas is vented through an H2S scrubber system. The process is monitored remotely via electronic sensors and controls. Operating condition data is captured to a data file. Remotely monitored cameras allow system management without entering the safety enclosure built around the unit.

in Table 1. The numbers are the actual analytical results, not normalized. Oxygen analysis is the actual result, not by difference. The results show effective hydrodeoxygenation. There was no evidence of pressure-drop buildup over the period of operation although the catalyst bed was not yet recovered for analysis of carbon buildup.

This test was the first large-scale hydroprocessing of

Table 1. Analysis (wet basis, as received) of feed and product of scaled-up reactor

	Carbon	Hydrogen	Oxygen	Nitrogen	Sulfur	Moisture	TAN
Feed	45.1	7.1	43.4	<0.05	<0.03	19	117
Product*	85.7	14.7	0.6	<0.05	<0.03	<0.3	<0.1

*initial product contained approximately 12% decane from catalyst sulfurizing during start-up.

During 2015, the distillation tower was brought on line to perform fractionations hydrotreated bio-oil products from earlier laboratory operations. This past summer (2016), the hydrotreater was operated initially to test pressure, temperature and flow systems with a liquid petroleum feedstock. In the recent test, actual bio-oil was processed over a sulfided Ru/C and CoMo catalyst to produce liquid hydrocarbon product. A total of 12.5 liters of bio-oil were treated over a 24 hour run. The yield of hydrocarbon liquid product was approximately 4.5 liters with 6.5 liters of aqueous byproduct. Analyses of the feedstock and product streams are presented

fast pyrolysis bio-oil. It is only the first of many expected at PNNL, whose research plan for the U.S. Department of Energy's Bioenergy Technologies Office is focused on a large scale process demonstration within FY2017 (before September 30, 2017). Additional work planned for the unit includes large scale hydroprocessing of hydrothermal liquefaction biocrude to produce fuel grade products.

Reference

Elliott, D.C. "Historical Developments in Hydroprocessing Bio-oils." **Energy & Fuels**, *21*, **2007,** 1792-1815.

Figure 2. PNNL Hydrotreater Commissioning Team

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Combustion Emissions from Products of a Fast-pyrolysis Pilot Reactor

Figure 1. Burner flame on bio-oil (left) and diesel fuel (right)

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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 ton/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 Navy and the Department of Energy. 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. 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. MEC is also targeting commercial applications—being a Florida company, initial waste biomass feedstock testing has focused pine logging residues from the northern part of the state.

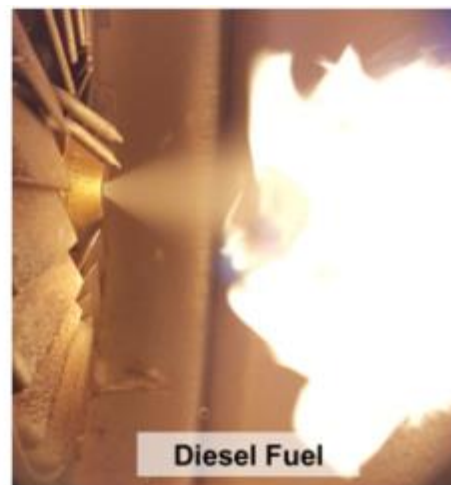MEC's focus has been on circumventing technical and cost barriers that have prevented small-scale pyrolysis from taking hold commercially, namely keeping the unit production costs low, finding a viable near-term offtake route for raw or mildy upgraded bio-oil, and demonstrating emissions compliance. The pilot reactor is fully operational and the company runs it approximately once per month as it works through various process improvements. The pilot reactor is described in more detail in PyNe 37 (June 2015).[1]

Recent additions and upgrades to the pilot reactor include on-stream regeneration of the hot-gas filter, a tunable high-voltage electrostatic precipitator, and an improved bio-oil collection filter media. The pilot-scale bubbling fluidized bed reactor (41 cm ID) was also recently outfitted with a high-temperature borescope to allow visualization of sand bed and screw feeder during operation. Wood-derived bio-oil from the pilot has been tested in-house and shown to comply with ASTM 7544-12 Grade D. The oil is particularly low in ash and solids because of the hot-gas filtration, making it attractive for bio-oil upgrading studies. For those interested, research quantities of bio-oil (2 L minimum order) are available for purchase from the email below.

Recently, MEC has focused on characterizing the combustion emissions from all three products of the fast pyrolysis process (bio-oil, biochar, and non-condensable process gas). Emissions measurements for bio-oil blends and the process gas have been taken at MEC. Bio-oil/ethanol blends (20%/80% by mass) were burned in a nominally 2 gal/hr (7.6 L/hr) modified fuel-oil burner. The bio-oil blend flame had similar stability and morphology as a baseline diesel flame (see Figure 1). The blending approach was adopted after attempts to burn neat bio-oil in this burner were unsuccessful. The process gas surrogate mixture was burned in a commercial burner designed for low-energy-content gaseous fuels. Emissions measurements for the biochar were taken as part of a project with the Energy & Environmental Research Center (EERC) in Grand Forks, ID using a pilot-scale fluidized bed combustor. For all three burners, measurements were made for CO, CO_2, NOX, SOX, and particular matter (PM).

The emissions from the three burners were treated holistically to simulate a small, distributed, fast-pyrolysis installation where the bio-oil is used

Combustion Emissions from Products...continued

on-site. The emissions were compared to the Environmental Protection Agency's standard for Other Small Waste Incinerators (OSWI). The EPA OSWI standard includes limits for four common emissions species (CO, NOx, SOx, and PM) and five other air toxics (dioxins, cadmium, lead, mercury, and HCl). A combined emissions metric was calculated by weighting the emissions concentration of each burner by the flow rate of its exhaust stream, which is in turn related to the yield of each product and the amount of excess air in the burners. The combined emissions were corrected to a dry basis with 7% O_2 in the exhaust, as prescribed by the OSWI standard.
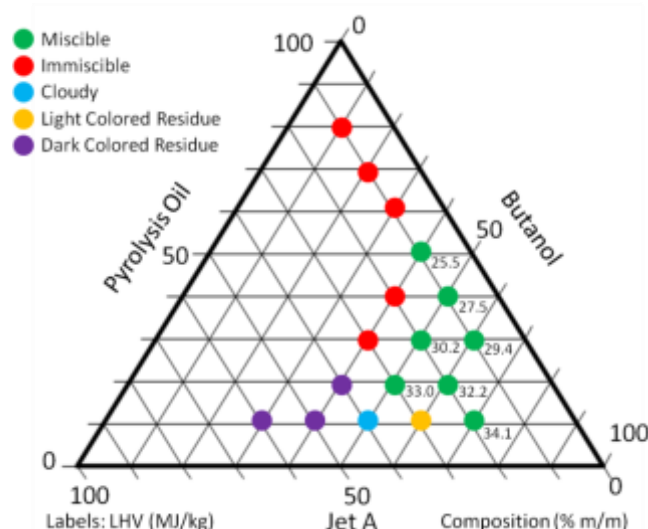
With a pine feedstock, the combined emissions of CO, NOX, and SOX were observed to fall below the EPA OSWI limit without any aftertreatment of the exhaust. PM was about twice the OSWI limit without aftertreatment suggesting that a baghouse filter should be used to meet the standard. Interestingly, the char burner and the bio-oil burner contributed nearly equally to the combined PM emissions. The char burner had a much higher PM emissions factor than the bio-oil burner, but its contribution to the combined emissions was weaker because the bio-oil yield is several times higher than the char yield.[2]

MEC has also been studying the blending of fast-pyrolysis bio-oil with jet fuel. Since jet fuel is not directly

soluble with bio-oil, co-solvents are required to produce a single-phase blend including jet fuel and bio-oil. Unlike with diesel fuel and bio-oil blends, ethanol was not a good co-solvent for jet fuel. Butanol, on the other hand, was able to produce single phase blends with bio-oil and jet fuel when composing at least 40% (m/m) of the blend (see Figure 2). For a blend containing 50% (m/m) butanol, the fuels were miscible for bio-oil fractions ranging from 20 to 40%, with the balance jet fuel, allowing for some blending flexibility.[3]

In addition to blending, MEC is extracting bio-oil with supercritical solvents to study processing these extracts individually. Supercritical CO2 at 60 °C and 2500 psig (170 atm) is able to extract over 10% (m/m) of the pyrolysis oil. Compared to the raw oil, the extract is characterized by lower water content, lower boiling range, and better solubility with butanol and jet fuel.[3] Future experiments will focus on treating this extract to produce value-added fuels and chemicals.

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

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PyNe: Historical Review

Honoring a legacy of pyrolysis research

In 2017, our research successes here are built on a foundation constructed by Giants.

The members of PyNE 1 in March of 1996 were: Tony Bridgwater, Wolter Prins, Yrjo Solantausta, Dietrich Meier, Leonetto Conti, Morten Fossum, Baldauf, Philippe Girard, Spitzer, Rosanna Maggi, Winther, Yannis Boukis, Karseten Pederson, Erik Rensfelt, Filomena Pinto, Jesus Arauzo, Angel Cuevas.

> *"If I have seen further, it is by standing on the shoulders of giants."*
> - Isaac Newton.

Thank you for the dedicated and tireless effort of Coordinator Tony Bridgwater and the amazing efforts of the long line of hard working Editors: Karen Dowden, Claire Humphreys, Emily Wakefield, Sara

PyNE 1: http://task34.ieabioenergy.com

Past Coordinator and Editors of PyNe from 1996 to 2015

Tony Bridgwater
PyNe 1-38
Co-ordinator

Claire Humphreys
PyNe 3-17
Editor

Emily Wakefield
PyNe 18-24
Editor

Irene Watkinson
PyNe 27-38
Editor

Kerri Lyon
PyNe 34-38
Editor

Not Pictured: Editors Karen Dowden (PyNe 1-2) and Sara Burrowes (Pvne 25-26)

Take time to celebrate these Giants of Pyrolysis, whose steadfast research has set the stage for the thermal liquefaction successes of the present, and have equipped you for making meaningful change to our global energy landscape through renewable energy. On the anniversary of the 40th issue of PyNe, Read again about those Giants and learn from their history in order to continue it. I hope that you spend time reading through selected prior issues of PyNE to celebrate the successes of those Giants, to avoid repeating what has already been tried, and to gain inspiration from paths not yet taken.

To start: Thank you for the fine work by the team at Aston University from 1996 to 2015 for keeping the flame of the PyNe newsletter burning brightly for 20 years.

Burrowes, Irene Watkinson, and Kerri Lyon. You are each greatly appreciated and missed.

PyNe was born in 1996, coordinated by Tony Bridgwater out of Aston

> "Welcome to PyNE's first newsletter, wherein we aim to heighten the awareness and opportunities for biomass pyrolysis and related technologies for liquid fuels, electricity, and other high added value products."
> - PyNE 1, March 1996.

University. It is difficult to think of biomass pyrolysis without thinking about Tony, whose strong leadership in this area has shaped this history of pyrolysis research to where it stands today.

PyNE was established in order to form a unified community out of activities supported by IEA Bioenergy as PYRA and the European Commission as PyNE. This original issue captures much of the excitement and promise of the pyrolysis community at that time. Its primary focus was to provide a forum for shaping the international dialogue on thermochemical liquefaction, identify research needs and priorities, encourage the active involvement of industry, and advance information dissemination and improve cooperation. History evidences the success the original PyNE pioneers.

PyNe: Historical Review...continued

(Continued from page 2)

PyNe 5: http://task34.ieabioenergy.com
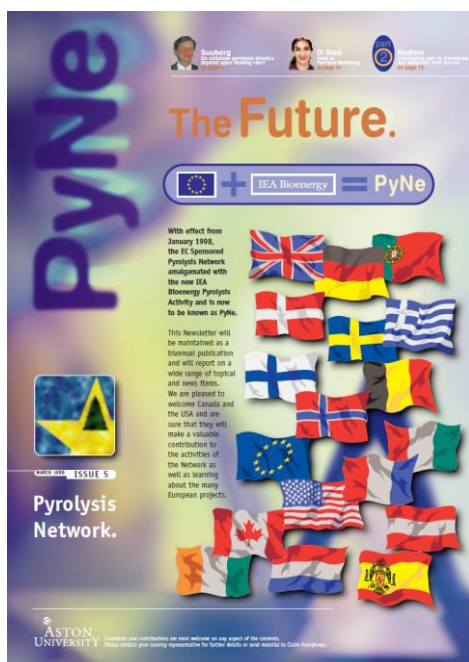
When PyNe 5 was published in January of 1998, PyNE became PyNe, an amalgamation of the EC Sponsored Pyrolysis Netowrk and the IEA Bioenergy Pyrolysis Activity. The membership increased with Ireland as a recent addition, with Pearse Buckley serving at the representative, (who in 2017 serves as the Secretary of the IEA Bioenergy.) In addition, PyNe reached across the Atlantic, as our friends in Canada and the USA formally joined as members, a recognition of the value of gathering together in cooperation to advance pyrolysis as a solution to our global energy future.

Bolstering the team were a new crop of pyrolysis giants, including Anja Oasmaa, Jan Piskorz, Stefan Czernik, Maximilian Lauer, Morten Gronli.

Articles feature a range of research organization as well as topics such as

pyrolysis modelling, co-combustion, catalytic upgrading, chemicals and materials, waste to energy, in addition to solar pyrolysis. Articles featured articles on a range of research organization including U. of Zaragoza (Spain), THERMIE and JOULE in Belgium, and INETI in Portugal. Pyne 5 also included topics such as pyrolysis kinetics, combined pyrolysis/gasification, catalytic upgrading of bio-oils, chemicals and materials from bio-oil, waste to energy, in addition to solar pyrolysis. Two years later, with the addition of Brazil, PyNe would see its largest historical membership, boasting participants from 18 countries: UK, Austria, Belgium, Canada, Denmark, Finland, France, Germany, Greece, Ireland, Italy, Netherlands, Norway, Portugal, Spain, Sweden, and USA.

PyNe 15: http://task34.ieabioenergy.com

PyNe 15 was published in 2003 with participation of 16 member countries in the community. By this time, we had been introduced to new names such as Doug Elliott and Yves Schenkle.

By this point, the growth of articles reflected the expanding nature of the questions and challenges in pyrolysis research, as well as reports and assessments from various collaborations and institutions, such as Schenkel's report on activities in Belgium.

Topics in Pyne 15 included:

- Coproducts: Stucley's report on simultaneous activated carbon and Eucalyptus oil production using pyrolysis for electricity in Australia
- Products: Tony's announcement of collaborations towards renewable resins from bio-oil
- Coproducts: Jean-Guy's discussion of solvent extracted chemicals during slow pyrolysis charcoal production in France.
- Technology: Cyclone reactor work at CNRS in France.
- Analysis: Girard's report on understanding the toxicity of pyrolysis oil.
- Heat and Power: Yrjo's contribution on pyrolysis oil for heat production in Finland
- Upgrading: Doug's note on the restart of catalytic upgrading to fuels in the USA
- Forward Thinking: Wolter's discussion on the technical and non-technical barriers to implementation.
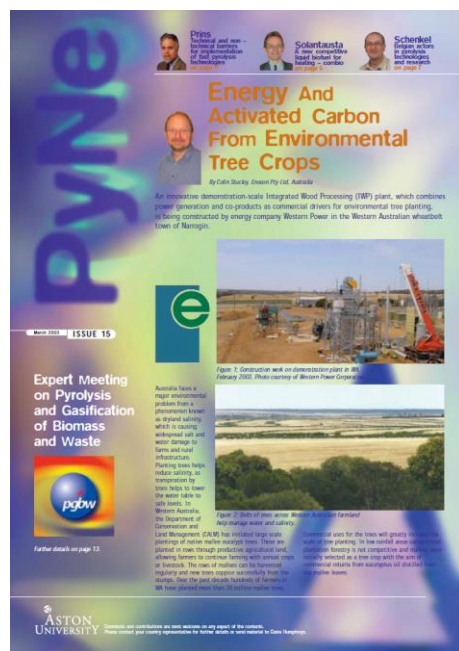
By PyNe 15, we had also been introduced to a range of commercial names: BtG, Fortum, Ensyn, Neste, Dynamotive, RTI, and others.

PyNe: Historical Review…continued

PyNe 25 in December of 2008 catalogued a number of changes within the community. As the Silver Jubilee issue, it also has an excellent retrospective and summary of the first 12 years of PyNe and is well worth reading again.

PyNe 25: http://task34.ieabioenergy.com

In 2008, Task 34 began a new triennium in IEA Bioenergy, and the PyNe newsletter began rebranding towards an IEA Bioenergy Task 34 output. At the same time, Doug Elliott of PNNL in the USA stepped up to lead Task 34 to continue the strong and noble leadership tradition established by Tony Bridgwater, who continued to co-ordinate the publication. With the successful completion of Thermalnet, formal membership settled to 4 countries party to Task 34: Finland, Germany, Australia, and the USA along with both UK and Canada working towards formal membership.

It was also a year of bright promise for pyrolysis oils. UOP and Ensyn announced a joint venture to offer second-generation biomass technology

"Fast pyrolysis offers enormous potential benefits for fuels, chemicals, heat and power and PyNe offers an opportunity for the international community to work together to help achieve this potential."
-Tony Bridgwater, PyNe 25, March 2008.

and news was reported on the registration efforts of Fast Pyrolysis Liquids under REACH in Europe.

PyNe 30 in December of 2011 is a large, landmark issue and is an excellent snapshot of the Pyrolysis landscape at the time for anyone interested in understanding the blossoming research in thermal biomass conversion and related technologies.

PyNe 30: http://task34.ieabioenergy.com

Topics included:

- Pyrolysis: Sai Gu reporting from Southampton UK on fluid bed pyrolysis
- Catalytic Pyrolysis: Mullen and Kwasi's report on catalytic pyrolysis at USDA (USA).
- Lignin Pyrolysis: Dietrich's discussion of pyrolysis for

phenols, biorefinery work in Germany.
- Fast pyrolysis/catalytic steam gasification: update from Williams and Wu in Leeds (UK)
- Pyrolysis combustion: Thomson's work on combustion research at the University of Toronto, Canada
- Slow Pyrolysis: Masek's report on slow pyrolysis research in Edinburgh (UK)
- Upgrading: Armbruster's report on near-critical water upgrading to fuel components (Germany)
- Upgrading: Waste wood pyrolysis and upgrading out of PNNL (USA) and Canmet (Canada)
- Standards: Alakangas of VTT (Finland) discussing solid biofuels standards for use or thermal conversion
- Analysis: Anja's and Doug's discussion of the analytical in the 2011 Task 34 Round Robin
- Fundamentals: Dauenhauer's report on a mechanism for aerosol formation during pyrolysis
- Strategic collaboration: Tony's (UK) report on the new BRISK initiative, with strong backing from 14 countries, to develop European research infrastructure in thermochemical conversion
- Strategic collaboration: Holladay's first year report on the National Advanced Biofuels Consortium in the USA
- Forward thinking: Tooke and Jackson's discussion of barriers to waste biomass conversion and upgrading (UK)
- Forward thinking: Tews' consideration of North American forestry for bio-oil production in the USA

PyNe: Historical Review...continued

In addition, continuing a tradition from PyNe 27, country reports were provided rounding out the newsletter to its longest ever at 52 pages.

PyNe 35: http://task34.ieabioenergy.com

PyNe 35, published in June 2014 captured the increased progress, expanded collaboration, and news of commercialization in the pyrolysis community. Topics included:

- Strategic Collaboration: Welcoming Magnus Markland of Sweden to membership in Task 34
- Strategic Collaboration: Toven and Tony describe efforts in ReShip project for wood based marine fuels
- Mobile Pyrolysis: Doug's review of mobile pyrolysis for distributed oil production
- Mobile Pyrolysis: Sagi at EBRI (UK) offers insights into mobile pyrolysis work in India
- Lignin Pyrolysis: Franck discusses results from pyrolysis of Kraft lignin in Germany.
- Pyrolysis combustion: Beran and Axelsson conclude discussion of combustion in the Netherlands first featured in PyNe 33.

- Catalytic Pyrolysis: Dauenhauer discusses a catalytic method for increasing viscosity and value of bio-oils.
- Catalytic Pyrolysis: Kantarelis of KTH in Sweden evaluated catalytic steam pyrolysis potential.
- Standards and requirements: Laihanen, Karhunen, and Ranta discuss transportation requirements and considerations for bio-oil in Finland.
- Analysis: Girke at KIT discussed in-line water content determination during pyrolysis production in Germany.
- Fundamentals: Janis at University of Eastern Finland looked at molecular characterization of bio-oils.
- Commercialization: Muggen announces the commercial EMPYRO pyrolysis plant in Netherlands.

As this segment of PyNe history came to a close, the landscape of pyrolysis had come very far. Concrete progress has been

PyNe 38: http://task34.ieabioenergy.com

demonstrated, bio-oil is used for renewable energy at many locations around the world, and yet there are still many questions that need to be answered.

The Future of PyNe

2016 welcomed in a host of changes announced in **PyNe 38** and beyond: A broadened focus on Direct Thermochemical Liquefaction (more than just pyrolysis), changes in Task leadership, gains in new country membership, loss of some long-time member countries, change in the management of the newsletter and webpage, and retirement of many good friends and colleagues.

Recently, as Dietrich Meier retired, Tony Bridgwater departed from the Task, and Doug Elliot retired, it became obvious that most of the original Giants of Pyrolysis have confidently placed the legacy of Direct Thermochemical Liquefaction completely in the hands of you.

They answered many questions, solved decades of questions, and their work was instrumental in enabling the growing commercial and institutional ventures that are using liquefied biomass for energy today.

2016 did not signal the end of an era. It did not mark the beginning of a new one. 2016 demonstrated that the torch would be carried in unbroken succession by the next crop of Giants, solving the challenges and barriers towards adoption of renewable energy from liquefied biomass.

While the original Giants who once walked the land take the opportunity to enjoy the greener pastures of well-deserved rest, it is now up to you to "stand on the shoulders" of their research in order to see further and pursue the solutions that will be needed to solve future energy needs

PyNe: Historical Review...continued

upon the foundation that they have built.

So take some time to review the historical record of PyNe, to savor the successes of the past, to avoid repeating research that has already been done, and to identify the questions raised in the past that are still in search of answers that you will be able to provide.

Acknowledgements

Thank you for the privilege I have had of being able to experience the collaboration and friendship of the international pyrolysis giants past and current: Doug, Tony, Yrjo, Anja, Dietrich, Bert, Wolter, Fernando, Magnus, Ferran, Nicholaus, Christian, Kai, and many others who have influenced me.

Thank you for the fine work that the team at Aston University have done over 20 years keeping the flame of the PyNe newsletter burning brightly for 20 years up to PyNe 38.

Thank you for the sustained national commitments made to the PyNe collaboration by all of the countries and governments over the years as shown
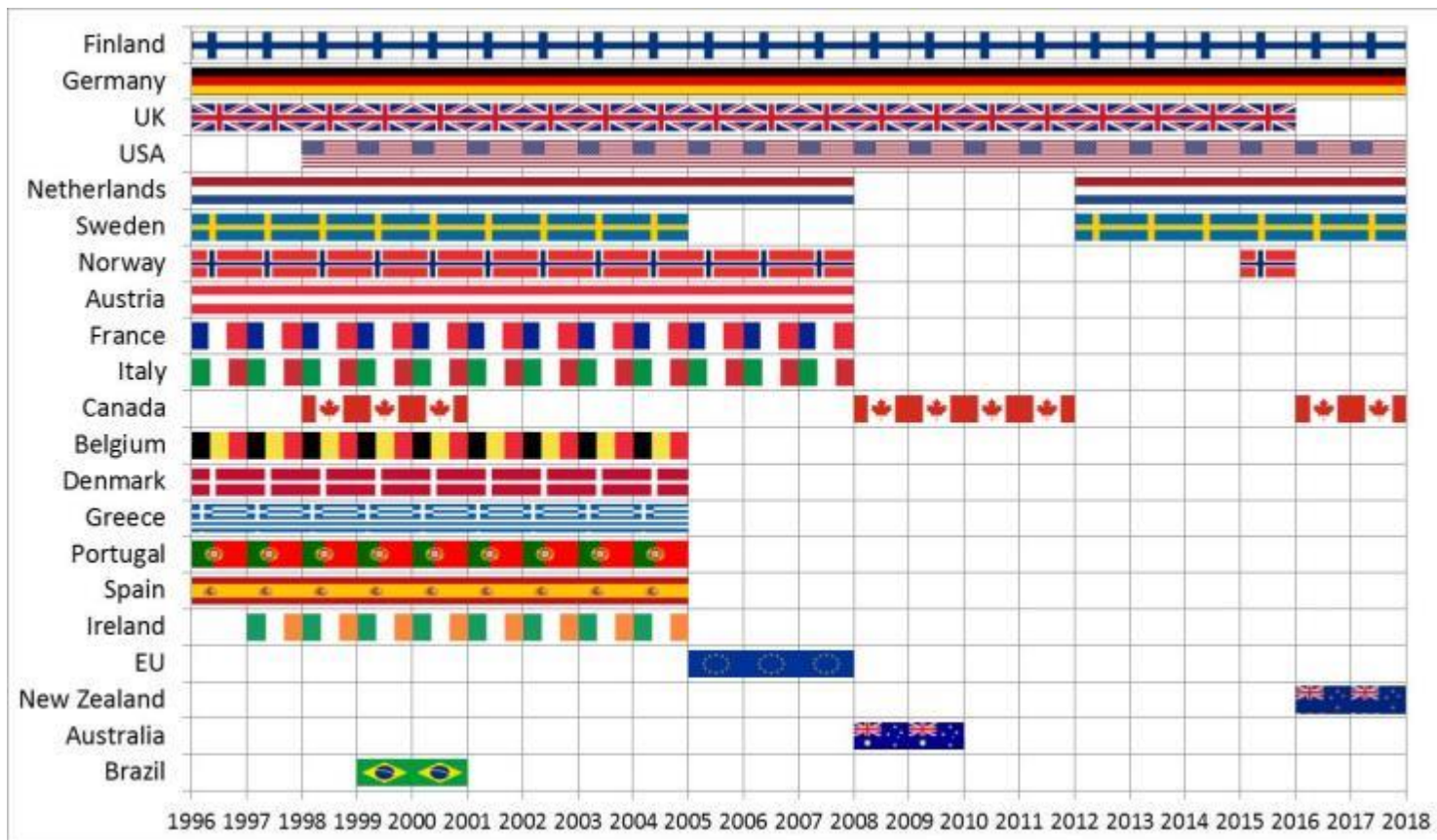

▲ IEA PyRA Group

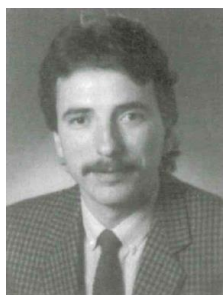in the figure, particularly during the years where renewable research was not popular.

Special thanks to the great countries of Finland and Germany and their researchers that have been steadfast every year, and to the UK, Netherlands, Sweden, and USA for their extensive commitments.
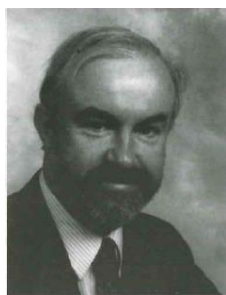
- Alan Zacher, Task 34

Faces of PyNe History

Dietrich Meier	Rosanna Maggi	Tony Bridgwater
Wolter Prins	Philippe Girard	Karsten Pederson

Dietrich Meier

Rosanna Maggi

Tony Bridgwater

Wolter Prins

Philippe Girard

Karsten Pederson

Josef Spitzer

Yrjo Solantausta

Erik Rensfelt

Morten Fossum

Filomena Pinto

Angel Cuevas

Jesus Arauzo

Anja Oasmaa

Jan Piskorz

Yannis Boukis

Colomba Di Blasi

Stefan Czernik

Ed Hogan

Doug Elliott

Max Lauer

Wolfgang Baldauf

Jan Barymin

Yves Schenkel

Elma Gyftopoulou

Robert Brown

Desmond Radlein

Cordner Peacocke

Robbie Venderbosch

Ton Beenackers

Task 34 Meeting in Rotorua, New Zealand...continued

Miguel Mercader, Magnus Marklund, Alan Zacher, Antti Arasto, Kirk Torr, and Luc Pelkmans.

Ferran hosted the tour of Scion which clearly demonstrated the commitment that the people of New Zealand have towards careful stewardship of their natural resources. Task members visited the nursery to see the results of decades long cultivation trials, integrated wood product processing research, thermochemical liquefaction and upgrading for both pyrolysis and hydrothermal liquefaction, and a range of wood derived product research including durable goods, packaging, biodegradable products, and even 3D printing with wood derived materials. One thing that was clear was the strategic thought that New Zealand puts into wood products. They calculate accurate yearly predictions of harvested wood biomass for next year, and each

subsequent one for the next 20 to 30 years. From this, they plan in advance what to do with that harvest, and if new technologies or new markets need to be created to make most efficient use of it, as well as determine if shorter or longer rotation plantations are needed to maintain effective supply decades in the future.

More information about the Task 34 meetings are available at
http://task34.ieabioenergy.com/

For Further Information

IEA Bioenergy Task 34 Website
  task34.ieabioenergy.com/

IEA Bioenergy
  www.ieabioenergy.com/

Past Issues of the Task 34 Newsletters
  task34.ieabioenergy.com/iea-publications/

Pyrolysis Demoplant Database
  task34.ieabioenergy.com/publications/pyrolysis-demoplant-database/

If you would like to contribute an article to the Task 34 newsletter, or have questions, please contact:

Alan Zacher: alan.zacher@pnnl.gov
          Or visit us at task34.ieabioenergy.com/

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Task 34
Direct Thermochemical Liquefaction
PyNe 40, March 2017