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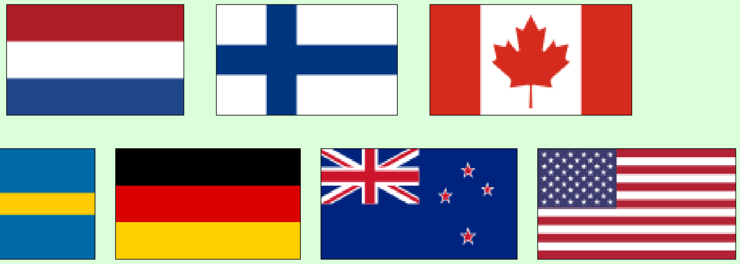

Task 34: Direct Thermochemical Liquefaction

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Demonstrating sustainable bioenergy...and Scaling it up

What do Canada, Sweden, and New Zealand have in common? All three are producing bioenergy and bioproducts from the same biomass, proving it can be grown sustainably over decades and generations.

It occurred to me arriving in Ottawa, Canada, for the Task 34 meeting held in November alongside ***Bioenergy for the Future***, where the IEA announced the new "Technology Roadmap: Delivering Sustainable Bioenergy", and *Scaling Up 2017*, an inspiring event highlighting the immediate need for scaled-up bioenergy.

Scaling Up was a uniquely refreshing experience, driven exclusively by topic centered Q&A panels with limited introductory remarks. The format breathed life into dynamic discussions of differing perspectives on a range of issues crucial to getting biofuels and bioenergy into the market, with hard questions from the audience generating interesting debate.

Topics included both global and Canadian perspectives on typical subjects, such as bioenergy production, biorefining, supply chain, policy drivers, and snapshots of the frontiers of commercialization. It included a **Direct Thermochemical Liquefaction** session entitled *Technology Commercialization – Achieving Success in Pyrolysis, Cellulosics, Hydrothermal Liquefaction, and Hydrofaction™ for Long-haul Transport.*

Fig. 1: Biomass production and fuel storage in Sweden destined for transport diesel fuel.

Yet there were also unusually fascinating panels on banking and financing, communication and collaboration, raising capital, and sourcing new research talent. Hidden gems included impassioned requests from environmental regulators for help in overcoming permitting and compliance barriers that are currently slowing adoption of some bioenergy.

This event was opportunity to see the collaboration of technologists and CEOs, bankers and regulators, which is needed for successful bionenergy.

What of the biomass used by Canada, Sweden, and New Zealand? It's no surprise that these countries share a common interest in bioenergy and bioproducts: the cold

Inside this Issue:

Demonstrating sustainable bioenergy...continued

climate of Canada and Sweden, and the location of New Zealand make these needs imperative. Yet I hadn't realized that all three countries were also world leaders in sustainably managing forests towards that goal.

It is easy to mistake a tree for a consumable in the short term. One day it is there, the next day it is not. Yet a tree may be just another energy and product crop if your farming perspective covers multiple decade investments.

Swedes, Canadians, and New Zealanders do this today. Seedlings planted today will have full impact in 20, 30, 50 years. So, in New Zealand, they forecast wood tonnage yields every year in 20-30 year horizons. In Sweden and Canada, where growing cycles are slower, those yield forecasts stretch out to 50 or more years

Fig. 2: Pyrolysis oil combustion.

Historically, these countries have sustainably farmed and harvested these natural resources for decades, and in some cases hundreds, of years. The difference is that today, their products are starting to displace petroleum use. In Sweden, Preem is making diesel fuel from tall oil and looking to advanced technology. In Canada, Ensyn is actively delivering pyrolysis oil to heat commercial buildings. In New Zealand, Scion is developing packaging material, expanded foams, and bio-plastics from wood sourced materials.

While there is no one-size-fits-all solution to our international energy needs, it is clear that sustainably managed forestry products are already filling an important role in both renewable bioenergy and bioproducts.

And with a decades of evidence that it can be managed sustainably, it will certainly contribute for years to come. . – Alan Zacher, Task 34 US NTL

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Comparison of intermediate and fast pyrolysis in screw-type reactors

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Intermediate pyrolysis is a well investigated process with distinct differences to the commonly known slow and fast pyrolysis. Its primary aim is to produce a liquid product with transportation fuel quality (Neumann et al., 2015; Tomasi Morgano et al., 2015). It operates at a solid residence time of minutes rather than hours, as for the case of slow pyrolysis, or seconds, as for the case of fast pyrolysis. The biomass particles are heated with a heating rate of around 100 K min-1, which is orders of magnitude below that of fast pyrolysis. Another important characteristic is the vapour residence time at reactor temperature. In contrast to fast pyrolysis, secondary pyrolysis reactions of the vapour products are allowed or even promoted with special reforming steps. It is obvious and well-known that these operating conditions lead to a lower bio-oil and higher reaction water yield. This price of low yields is paid to obtain a bio-oil product that shows more favourable characteristics as a transportation fuel than typical fast pyrolysis bio-oil (Neumann et al., 2015). It is interesting to note that to date there was no concerted effort to actually quantify the differences in yields from intermediate and fast pyrolysis, which both aim at producing a bio-oil as main product.

The aim of the present study is to close this gap by comparing the product distribution of two pilot scale pyrolysis units with 10 kg h-1 feed capacity that are operated with intermediate and fast pyrolysis conditions for the same set of biomass (Funke et al., 2017). The type of biomass used was beech wood, hybrid poplar wood, wheat straw, and a blend (hybrid poplar, forest thinnings, wheat straw). The latter three feedstocks have been supplied as part of a Round Robin organized by the IEA Bioenergy Task 34 and the bio-oils obtained from the fast pyrolysis trials presented here have been supplied for analysis within this Round Robin (Elliott et al., 2017). The intention was to establish a broader context to compare bio-oil yields. Unfortunately, the results of aforementioned Round Robin have finally been published without an indication of bio-oils yields from the different laboratories. In addition to these three feedstocks, beech wood was chosen as one of the few biomass resources that are commercially available with a relevant quality control (particle size, ash content, bulk density, moisture content). Analyses of these feedstocks are summarized in Table 1. It is pointed out that the ash content covers a broad range between 1-13 % (dry mass basis) The setup of the test rigs and general experimental procedures are described in detail elsewhere (Funke et al., 2016; Tomasi Morgano et al., 2015). Both test rigs incorporate screw type reactors. High heat transfer for fast pyrolysis conditions is achieved by adding a preheated heat carrier to the reactor, which is then mechanically mixed with the feedstock by two interlacing screws. The process conditions have been chosen to both reflect the different intermediate/fast pyrolysis process conditions and at the same time be as close as possible for comparison (see Table 2). They do not necessarily reflect optimum process conditions. Reactor temperature was controlled closely at the same level, which reflects the temperature of secondary vapour phase reactions and also the mixing temperature of heat carrier/biomass particles in case of fast pyrolysis. The feed rate was in the same range and limited by the material with the lowest volumetric density (wheat straw). The condensation strategy of the two test rigs has been adapted for the specific products and shows significant differences. Final condensation temperature was kept as close as possible with the existing equipment so that the overall bio-oil yield (and its components) can be compared directly. A comparison of the bio-oil quality was not aim of this study and requires alignment of the

Table 1: Analyses of the selected feedstocks.

	Water (ar) (%)	Ash (d) (%)	C (d) (%)	H (d) (%)	O* (d) (%)	HHV (d) (kJ g-1)	Volatiles (d) (%)
Beech wood	9.0	1.2	49.6	6.0	42.5	18.7	83.1
Poplar wood	7.8	2.0	48.9	5.9	43.2	18.7	82.1
Blend	7.0	4.0	47.7	5.8	42.5	18.6	77.3
Wheat straw	5.7	12.9	42.8	5.4	38.9	16.6	67.0

* by difference; ar: as received;, d: dry

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Comparison of pyrolysis in screw-type reactors…Continued

condensation strategies to allow for a feasible data basis.

Table 2: Process conditions of the experiments

	Dur.	Feed rate	Rxtr. temp.	Heating rate	Vapour res. time	Condens. temp(s)
Python	4-5 h	5-6 kg h^{-1}	500°C	>10.000 K min^{-1}	<4 s	90°C; 20°C
STYX	3-4 h	3 kg h^{-1}	500°C	≈100 K min^{-1}	<20 s	80°C; 15°C

Screw-type reactors have been questioned to be representative for fast pyrolysis (Elliott et al., 2017). This hypothesis can be investigated with the present study because fast pyrolysis experiments have been conducted as part of the IEA Bioenergy Task 34 Round Robin and also because beech wood has been used additionally. The most meaningful basis to compare bio-oil yields is on the basis of the organic liquid yield, which excludes the water content of liquid product(s) (see Figure 1). The organic liquid yield obtained in this study from beech wood fast pyrolysis is comparable to the range of 50-55 % reported elsewhere for beech wood (Beaumont & Schwob, 1984; Greenhalf et al., 2013). Unfortunately, results in literature are often only reported for the bio-oil yield, i.e. including water. Such data for beech wood fast pyrolysis reports bio-oil yields of around 61-70 % (Beaumont & Schwob, 1984; Di Blasi & Branca, 2001; Jendoubi et al., 2011; Wang et al., 2005). These results are in line with bio-oil yields obtained from beech wood fast pyrolysis in the present study, too (69.9±0.9 %).

Finally, the quality of the produced fast pyrolysis bio-oil from the feedstocks supplied by the IEA Bioenergy Task 34 Round Robin does not show a significant deviation from bio-oils produced by fluidized bed or ablative reactors (Elliott et al., 2017). Values can be easily checked because there has been only one participating laboratory that applied a twin-screw technology. The only exception to the quality parameters is the high solids content. The comparably poor solid separation prior to condensation is due to the current project requirements in which the condensate(s) are mixed with the solids to produce a bioslurry for subsequent gasification (Dahmen et al., 2012; Nicoleit et al., 2016).

Obviously, the reactor type used to achieve fast pyrolysis conditions is of minor importance as long as heating rate and hot vapour residence time requirements are met. It is concluded that the screw-type reactor used in this study is suitable to achieve all necessary fast pyrolysis conditions and in consequence to produce a 'typical' fast pyrolysis bio-oil. All data indicate that it is a suitable representative for fast pyrolysis to allow for a comparison with intermediate pyrolysis.

The organic liquid yields obtained from fast pyrolysis are significantly higher than from intermediate pyrolysis, as expected. It is

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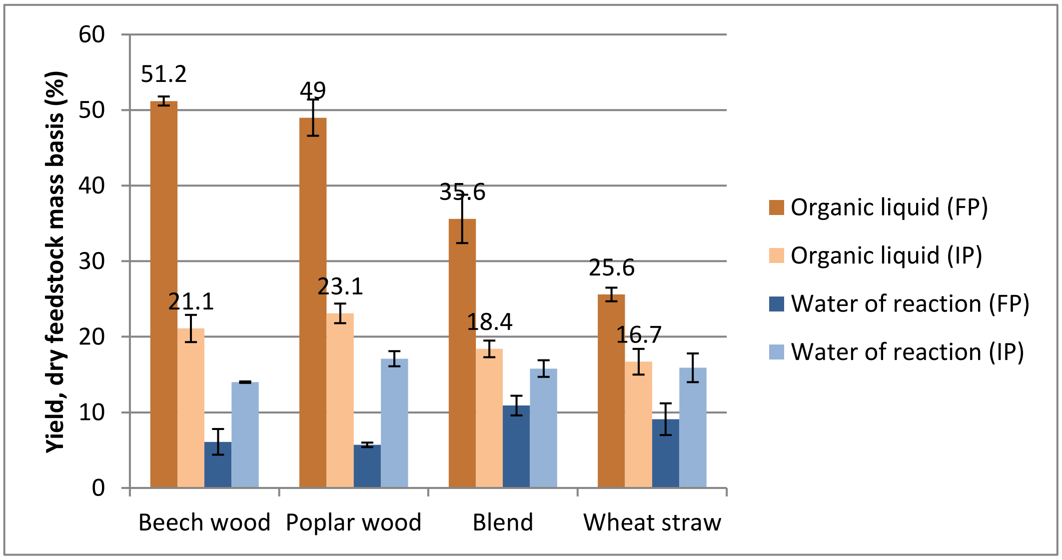

Figure 1: Organic liquid and water of reaction yields (FP: fast pyrolysis, IP: intermediate pyrolysis). Error bars indicate the difference between two experimental runs.

Comparison of pyrolysis in screw-type reactors...Continued

interesting to observe that the yields from fast pyrolysis are more heavily affected by the ash content of the feedstock. While more than twice as much organic liquid is produced in case of beech wood only 50 % more is produced for the ash-rich wheat straw. Consequently, the advantage of high organic liquid yields has to be evaluated with special consideration of the type of feedstock used. The high amount of reaction water produced during intermediate pyrolysis does not affect bio-oil quality negatively. Water content in the intermediate pyrolysis bio-oil of around 10 % has been observed with the current condensation and product recovery design.

The yield of several marker species has been evaluated for the obtained bio-oils. The results support the expected ongoing pyrolytic reactions in case of intermediate pyrolysis. Acetic acid yields are increased and so is the yield of phenol on the expense of guaiacol. It can even be observed that benzene and naphthalene are produced with yields one order of magnitude higher than for fast pyrolysis.

Surely, this study is a first step to allow for a more detailed comparison of these two pyrolysis technologies. It provides the required quantitative data to show differences in product distribution. The next step is to directly compare bio-oil quality and relate it to the differences in bio-oil yield. Such data is a mandatory prerequisite to allow for a rational decision for suitable pyrolysis technology dependent on feedstock and product use.

References

Beaumont, O., Schwob, Y. 1984. Influence of Physical and Chemical Parameters on Wood Pyrolysis. Ind Eng Chem Process Des Dev, 23, 637-641.

Dahmen, N., Henrich, E., Dinjus, E., Weirich, F. 2012. The bioliq bioslurry gasification process for the production of biosynfuels, organic chemicals, and energy. Energ Sust Soc, 2(3).

Di Blasi, C., Branca, C. 2001. Kinetics of Primary Product Formation from Wood Pyrolysis. Ind Eng Chem Res, 40(23), 5547-5556.

Elliott, D.C., Meier, D., Oasmaa, A., van de Beld, B., Bridgwater, A.V., Marklund, M. 2017. Results of the International Energy Agency Round Robin on Fast Pyrolysis Bio-oil Production. Energ Fuel, 31(5), 5111-5119.

Funke, A., Richter, D., Niebel, A., Dahmen, N., Sauer, J. 2016. Fast Pyrolysis of Biomass Residues in a Twin-screw Mixing Reactor. J Vis Exp, 115, e54395.

Funke, A., Tomasi Morgano, M., Leibold, H., Dahmen, N. 2017. Experimental Comparison of Fast and Intermediate Pyrolysis. J Anal Appl Pyr, 124, 504-514.

Greenhalf, C.E., Nowakowski, D.J., Harms, A.B., Titiloye, J.O., Bridgwater, A.V. 2013. A comparative study of straw, perennial grasses and hardwoods in terms of fast pyrolysis products. Fuel, 108, 216-230.

Jendoubi, N., Broust, F., Commandre, J.M., Mauviel, G., Sardin, M., Lede, J. 2011. Inorganics distribution in bio oils and char produced by biomass fast pyrolysis: The key role of aerosols. J Anal Appl Pyr, 92(1), 59-67.

Neumann, J., Binder, S., Apfelbacher, A., Gasson, J.R., Ramírez García, P., Hornung, A. 2015. Production and characterization of a new quality pyrolysis oil, char and syngas from digestate - Introducing the thermo-catalytic reforming process. Journal of Analytical and Applied Pyrolysis, 113, 137-142.

Nicoleit, T., Dahmen, N., Sauer, J. 2016. Production and Storage of Gasifiable Slurries Based on Flash-Pyrolyzed Straw. Energy Technology, 4(1), 221-229.

Tomasi Morgano, M., Leibold, H., Richter, F., Seifert, H. 2015. Screw pyrolysis with integrated sequential hot gas filtration. Journal of Analytical and Applied Pyrolysis, 113, 216-224.

Wang, X., Kersten, S., Prins, W., van Swaaij, W.P.M. 2005. Biomass Pyrolysis in a Fluidized Bed Reactor. Part 2: Experimental Validation of Model Results. Ind Eng Chem Res, 44, 8786-8795.

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Increasing production and isolation of phenols via pyrolysis of lignocellulosic biomass

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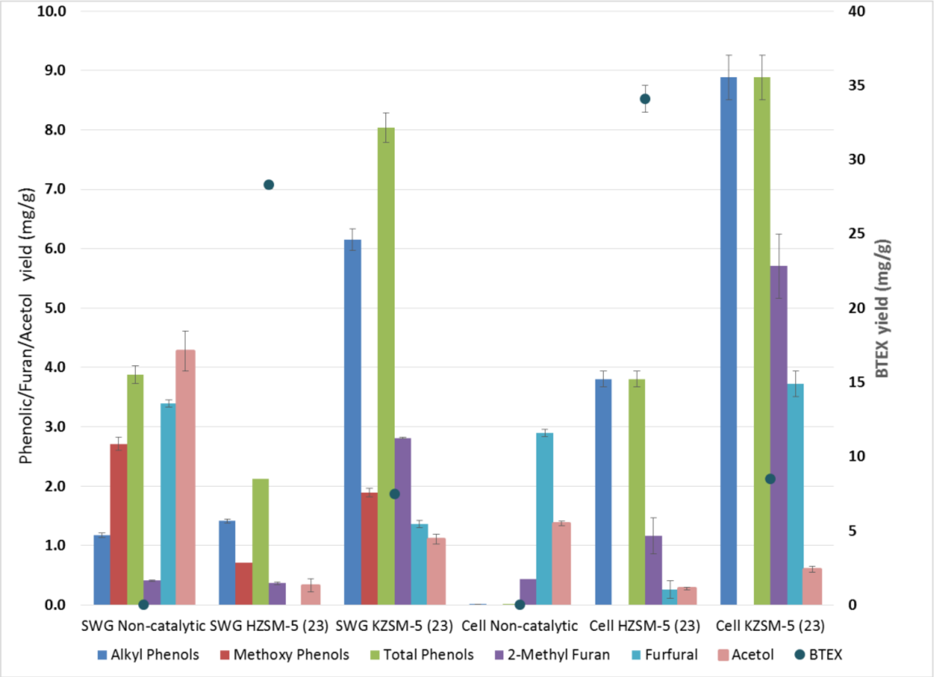

Figure 1. Comparison of yields from selected compounds from switchgrass (SWG) and Cellulose (Cell) over HZSM-5 (23) and KZSM-5 (23) at 5/1 catalyst/biomass and 500 ºC. Alkyl phenols = phenol, o-,m-,p-cresols, 2,4-dimethyl phenol and 4-ethyl phenol. Methoxy phenols = guaiacol, 4-methylguaiacol, syringol. BTEX = benzene, toluene, ethyl benzene, xylenes. Error bars represent one standard deviation.

Much of the research in biomass pyrolysis over the last decade has focused on modifications to the pyrolysis process to produce stable, partially deoxygenated bio-oils. This has been done, usually, with the ultimate goal of reducing the oxygen content, after upgrading, to near zero for use in advanced hydrocarbon bio-fuels. However, there is now a realization that to be commercially viable, biorefineries will need to produce high value chemical or materials co-products in addition to fuels, just as petroleum refineries do. This is where preservation of some of the inherent oxygen content, that we have long sought to remove, may be an advantage. Nearly limitless useful oxygenated chemicals, from high volume commodities to premium pharmaceutical precursors are produced through oxidation of petroleum hydrocarbons, so oxygenated biomass derived replacements may be advantageous. USDA-ARS has begun researching ways to increase the yield of certain targeted oxygenated hydrocarbons during pyrolysis and also isolate them from the complex mixture. One examples is phenolics. The phenolic aromatic C-O bond is among the most difficult of all the C-O bonds found in bio-oils to break, and phenols are found among the remaining oxygenates in both the CFP and TGRP processes. Furthermore, phenol is more valuable than its completely deoxygenated analog benzene. For these reasons phenols are among the first oxygenated chemicals we are targeting for increased production during pyrolysis.

Two types of phenols are produced from pyrolysis of lignocellulosic biomass, alkyl phenols which can be derived from either the cellulose or lignin polymer, and methoxylated phenols which are generated directly from lignin depolymerization. Recent developments in our laboratory have increased the production of both classes of phenols from pyrolysis of biomass. In many studies of HZSM-5 zeolite catalyst deactivation, alkyl phenols are often found as an “intermediate” product, not produced by fresh catalysts, but by partially deactivated catalysts at levels well above non-catalytic pyrolysis. For this reason, we sought to understand the properties of these partially deactivated zeolites, and mimic them to maximize production of alkyl phenols. Catalyst deactivation can occur by deposition of carbon deposits on catalysts or by poisoning by alkali metals; both of these have the effect of decreasing the Brønsted acid site density. We therefore produced a simple series of catalysts, reducing the acid site density by exchanging the acid sites with potassium (K).

As shown in Figure 1, when the KZSM-5 catalyst was used for the CFP of switchgrass, there was a 74% decrease in the production of aromatic hydrocarbons compounds and ~3-fold increase in the production of the selected alkyl- and methoxy phenols compared to the parent HZSM-5. In the case of methoxy phenols, the yield was lower than that achieved non-catalytically, which suggests they were not formed catalytically but rather their

(Continued on page 5)

Increasing production and isolation of phenols…continued

catalytic conversion to other products was limited by the use of a less active catalyst. However, the alkyl phenol yield was substantially higher (>4-fold increase) than that produced non-catalytically, meaning the alkyl phenols were the product of a catalytic reaction, not merely a consequence of diminished catalytic conversion. Similarly, there was an increase in the production of furans, particularly 2-, whose production increased to a yield of 4.6 mg/g, whereas only trace amounts were observed for HZSM-5 (23) and non-catalytic pyrolysis.

Table 1. Effect of adding 1,4-butandiol to lignin during microwave pyrolysis on bio-oil yield, molecular weight, dispersity index and phenolic selectivity

Eqs. of 1,4-Butanediol added	-	0.125	0.250	0.500	1.000
Bio-oil Yield	30.4	37.8	40.1	39.7	44.3
Bio-oil M_w	1187.9	637.6	443.4	332.0	134.9
Bio-oil M_n	350.5	261.8	221.9	181.3	102.7
Bio-oil PDI	3.39	2.44	2.00	1.83	1.31
Methoxy-phenols selectivity(wt%)	5	9	31	55	62
Alkyl-phenols selectivity (wt%)	95	91	69	45	38

When cellulose was used as the starting material rather than switchgrass, the same trend is observed, and the production of alkyl phenols from cellulose (not just lignin) is verified. Selected alkyl phenols were produced in a yield of about 9 mg/g from cellulose over KZSM-5 (23), compared with 3.8 mg/g over HZSM-5 (23) and only trace amounts non-catalytically. Similarly, the yield of 2-methyl furan increased to over 5 mg/g over KZSM-5 (23), compared with ~1 mg/g using HZSM-5 (23). More details of this work can be found in our recent ACS Sustainable Chemistry and Engineering publication [1].

Meanwhile, in another development in our laboratory we have also found that microwave co-pyrolysis of lignin with high boiling diols can increase its net depolymerization, resulting in an increase in production of methoxyphenols along with an overall decrease in the average molecular weight of the bio-oil. Lignin is also the most abundant natural source of aromatic compounds in the biosphere, which makes it an attractive renewable feedstock for the production of biofuels, commodity chemicals, and other value added products. Unfortunately, limited success has been achieved in development of effective depolymerization strategies to unlock this potential.

In our work, lab scale microwave pyrolysis of lignin has been performed and the liquid products obtained are composed of smaller polymeric components and moderate yields of monomeric phenols. However, upon the addition of 1,4-butanediol, repolymerization reactions that limit the yield of monomeric and other reduced molecular weight products are inhibited. As shown in Table 1, a 85-90% reduction in the average molecular weight of the liquid products was observed concurrent to an overall increase in liquid yield. At the optimized ratio of 2:1 lignin to 1,4-butanediol (w/w), the yield of selected monomeric phenols increased three-fold to ~3.4 wt% (based on feedstock), while the yield of mono-aromatic hydrocarbons decreased by approximately 90%. The addition of the diol co-reactant also led to a significant shift in selectivity towards the production of methoxy-phenols (guaiacols, syringols) over non-methoxylated alkyl-phenols (phenol, cresols, etc.). The results obtained may help lead to the development of novel lignin co-processing methods. We believe that the addition of the diol may quench radical or acid initiated reploymerization reactions leading to the observed higher yield and lower molecular weight, and also that preservation of the methoxy groups may also decrease the occurrence of repolyemrization reactions during pyrolysis. More details on this development can be found in our recent journal publication [2].

We are currently building off these developments to further increase the production of phenolics from cellulose, lignin and biomass. This includes development of catalysts more selective for phenols, transfer of operations to a continuous larger scale process and development of methods for the selective isolation of phenols from bio-oil.

References

[1] Mullen, C.A., Tarves, P.C., Boateng, A.A. Role of Potassium Exchange in Catalytic Pyrolysis of Biomass over ZSM-5: Formation of Alkyl phenols and Furans. ACS Sustainable Chemistry and Engineering, 5, 2154-2162. 2017.

[2] Tarves, P. C., Mullen, C.A., Strahan, G. D., Boateng, A.A. Depolymerization of Lignin via Co-pyrolysis with 1,4-Butanediol in a Microwave Reactor. ACS Sustainable Chemistry and Engineering, 5, 988-994. 2017

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Applications of Phenolic Oil Derived from Fast Pyrolysis

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Fast pyrolysis of lignin results in a mixture of phenolic monomers and oligomers sometimes referred to as pyrolytic lignin although phenolic oil is a more accurate characterization. Iowa State University (ISU) has developed a fractionating recovery system that collects phenolic oil has part of a heavy ends fraction [1, 2]. A simple water extraction is able to separate the water-insoluble phenolic oil from water soluble sugars and anhydrosugars [3].

Phenolic oil presents 40-45% of the carbon content of the products of pyrolysis. Most of the aromatic content of the lignin is preserved. Its oxygen content is approximately 20-24%, much lower than that of the carbohydrate-derived products of pyrolysis, giving it an attractive heating value for production of fuels. However, it is extremely reactive in storage or during thermal processing, which can complicate its refining, although in some cases this reactivity can be exploited. This paper explores some options for upgrading phenolic oil into various products.

Low-temperature, low-pressure hydrogenation

The superficial similarities between petroleum and bio-oil have encouraged efforts to upgrade it in the same way as petroleum. Any facile comparison is overshadowed by the fact that petroleum contains non-polar hydrocarbons that are relatively stable, requiring elevated temperatures and pressures to encourage chemical transformations, whereas bio-oil consists of oxygenated organic compounds whose high degree of functionality makes them chemically reactive even at low temperatures and pressures. Due to the reactive nature of the phenolic oil, low-temperature, low-pressure hydrogenation (LTLP-H) was utilized to produce a stable, low viscosity product at high yields [4].

Low-temperature, low-pressure hydrogenation, which was performed at 21 °C and 1 bar pressure, resulted in high carbon yields: 98.2% to 98.7% for phenolic oils from corn stover and red oak, respectively. The viscosities of phenolic oil samples (measured at 60 °C) dropped dramatically after hydrogenation: cornstover fraction 1 decreased by 81% and fraction 2 decreased by 47%. Red oak fraction 2 heavy ends showed a more dramatic drop in viscosity, decreasing by 99%. This viscosity thinning after hydrogenation is in sharp contrast to the viscosity thickening observed by researchers who used higher temperatures and pressures to hydroprocess bio-oil. Viscosity reductions are usually associated with more severe hydrocracking, which reduces the molecular weight of heavy organic compounds. Cracking of phenolics clearly did not occur during LTLP-H. Further analytical testing suggested that viscosity thinning was the result of the self-solvation power of produced alcohol during hydrogenation.

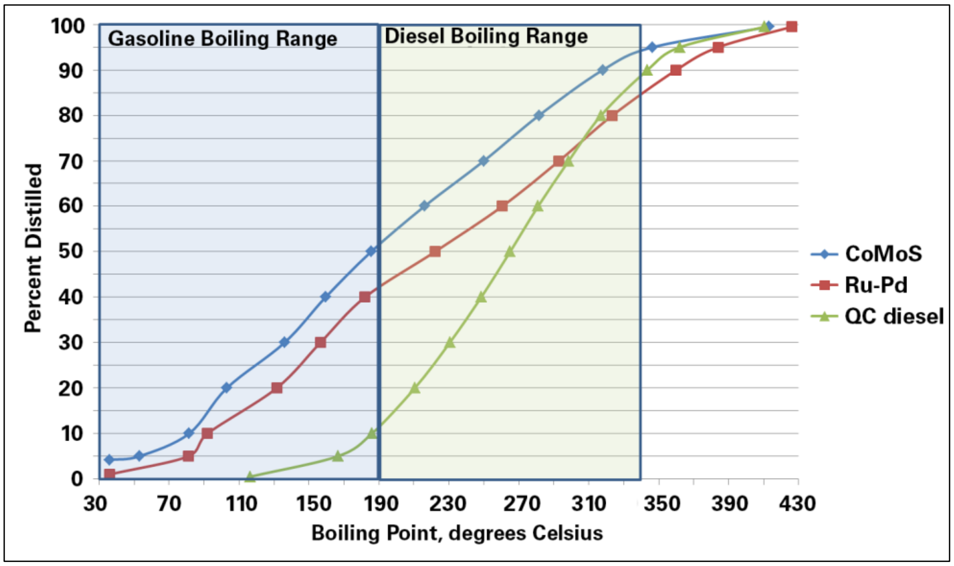

Fig. 1 - Gas chromatography simulated distillation (SimDist ASTM D2887) of hydrotreated phenolic oil utilizing sulfided CoMo and Ru-Pd catalysts.

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Applications of Phenolic Oil Derived from Fast Pyrolysis...continued

Catalytic hydroprocessing of phenolic oils

Hydroprocessing can deoxygenate and crack phenolic oil into fuel-range hydrocarbon molecules as demonstrated in a collaboration between ISU and Pacific Northwest National Laboratory (PNNL) [5]. Red oak and corn stover were pyrolyzed and the phenolic oil recovered using water extraction of the heavy ends at ISU. The phenolic oils from these two feedstocks were shipped to PNNL where they were catalytically hydrotreated to remove heteroatoms. The carbon yields were as high as 90% carbon yield to liquid hydrocarbons from the phenolic oil.

The liquid product from hydrotreated red oak phenolic oil was analyzed by gas chromatography simulated distillation. Figure 1 indicates a significant portion of the hydrotreated products fell within gasoline range molecules (42-52%), whereas, 43% fell within diesel range molecules [3].

Coal substitute from curing phenolic oil

The reactivity of phenolic oil can be exploited to produce an attractive low ash, low sulfur coal substitute called Lignocol. Phenolic oil heated to 105-220 °C for ≤ 2 hours polymerizes to a vitreous solid resembling coal with yields of 87.4-94.5 % depending on the heating temperature, length of time, and moisture content. The optimum temperature for these experiments was ≤160 °C for 45 min. This process is illustrated schematically in Figure 2 [6].

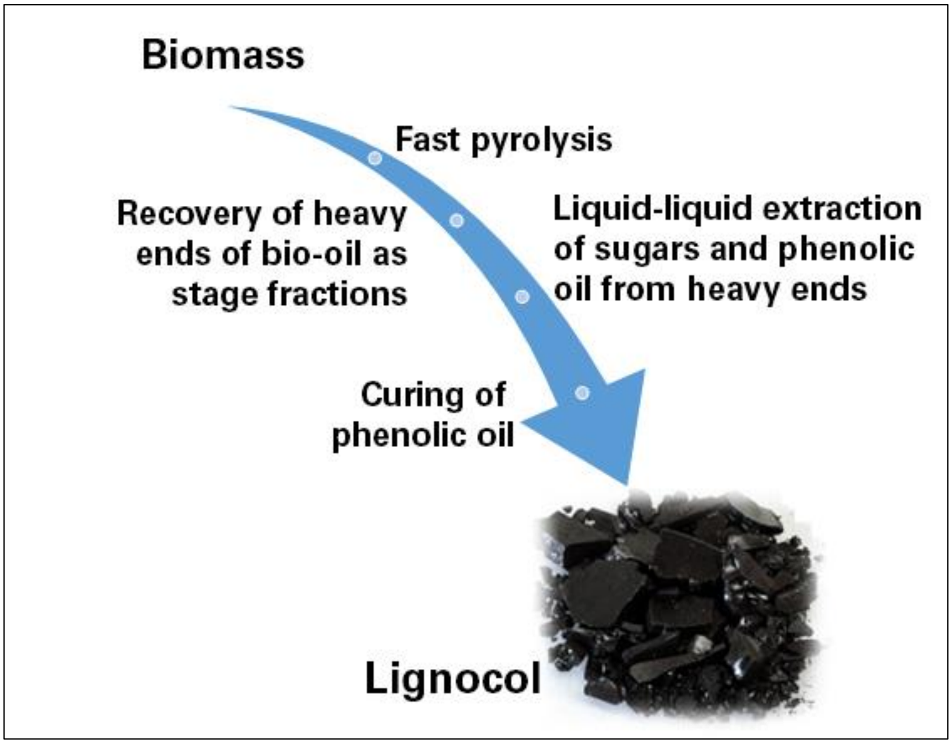

Fig.2 - Process for the production of Lignocol from lignocellulosic biomass.

The higher heating value of Lignocol was similar to that for a variety of coals in the United States, whereas, the nitrogen and sulfur content were lower than coal, 65-85% and 97-99%, respectively. The metal content of Lignocol was well below that of most coals.

Fractionated phenolic oil as binder in asphalt and pavement

Asphalt is used in approximately 90% of U.S. paved highways. It is also used for crack sealing and surface treatments of pavements. Research at ISU has demonstrated that bioasphalt can be used as a modifier, extender, or even as an antioxidant when added to petroleum-based asphalt [7, 8].

Phenolic oil derived from cornstover, red oak wood, and switchgrass were used to formulate bioasphalt. The phenolic oil was blended with three common asphalt binders and evaluated for high temperature rheological properties, short term aging, inter temperature rheological properties, long term aging, and low and high temperature rheological properties. The addition of phenolic oil to the asphalt binders caused a stiffening effect resulting in increased high and low critical temperatures. Overall, the tests showed beneficial effects of using phenolic oil in asphalt at high and medium temperatures.

A section of the Waveland Bike Trail, Des Moines, IA, was selected for a demonstration project. Approximately 900 feet of the 10 foot wide trail was paved in fall of 2010 with a 2 inch layer of asphalt containing 3% phenolic oil from heavy ends bio-oil (Figure 3). Evaluation of the project is still ongoing and has been successful to date [9].

Acknowledgements

The author wishes to acknowledge the contributions of co-workers and collaborators. Robert Brown, Bioeconomy Institute Director, was the Principal Investigator for hydrotreating project, which was supported by the

(Continued on page 10)

Applications of Phenolic Oil Derived from Fast Pyrolysis...continued

U.S. DOE. Ryan Smith managed the projects LTLP-H and Lignocol projects, which were funded by the Bioeconomy Institute, Iowa State University. Douglas C. Elliott and Huamin Wang of Pacific Northwest National Laboratory performed the hydrotreating experiments. The bioasphalt experiments were done under the direction of R. Christopher Williams in his laboratory at ISU. He also oversaw the Waveland Bike Trail demonstration project. Lysle Whitmer managed the production of all oils used in the experiments while Jordan Funkhouser and Andrew Friend helped in the operation and maintenance of the pyrolysis system. Patrick Hall and Patrick Johnston helped in analyzing the bio-oil samples. Bob Mills assisted in preparing this article.

Fig. 3 – Paving Waveland Bike Trail, Des Moines, IA with a mixture of petroleum-based asphalt and phenolic oil.

References

[1] Pollard, A. S.; Rover, M. R.; Brown, R. C., Characterization of bio-oil recovered as stage fractions with unique chemical and physical properties. *Journal of Analytical and Applied Pyrolysis* **2012,** 93, 129-138.

[2] Rover, M. R.; Johnston, P. A.; Whitmer, L. E.; Smith, R. G.; Brown, R. C., The effect of pyrolysis temperature on recovery of bio-oil as distinctive stage fractions. *Journal of Analytical and Applied Pyrolysis* **2014,** 105, (0), 262-268.

[3] Rover, M. R.; Johnston, P. A.; Jin, T.; Smith, R. G.; Brown, R. C.; Jarboe, L., Production of Clean Pyrolytic Sugars for Fermentation. *ChemSusChem* **2014**, 1662-1668.

[4] Rover, M. R.; Hall, P. H.; Johnston, P. A.; Smith, R. G.; Brown, R. C., Stabilization of bio-oils using low temperature, low pressure hydrogenation. *Fuel* **2015,** 153, 224-230.

[5] Elliott, D. C.; Wang, H.; Rover, M.; Whitmer, L.; Smith, R.; Brown, R., Hydrocarbon Liquid Production via Catalytic Hydroprocessing of Phenolic Oils Fractionated from Fast Pyrolysis of Red Oak and Corn Stover. *ACS Sustainable Chemistry & Engineering* **2015,** 3, (5), 892-902.

[6] Rover, M.; Smith, R.; Brown, R. C., Enabling biomass combustion and co-firing through the use of Lignocol. *Fuel* **2018,** 211, 312-317.

[7] Peralta, J.; Williams, R. C.; Rover, M. R.; Silva, H. M. R. D., Development of Rubber-Modified Fractionated Bio-Oil for Use as Noncrude Petroleum Binder in Flexible Pavements. In *Alternative Binders for Sustainable Asphalt Pavements*, Transportation Research Board: Washington D.C., 2012; pp 23-36.

[8] Williams, R. C.; Satrio, J.; Rover, M. R.; Brown, R. C.; Teng, S., Utilization of Fractionated Bio Oil in Asphalt. In *Transportation Research Board 88th Annual Meeting*, Transportation Research Board: Washington DC, 2009.

[9] www.iowaltap.iastate.edu/documents/TN/2011/Oct-Dec/2011%20TN%20Oct-Dec-5-6%20bio-asphalt.pdf Iowa experiments with a "greener" pavement option.

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The use of fast pyrolysis bio-oil in a modified diesel engine

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The use of Fast Pyrolysis Bio-Oil (FPBO) in stationary diesel engines can be a valuable approach for small scale, combined heat & power (CHP) applications. However, direct application (i.e. without chemical upgrading) is challenging due to the specific properties of FPBO. The pH of FPBO is below 3 and the water content is in the range of 20 -25 wt%. As a result standard diesel engine components will quickly corrode when contacted with FPBO.

To enable fast and complete combustion of FPBO, proper atomization is of utmost importance. Compared to conventional diesel FPBO, has a higher viscosity and a higher density which will result in larger droplets. Additionally, the dynamic surface tension of FPBO is significantly higher than for diesel causing a further increase in droplet size [3,4]. Adding some ethanol to the FPBO strongly improves the atomization properties.

FPBO is difficult to ignite and special measures are required. Different approaches can be used such as increasing the air inlet temperature,

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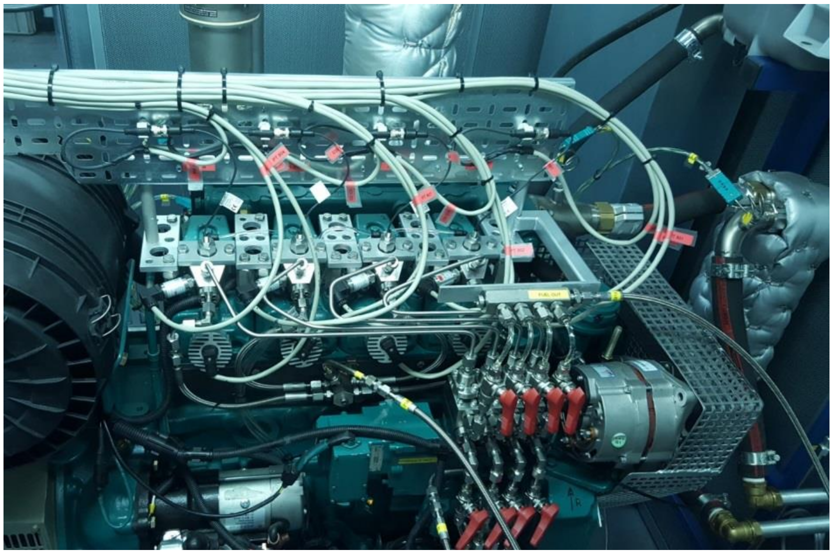

Fig. 1: Modified 4 cylinder diesel engine

Fig 2: Fuel feeding skid

The use of fast pyrolysis bio-oil in a modified diesel engine

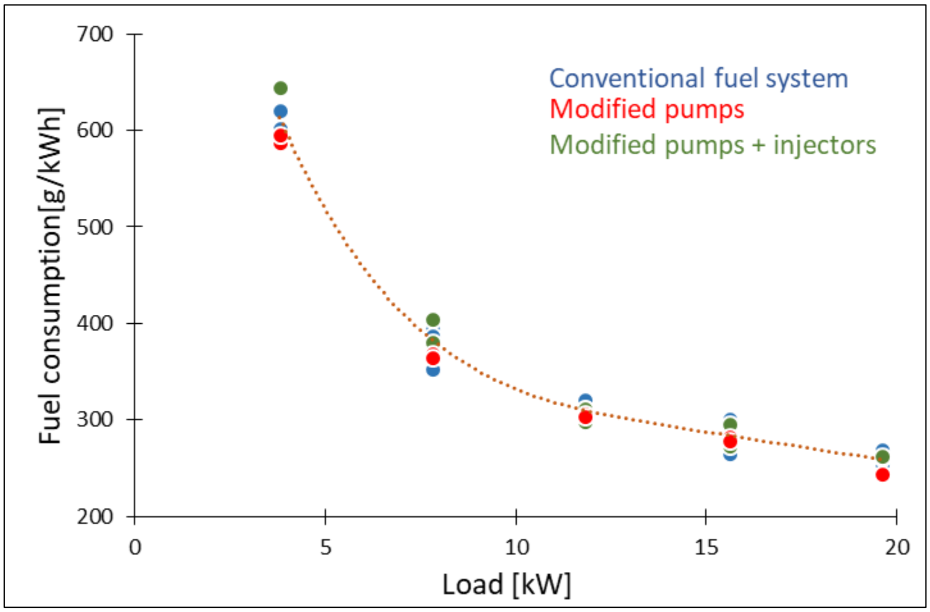

Fig. 3A: Specific fuel consumption as a function of the load

increasing the compression ratio, adding cetane improvers to the fuel, or pilot fuel injection.

Engine modification

BTG has modified two compression-ignition engines to develop this application, viz. a one-cylinder and a four-cylinder prototype. Initial work was done with the 1-cylinder engine which has the advantage that only 1 fuel injection system needs to be constructed and installed. More recently, the modification of the four cylinder engine started which can be seen as a prototype for a commercial size CHP system.

The prototype is based on the Weichai 226B engine, and the complete gen-set has been assembled and supplied by ABATO Motoren BV, the Netherlands. Subsequently, the unit has been modified by BTG to enable FPBO fueling. Four corrosion resistant fuel pumps and fuel injectors have been constructed in-house. The fuel pump is a two-stage system meaning that the original fuel pump is driving a 2nd fuel pump. The latter pump is connected to the fuel injector, and direct contact of FPBO with original parts of the engine is avoided. To overcome the poor ignition of FPBO the incoming air can be preheated; the compression ratio is kept to the original value of 18. Some pictures of the unit are shown in Fig. 1 and 2.

The engine is started on diesel, and subsequently the inlet air heater is switched on. If the engine is running smoothly and stable the fuel type is switched to rinsing liquid (ethanol or butanol) and engine will run for 5 or 10 minutes on this fuel. Finally, the switch is made to FPBO. So far all tests have been carried out with FPBO containing 20 wt% ethanol. The FPBO was produced by the Empyro plant from woody biomass.

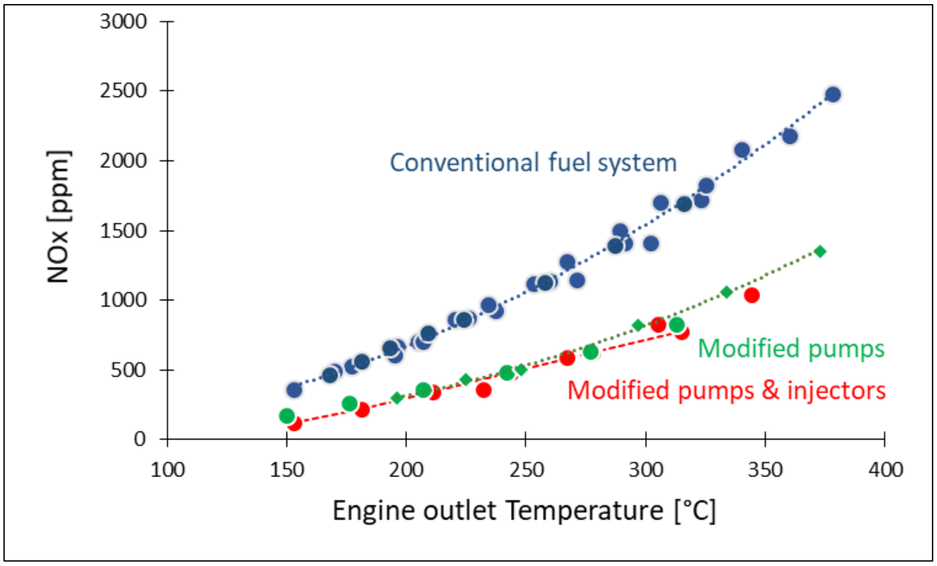

Fig. 3A: Specific fuel consumption as a function of the load

Initial results

The major modification to the engine concerns the fuel feeding pumps and fuel injectors. To evaluate the new components their performance has been compared to the standard ones. Initially, reference runs have been carried out with diesel and the standard fuel pumps and injectors. Next, only the four fuel pumps were replaced with the modified fuel pumps, and the test runs were repeated with diesel as fuel. Finally, the new fuel injectors were installed and the same tests were carried out again. In Fig 3A and 3B the results of these tests are shown. Fig. 3A shows the fuel consumption for the three configurations as a function of the electrical load. Hardly any difference is

(Continued on page 13)

The use of fast pyrolysis bio-oil in a modified diesel engine

observed indicating that the system is working reasonably well. In Fig. 3B the NO_x concentration in the flue gas is shown as a function of the flue gas temperature. Tests were carried out at different engine loads (up to 20 kW_e) and different air inlet temperatures (50 – 200 °C). The new system leads to a lower NO_x content probably due to some delay in the fuel injection caused by the indirect pump system. A small change in the fuel injection timing might be implemented to get similar performance.

The fully modified system was tested with different fuels including FPBO. In Fig. 3 the specific fuel consumption is plotted in g/kWh as a function of the electrical load for diesel, butanol, ethanol and FPBO. Obviously, due to the lower heating value the consumption of FPBO will be the highest, and the specific fuel consumption will decrease with increasing load. Please note that 20 kW_e corresponds to only 40% engine load. However, the overall efficiency is nearly the same for the different fuels (see [3, 4] for further details).

In summary, it can be concluded that the 4 cylinder engine has successfully been modified to enable FPBO fueling. In 2017/2018 an extensive test program will be carried out to continue the development.

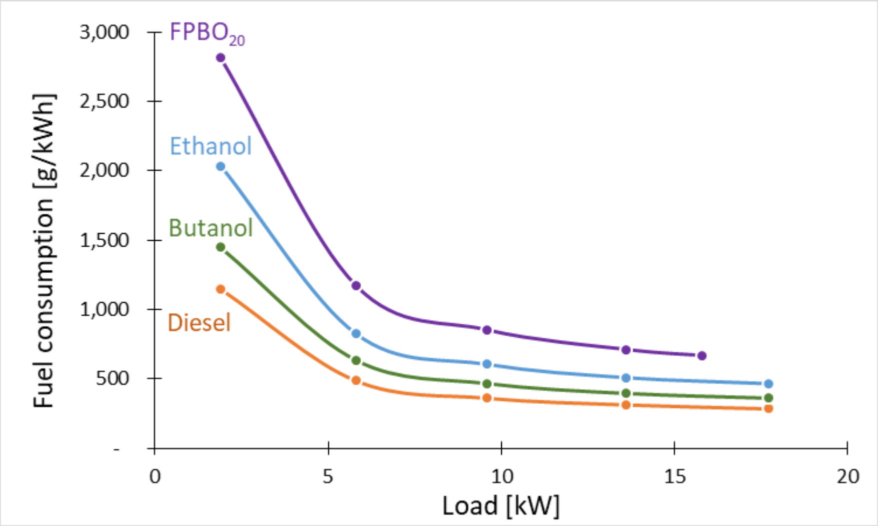

Fig. 4: Specific fuel consumption as a function of the electrical load for different fuels

References

Bert van de Beld, Elmar Holle and Jan Florijn, An experimental study on the use of pyrolysis oil in diesel engines for CHP applications, 19th European Biomass Conference and Exhibition, Berlin-Germany (2011) 1181 - 1187.

Bert van de Beld, Elmar Holle and Jan Florijn, The use of pyrolysis oil and pyrolysis oil derived fuels in diesel engines for CHP applications, Applied Energy, 102 – issue C (2013) 190 - 197.

Bert van de Beld, Elmar Holle and Jan Florijn, The use of fast pyrolysis oil in diesel engines for CHP application, 25th European Biomass Conference and Exhibition, Stockholm-Sweden (2017) 1932 - 1937.

Bert van de Beld, Elmar Holle and Jan Florijn, The use of fast pyrolysis oil in diesel engines for CHP application, submitted to Biomass & Bioenergy (2017).

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Biorenewable calcined coke as a pyrolysis co-product

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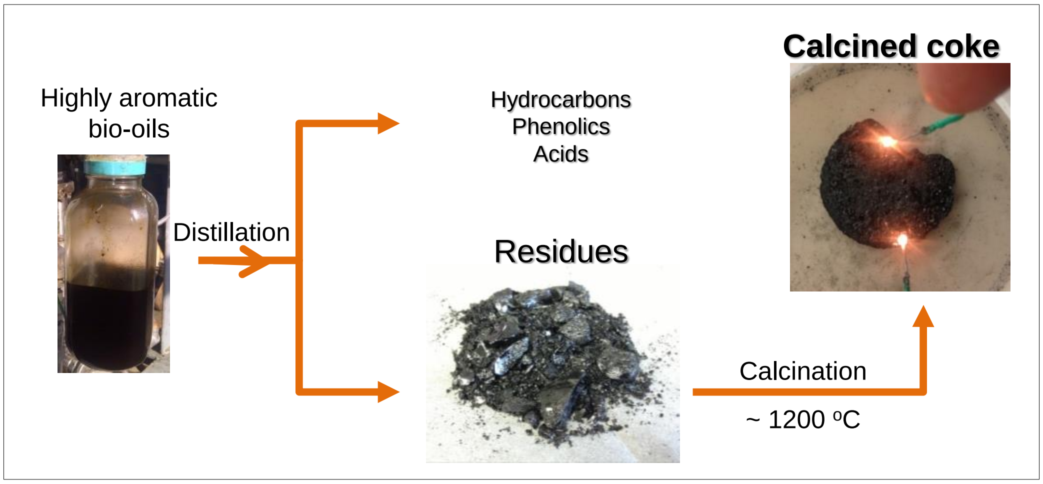

Figure 1. Overview of how renewable calcined coke is made from bio-oils.

Typically, the distillation of petroleum, followed by coking of the residues, produces ‘green petcoke’. The green coke is then sent to an industrial calciner for conversion into calcined petroleum coke (CPC). CPC is the only known material which can serve as anode material for the electrochemical reduction of Al_2O_3 into aluminium metal at industrially relevant scales. The main reason for this exclusivity revolves around the combination of properties, such as high electrical conductivity, high thermal tolerance, low ash and impurities (S, Ni, V, et. al.), high bulk density, and low coefficient of thermal expansion (CTE) [1].

Aluminum smelting uses consumable anodes which produce 1.5 tonne CO_2/ tonne Al. Although some smelters can utilize hydroelectric power, at least a third of their total CO_2 footprint originates from aluminum production. Furthermore, petroleum-based cokes are plagued by continually waning quality; high sulfur concentrations (5 – 6 wt%) often prevent smelters from meeting regulatory limits on emissions. Metallic impurities such as Ni, V, and alkali metals can either reduce current efficiency or otherwise contaminate the aluminum product, leading up to $100/tonne coke in financial losses. One option to reduce the CO_2 footprint is to source coke from biorenewable sources.

At USDA-ARS, our goal has been to follow an analogous approach towards production of green and calcined cokes [1, 2], using catalytic and/or tail-gas reactive pyrolysis (TGRP) bio-oils (Figure 1). The bio-oils underwent batch distillation in typical laboratory glassware, making sure to maintain the residues in a molten state at elevated temperatures while collecting the distillates. The remaining residues typically have 30 – 45 wt% volatiles remaining. Subsequently, the residues undergo complete devolatilization (appx 900 °C) followed by calcination under inert atmosphere (1000 – 1200 °C).

While our initial product’s elemental properties met and/or exceeded many critical criteria measured for petroleum (Table 1), physical properties had yet to be tested. In particular, the degree of polyaromatic crystallite stacking is tied to many other important physical properties such as real density and the coefficient of thermal expansion. One primary requirement for ensuring adequate quality of crystallite structure is for the oil to contain elevated aromaticity. Heteroatoms such as

(Continued on page 15)

Table 1. Typical properties for both petroleum and biomass-derived calcined cokes

	Calcined petroleum coke	Calcined biocoke (hardwood)
(wt%) C	>96	98.5
H	< 0.1	0.2
N	1 – 1.5	0.3
O	0	< 1.0
S	3 – 4	<0.05
(ppm) Ni	< 200	< 10
V	< 300	< 10
Na	< 100	220
K	--	220
Ca	< 200	166
Si	< 250	240
Zn	< 10	22
P	< 10	9
Resistivity (mΩ*m)	< 100	100 – 200
% ash	< 0.4	< 0.2
%volatiles	< 0.4	< 0.2

Biorenewable calcined coke as a pyrolysis co-product...continued

oxygen prevent crystalline alignment of PAHs via elevated viscosity and cross-linking reactions. However, we have demonstrated that this common rule of thumb is not necessarily the case for bio-oils with less than 15 – 17 wt% oxygen.

By modifying the distillation procedure, we produced coke samples with high degrees of anisotropy. Images from polarized light microscopy (Figure 2) illustrate the increase in anisotropy, compared with what was produced beforehand. Anisotropic textures are the most favorable for smelting anodes and comprise the majority of anodes. Isotropic textures can be used as blends with anisotropic cokes. Amorphous cokes cannot be used at all due to their tendency to crack under thermal shock. When compared with these standards, the coke we've produced constitutes isotropic coke with largely anisotropic domains, as indicated by the stacking and alternation of colored regions.

We are currently focusing on developing larger-scale and/or continuous processing of bio-oil distillation residues. Recently, our lab acquired a laboratory-scale tube furnace that more closely mimics rotary kilns used to calcine petroleum coke industrially. More industrially relevant process parameters should now be obtained since there would be a more accurate emulation of heat and mass transport phenomena. The tube furnace can also attain a maximum temperature of 1600 ^{o}C, significantly beyond that limits of our muffle furnaces. Our goal is to produce larger-scale batches of biorenewable calcined coke for use in pilot-scale anode testing and for characterization of mechanical properties.

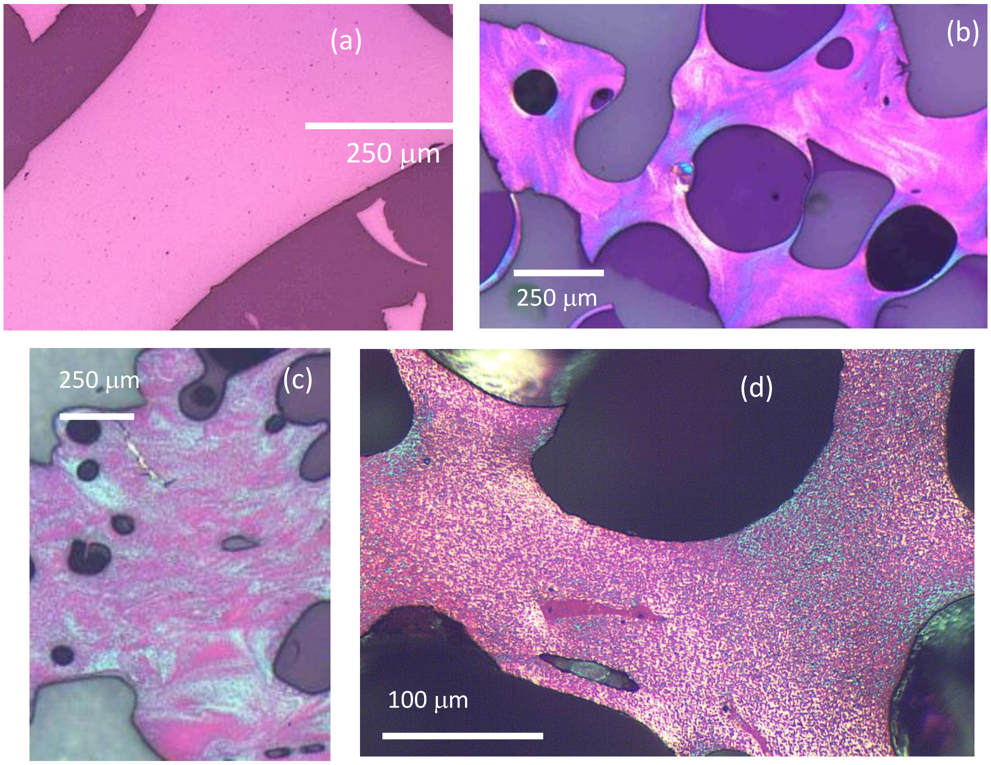

Figure 2. Polarized light microscopy images of pyrolysis oil-based calcined coke (a) initial amorphous samples. Subsequent improvements produced (b and c) mixed isotropic and anisotropic samples. (d) higher resolution image of mostly isotropic region.

References

[1] Y. Elkasabi, A.A. Boateng, M.A. Jackson, "Upgrading of bio-oil distillation bottoms into biorenewable calcined coke" Biomass and Bioenergy (2015), 81, 415 – 423.

[2] Y. Elkasabi, H. Darmstadt, A.A. Boateng, "Coke produced from lower-oxygen fast-pyrolysis oil: a new approach to produce renewable anode raw materials" in Light Metals 2017, The Minerals, Metals, & Materials Society (2017), A.P. Ratvik (ed.), 1221 – 1227.

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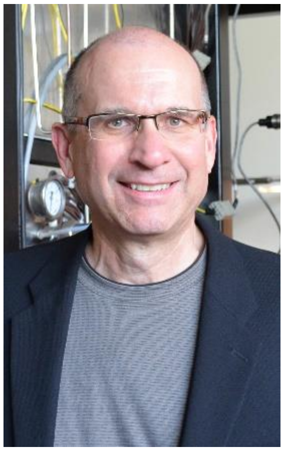
Continuous solvent liquefaction research at Iowa State University



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Iowa State University

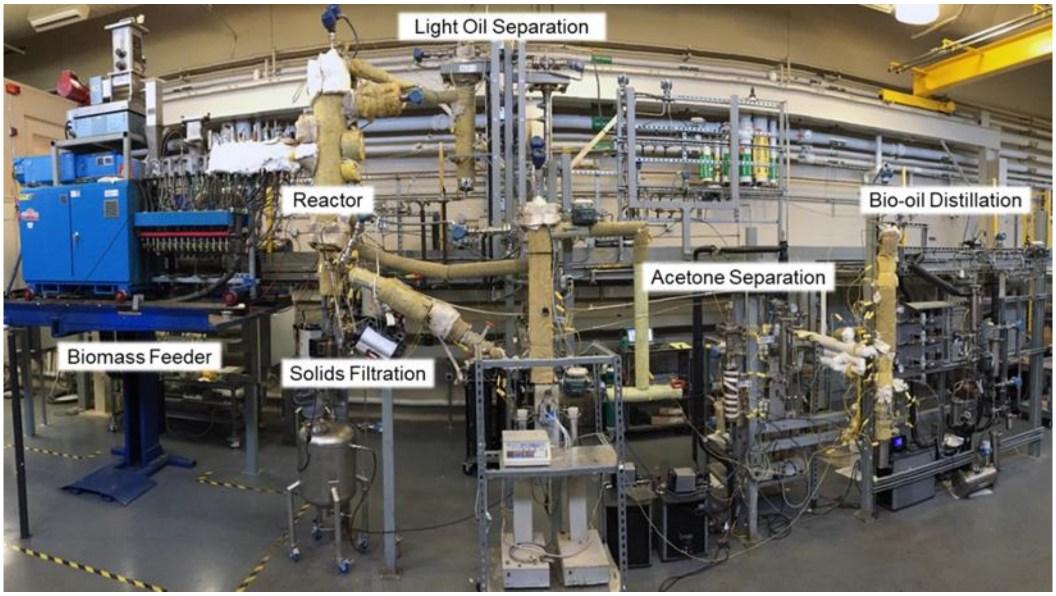

Fig. 1 - A 1 kg/h continuous pilot plant was constructed to evaluate the performance of solvent liquefaction of southern yellow pine in a hydrocarbon solvent

Solvent liquefaction (SL) of biomass is a promising technology for the conversion of biomass to renewable fuels and chemicals. Liquid-phase thermal deconstruction of biomass in the presence of hydrocarbon-based hydrogen-donating solvents can result in bio-oils with low moisture and low oxygen content. These oils are thermally stable and highly miscible with hydrocarbon streams, which make them a promising biorenewable blendstock for petroleum refineries.

At Iowa State University, we have developed a 1 kg hr-1 continuous SL pilot plant (Figure 1) to evaluate the performance of SL of southern yellow pine in a hydrocarbon solvent [1]. The process development unit (PDU) was also designed to evaluate several unit operations critical to large-scale operations.

PDU Operation

Three separate experiments, each more than twelve hours long, were conducted with the unit using Southern yellow pine sawmill residue dried to 4% moisture and ground and sieved to 6.4 mm (0.25 in) size.

The solvent was a blend of two hydrocarbon liquids. The majority of the solvent was comprised of commercially available naphthalene-depleted heavy aromatic solvent (CAS # 64742-94-5). The hydrogen donor solvent was a proprietary cut of light cycle oil (LCO) (CAS # 64741-59-9) that was specially hydrotreated.

Biomass feeding was done in a two-stage process. The first feeder consisted of a 15 L hopper on top of a single-screw auger that metered biomass at a constant rate of 0.7 kg/h. The second stage was an extruder with two co-rotating, intermeshed screws where solvent was injected into the feed stream with a solvent-to-biomass ratio of approximately 4:1. Pressures in the extruder ranged from 42 to 53 bar. The biomass/solvent slurry was injected directly from the extruder exit into the side of the reaction vessel operated at 400 °C and 43 bar. The solvent vapor pressure at this temperature was estimated to be 12.3 bar.

Liquids and solids exited the bottom of the reactor and entered a solids filtration vessel. A 50 µm stainless steel pleated mesh filter separated the particulate matter from the heavy liquid as it was pumped out of the vessel with a high-viscosity pump, passing through a 5 µm stainless steel filter to a vessel where the liquid, a mixture of heavy product bio-oil and solvent, was stored for subsequent bio-oil fractionation.

Vapors and non-condensable gas products exited the top of the reactor and entered the first of three stages of liquid recovery. The first stage condensed vapors to liquids at 260 °C with the goal of recovering hydrocarbons and/or phenolic monomers produced during solvent liquefaction. Any remaining condensable vapors were collected in the second stage of liquid recovery, which was mostly water

(Continued on page 17)

Continuous solvent liquefaction research at ISU...continued

and light oxygenated compounds. Gases exiting this second stage passed through a 10 µm barrier filter and into the third stage of recovery, which was a knockout vessel designed to remove any fume from the non-condensable gas stream before gas analysis.

To improve separation of heavy bio-oil and solid residue recovered from the bottom of the reactor, an optional system for injecting acetone into this mixture and subsequently recovering the acetone was constructed. The liquid stream entered this step at approximately 120 °C, while the vessel itself was controlled to 93 °C and 1.1 bar. The operating conditions were established such that acetone would flash from the liquid phase and carry overhead into the next separation unit. No other compounds were expected to flash off with acetone due to the low volatility of the compounds present in this portion of the system.

After solids and acetone were removed from the liquid stream, bio-oil was transferred to the bio-oil fractionation system. The primary goal of this system was to separate a cut of the bio-oil for use as a potential recycle solvent. This cut was targeted to contain molecules near the boiling point range of the hydrocarbon solvent. Hot nitrogen gas was used as the stripping agent. The overheads stream passed through a heat exchanger that condensed products at 5 °C and were collected in another separator.

Liquefaction Performance

Three tests were conducted to evaluate the overall liquefaction performance and repeatability of the SL PDU. At least three steady-state samples were collected for each run to determine averages. Most of the product gas was accounted for in the overhead products system; however, some degassing did occur in the solids filtration and acetone recovery system due to the pressure letdown in solids removal system.

Primary gases produced during liquefaction were CO2 and CO, products of biomass decarboxylation and decarbonylation, respectively. Minor gaseous products were light hydrocarbons (CH4, C2H4, and C2H6).The bio-oil yield for the system ranged from 47.2 wt% to 54.1 wt%, with an average of 51.2 wt% across the three runs. On average, the mass fraction of remaining products was essentially equal: aqueous (13.4 wt%), gas (17.7 wt%), and char (18.8 wt%) products.

Due to the tendency of the bio-oils to separate into organic and aqueous phases, bio-oils had very low moisture content. This behavior is attributed to partial hydro-deoxygenation of the bio-oil by the hydrogen donor included in the solvent mixture. The higher heating value (HHV) was also higher than for bio-oil from fast pyrolysis, which is often in the range of 10-20 MJ/kg. The average oxygen balance across the three runs was determined (Figure 2). Approximately 17.6 wt% of the initial oxygen in the feedstock was recovered as water produced from dehydration and hydrodeoxygenation.

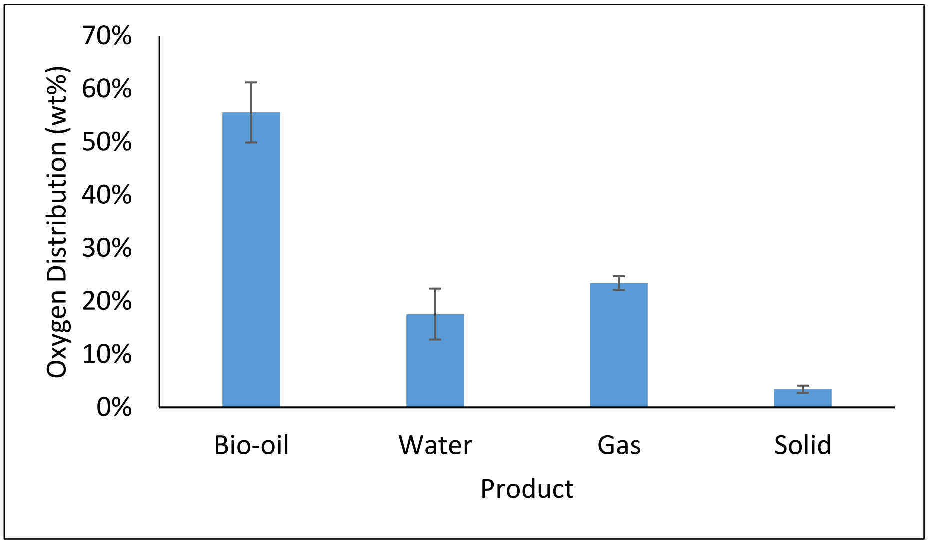

Fig. 2 - Oxygen balance across the whole system on an ash-free, moisture-free biomass basis. Error bars represent the standard error of the mean for the three runs.

Decarbonylation and decarboxylation were prominent means for deoxygenation. Over 23.4 wt% oxygen was rejected from the biomass through these reactions. This resulted in approximately 55.6 and 3.4 wt% of the oxygen remaining in the bio-oil and solid residue, respectively. Considering the initial oxygen content of the southern yellow pine was 41.7 wt% this results in a total oxygen content of 23.2 wt% in the bio-oil as a whole.

Char was removed with the acetone-free on-line filtration system for at least 6 h of continuous operation without clogging the filters. The total calculated filtration efficiency was 99.8%. Acetone separation from the heavy bio-oil achieved 97% efficiency (i.e. 3% acetone loss) at a flash temperature of 135 °C. Additional increases in the vessel temperature were expected to

(Continued on page 18)

Continuous solvent liquefaction research at ISU…continued

result in improved separation efficiency, but long-term thermal stability of the bio-oil was a concern at elevated temperatures.

Prior to implementation of the fractionation system, a series of tests were conducted to determine the thermal stability of the product stream. Only modest changes of about 5% or less were found for the bio-oil, and increasing temperature up to 300 °C appeared to have insignificant influence compared to lower temperatures. The conclusion was that the heavy oil product exhibited sufficient thermal stability to remain unchanged following thermal fractionation up to 300 °C.

After the operating conditions of the bio-oil fractionation system were established, several extended-duration experiments were conducted to verify its operational consistency. For more than 25 h of run time the average split was 24% bottoms and 76% overheads, each with a 1% standard error of the mean. The overheads were predominantly recovered hydrocarbon solvent and wood-derived monomers with boiling points below 204 °C. This stream accounts for approximately 93 wt% of the initial solvent input. The overheads product was a low-viscosity clear liquid with an amber hue. It is suitable for use as recycle solvent. Conversely, the bottoms product was black in color with a slightly higher viscosity, though still mobile at ambient conditions (Figure 3). This cut likely contained phenolic oligomers and anhydrosugars produced from lignin and carbohydrates, respectively, in the biomass, similar to heavy pyrolysis oils.

Fig. 3 - Acetone-free bio-oil from the solvent liquefaction process (left) is fed into the bio-oil fractionation system which separates the feed into a bottoms (center) and overheads (right) product, otherwise referred to as heavy bio-oil and medium oil, respectively.

Acknowledgements

The author wishes to acknowledge the contributions of several individuals. Martin Haverly, Lysle Whitmer, and Andrew Friend were responsible for most of the design and construction of the system. They were joined by Taylor Schulz and Jordan Funkhouser in operating and maintaining the system. Patrick Hall, Patrick Johnston and Marge Rover assisted in analyzing the bio-oil samples. Ryan Smith served as project manager. Bob Mills assisted in preparing this article. This work was supported by the U.S. Department of Energy and Chevron U.S.A, Inc.

References

[1] Haverly, M. R., Schulz, T. C., Whitmer, L. E., Friend, A. J., Funkhouser, J. M., Smith, R. G., Brown, R. C. (2018) Continuous solvent liquefaction of biomass in a hydrocarbon solvent, Fuel 211, 291-300.

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Licella and the Catalytic Hydrothermal Reactor (Cat-HTR™)

Steve Rogers
Licella

Licella has developed the Catalytic Hydrothermal Reactor (Cat-HTR™) platform as a hydrothermal upgrading process to transform a wide variety of low cost biomass feedstocks, wastes and residues into a stable biocrude. Licella's biocrude can be refined, using conventional refinery infrastructure, to a range of fuels and chemicals, including:

- Drop-in fuels, low Sulfur (Gasoline, Kerosene, Diesel, Gas and Fuel Oils) when co-processed with conventional petroleum feedstocks
- Chemicals, that can be used, for example, as components in products such as adhesives and tacifiers

The Cat-HTR™ has processed a wide variety of feedstocks that can be processed wet, removing the need for any pre-drying step.

The Cat-HTR™ is a highly controllable process, enabling it to process a wide range of feedstocks, typically taking between 15-25 minutes to produce the biocrude that is stable, miscible and for forest residues, normally has a calorific value of 34-36 Mj/kg (feedstock dependant).

The Cat-HTR™ process utilises equipment that is already in widespread use in other industries, meaning capital costs are kept to a minimum. Operationally most of the energy required to initiate the series of transformational cascading chemical reactions is recovered. In addition the process is able to utilise inexpensive and non-proprietary catalysts.

About Licella™

Licella™ was founded in 2007 and is a subsidiary of Ignite Energy Resources (IER). Licella ™ was formed to focus on commercialising the Cat-HTR™ platform for biomass. In 2007 the first design of the Cat-HTR™ (Generation 1) was completed and this very first plant was commissioned in early 2008, at Somersby on the New South Wales Central Coast, about an hour north of Sydney, Australia.

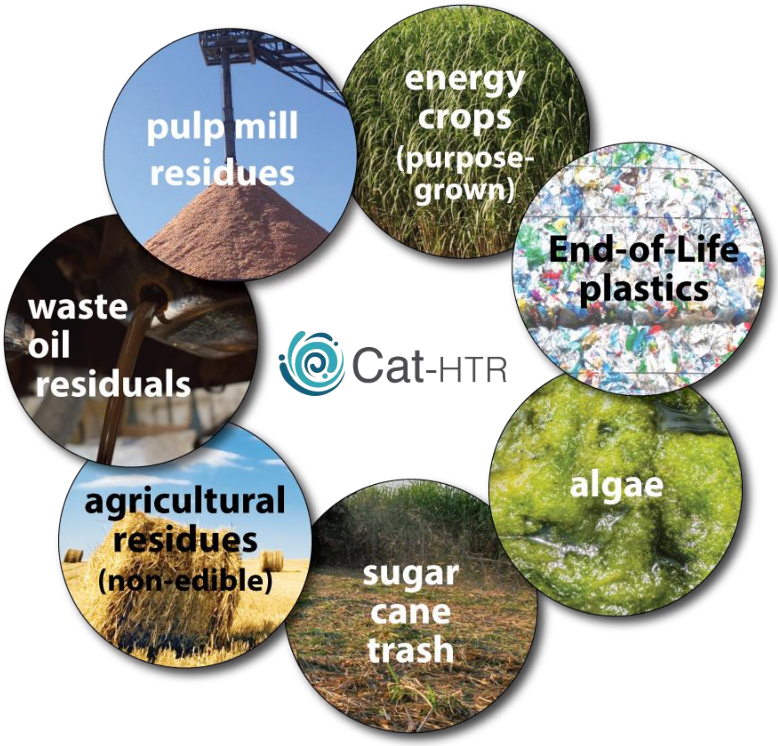

Fig. 1: Examples of feedstock that have been processed by the Cat-HTR™ platform experimental runs.

Since then, Licella™ has used the pilot plant facility, to refine the Cat-HTR™ process for optimal yield, product quality and economics. This has involved three separate scale-ups of the Cat-HTR™ technology, resulting in the construction of the current Large Pilot Plant. The final scale up to a commercial scale module is a x 2.2 scale up of the existing Large Pilot Plant reactors.

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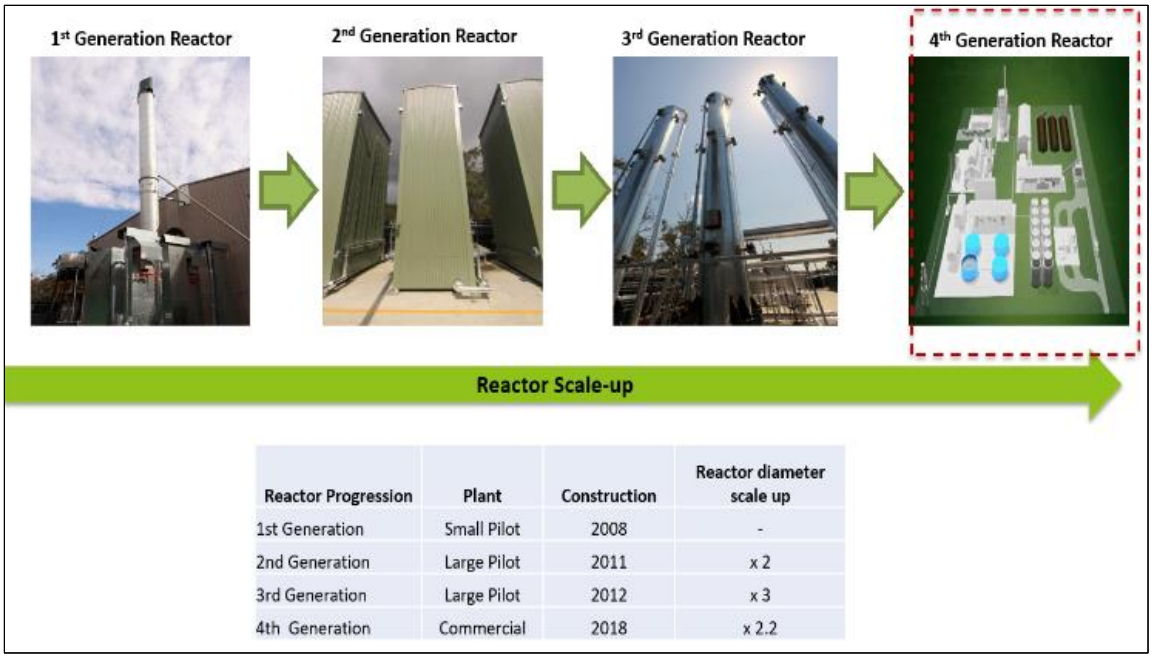
Licella and the Catalytic Hydrothermal Reactor (Cat-HTR™)



Reactor Progression	Plant	Construction	Reactor diameter scale up
1st Generation	Small Pilot	2008	-
2nd Generation	Large Pilot	2011	x 2
3rd Generation	Large Pilot	2012	x 3
4th Generation	Commercial	2018	x 2.2

Fig 2: Cat-HTR™ scale-up showing reactor progression

Cat-HTR™ Development

The Cat-HTR™ platform was invented in Australia by Dr Len Humphreys, Licella™ CEO, and Professor Thomas Maschmeyer, of the University of Sydney.

“We began developing the Cat-HTR™ technology in 2005, from a related approach involving the use of supercritical methanol to convert edible oils to biodiesel. We needed a feedstock which was non-edible, abundant and low cost. Lignite became the new feedstock, and water the processing medium in late 2006.”

“For many decades people had tried to upgrade lignite by drying it. The breakthrough for us happened when we turned this approach on its head – embracing water as the agent of change, not the enemy. This lead to a simpler and much more economical upgrading process.”

Dr Len Humphreys,
CEO & Co-Founder

Prof Dr Thomas Maschmeyer
FAA FTSE, Technology
Consultant & Co-Founder

IMAGE 3: Cat-HTR inventors Dr Len Humphreys and Professor Dr Thomas Maschmeyer

“The same Cat-HTR™ transformational principles that work for lignite can, with some modifications, also be applied to biomass, such as pulp and paper residues. We are today incredibly excited to be moving towards our fourth generation and commercial scale Cat-HTR™ plants with our partners.”

Technology Development to Commercialisation

Licella™ has formed a global joint venture with Canfor Pulp, a Canadian (TSX) listed leading global supplier of pulp and paper products. The joint venture was formed to integrate Licella’s Cat-HTR™ platform into kraft and mechanical pulp mills, utilising waste streams to create renewable fuels and chemicals. Canfor and Licella have formed a joint project team who are currently undertaking engineering work to integrate the Cat-HTR into Canfor Pulp’s Prince George (British Columbia) mill.

Licella and the Catalytic Hydrothermal Reactor (Cat-HTR™)

Once integrated, the Cat-HTR™ platform will convert wood residues from the kraft pulping processes, into renewable biocrude, to produce advanced biofuels and biochemicals. This additional residue stream refining would allow Canfor Pulp to further optimise their pulp production capacity.

The formation of the joint venture follows a successful program of trials conducted on feedstock from Canfor Pulp's Prince George pulp mill at Licella's pilot plants in Australia.

Upon successful integration of the Cat-HTR™ technology, the joint venture look towards offering the Cat-HTR™ solution to Kraft and mechanical pulp mills globally.

IMAGE 4: Licella's Generation 3 Cat-HTR™ reactors, at the Large Pilot Plant in Somersby, NSW

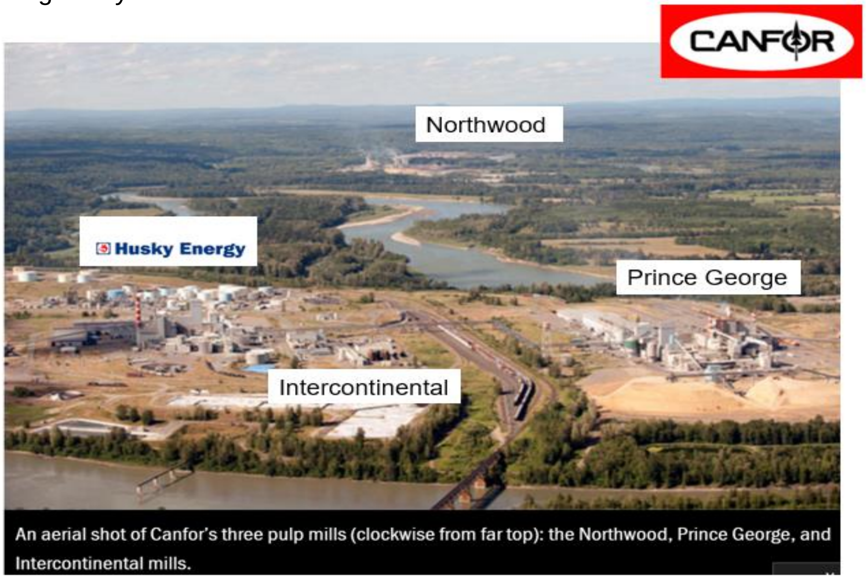


IMAGE 5: Canfor's 3 pulp mills in Prince George British Columbia and the Husky Energy refinery

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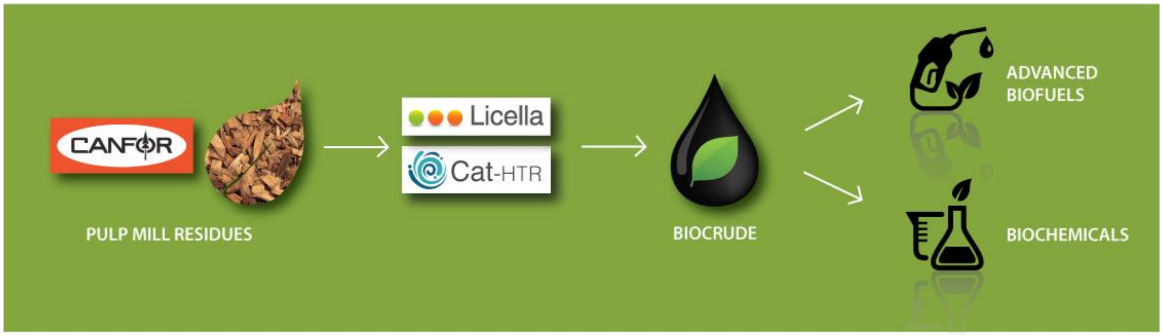

PYRENA: PYROLYSIS EQUIPMENT FOR NEW APPROACHES

Paul J. de Wild
Energy research Centre
of the Netherland (ECN)

PYRENA is a novel integrated system that features ONE reactor in which fast pyrolysis and combustion are combined. PYRENA is suitable for (catalytic) fast pyrolysis and offers continuous catalyst recycling in one heat-integrated system. Especially the flexibility regarding the use of catalysts is an attractive option, because it offers a route (via in-situ and ex-situ catalysis) to a better bio-oil that probably requires less downstream upgrading when compared to analogous pyrolysis systems. PYRENA consists of a bubbling fluidised bed reactor vessel, in the center of which an internal riser reactor is located for the pyrolysis, see Figure 1. Biomass is fed to the riser reactor at a maximum feed rate of 5 kg/hr and pyrolysed at 400 – 600°C. The required heat is provided by hot sand or catalyst that circulates from the surrounding bubbling bed into the riser. The sand is heated via the combustion of the pyrolysis char that is transported from the riser reactor via an internal cyclone. The hot pyrolysis vapours are quickly quenched and recovered via direct or fractionated condensation. The PYRENA system is roughly comparable to a circulating fluidised bed (CFB) system. A major difference is the integration; most state-of-the-art CFB reactors use an external reactor for combustion of the char and heating of the sand.

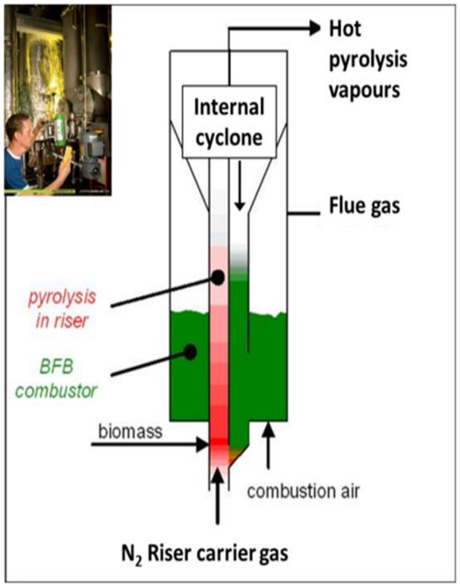

Figure 1: PYRENA consists of a bubbling fluidised bed reactor vessel, in the center of which an internal riser reactor is located for the pyrolysis

Figure 2 presents a detailed flow scheme of the reactor set-up, including product collection.

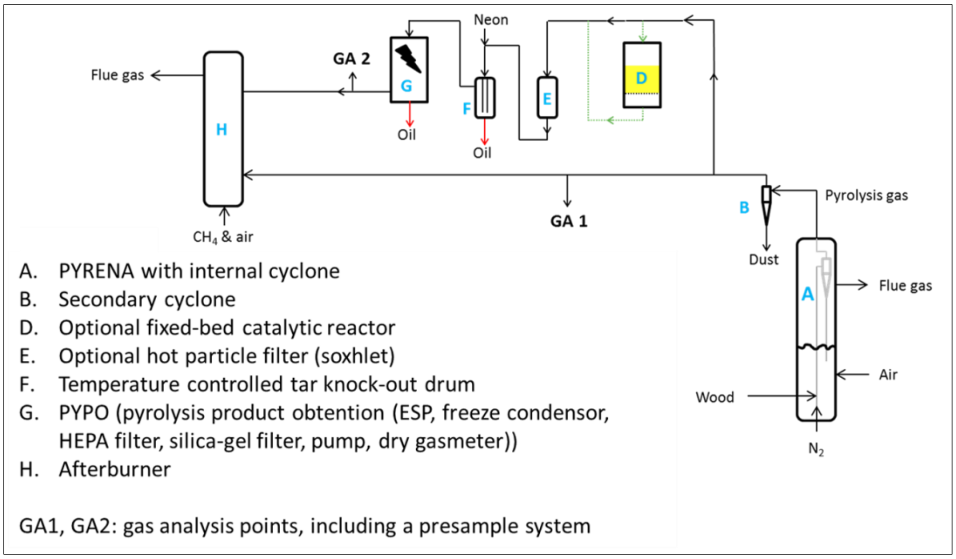

Figure 2: Detailed flow scheme of the PYRENA reactor set-up, including product collection

PYRENA has successfully participated in a recent international round robin test on fast pyrolysis [1]. PYRENA bio-oil from poplar and wheat straw was nicely comparable with other state-of-the art pyrolysis reactors. The pyrolysis of hybrid poplar fines (<0.5 mm), prepared by Idaho National Laboratories, yielded 64% of a one-phase oil (based on the poplar intake weight a.r.) containing 42% organics and 22% water. Overall mass balance was 98% (64% oil, 12% gas, 22% char). For the wheat straw fines (also prepared by Idaho National Laboratories, US) the results were remarkably different. A clear two-phase oil was obtained in a yield of 44% (based on the straw intake a.r.). Almost half of the liquid was water (24%) and 20% organic substances. Mass balance was incomplete at 82% (44% oil, 9% gas, 29% char).

The PYRENA set-up has been modelled in a coarse techno-economic evaluation, aimed at a scale of 300 kt/yr of dry biomass intake. Assuming 300 kton/a (dry) biomass (softwood),

(Continued on page 23)

PYRENA: PYROLYSIS EQUIPMENT FOR NEW APPROACHES…continued

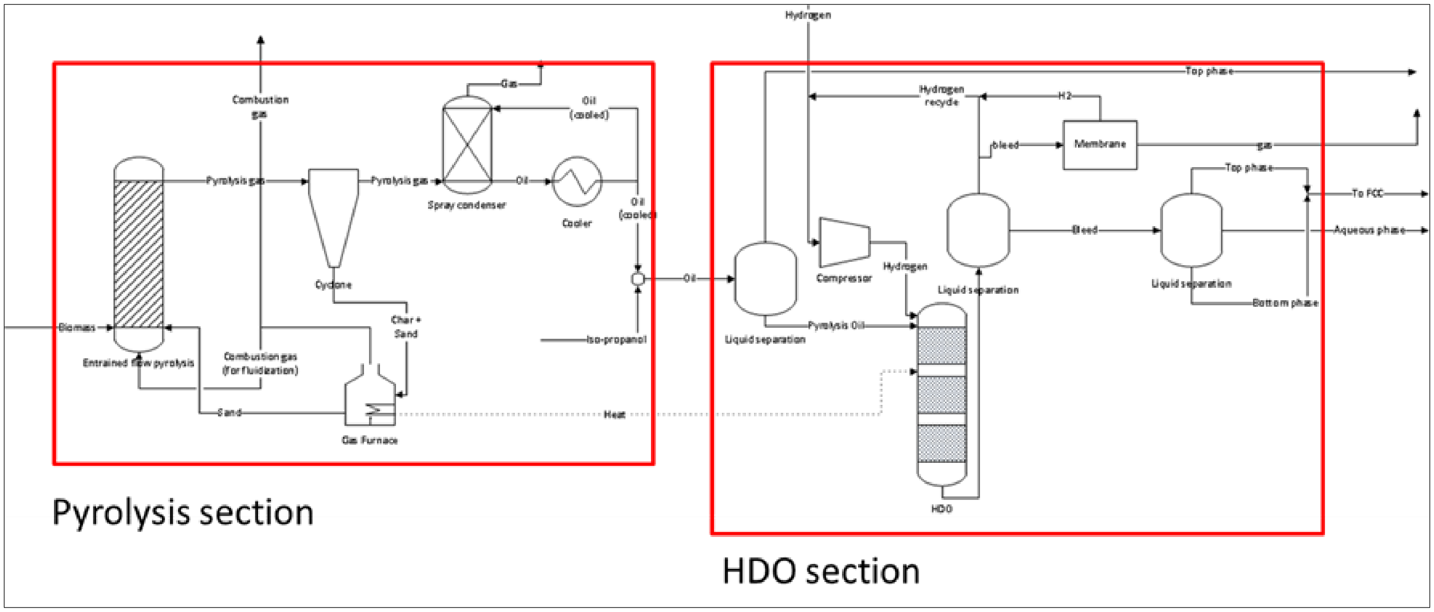

Figure 3: PYRENA process flow diagram for techno-economic evaluation including pyrolysis and hydrodeoxygenation

8000 hrs operation, CFB pyrolysis, thermal pyrolysis(TP) followed by catalytic hydrodeoxygenation (HDO) was compared with catalytic pyrolysis (CP) using state-of-the-art ZSM5 catalysts. TP→HDO was modelled using experimental data, while for CP literature data were used [2, 3]. An Excel model was constructed to calculate mass- and energy balances from both exp and literature data. Results indicate a higher oil yield (36%) and less char (13%) for the TP→HDO approach than for CP (17% oil, 24% char), while CAPEX was higher for TP→HDO when compared to CP (100 M€ vs 70 M€).

Summary

In future work, PYRENA will be used to study the effect of the environmentally benign mineral olivine as a mild, cheap and easily regenerable cracking catalyst on the fast pyrolysis of softwood. Presently, focus is on fractionated recovery of pyrolysis products from lignin and lignin-rich biomass types to produce ample samples in sufficient quantity for further processing and/or application trials.

PYRENA was deployed in a recent Dutch national Catalytic Pyrolysis project to produce bio-oil samples for the project consortium and to tests catalysts. The project dealt with the application of catalysis in dedicated pyrolysis reactors aiming at improving the quality of the produced oil. One of the target applications of the oil is a refinery co-feed. PYRENA is a promising candidate.

Acknowledgements

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References

1. D.C. Elliott, D. Meier, A. Oasmaa, B. van de Beld, A.V. Bridgwater, M. Marklund, K. Toven, “Results of the IEA Round Robin on fast pyrolysis bio-oil production”, Energy Fuels, 2017, 31 (5), pp 5111–5119.

2. F. de Miguel Mercader, Pyrolysis oil upgrading for co-processing in standard refinery units, PhD thesis Twente University, 2010.

3. V. Paasikallio, C. Lindfors, E. Kuoppala, Y. Solantausta, A. Oasmaa, J. Lehto, J. Lehtonen, Product quality and catalyst deactivation in a four day catalytic fast pyrolysis production run, Green Chem. 2014, 16, 3549

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Task 34: Direct Thermochemical Liquefaction

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