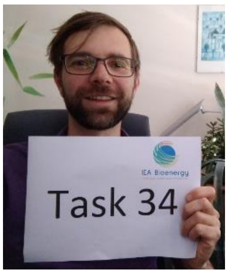
IEA Bioenergy

Task 34

Direct Thermochemical Liquefaction

PyNe 46

August 2020



IEA Bioenergy

Technology Collaboration Programme

Inside this Issue:

These days everybody is more or less affected by the ongoing Covid-19 pandemic and so was the work of IEA Bioenergy Task 34. Unfortunately, we had to cancel a meeting in Finland at VTT, an event we were looking forward to very much.

Christian Lindfors has already attracted many interesting Finish stakeholders from research and industry for a joint workshop and the organization for this event was well on its way. We had to retreat to a series of virtual meetings to continue our work – not unlike many others in the world.

So this time Task 34 NTLs send around their warmest greetings virtually. It surely does not replace meeting stakeholders, but we could push forward an update of our website content, which is excellent timing with the launch of the brand new IEA Bioenergy corporate design.
(please check www.ieabioenergy.com for more) Our website update is still work in progress and we aim at sharing it with you in the upcoming PyNe newsletter.
In the meantime, we've also published our first two reports of this triennium. The Country Report 2019 features latest DTL activities in Finland, Germany, The Netherlands, and Sweden.

We also compiled background knowledge around DTL principles, technologies, and product characteristics in a 'Direct Thermochemical Liquefaction Brochure'. This report aims at explaining DTL to a broader audience. Both reports are available online and can be downloaded from our website www.task34.ieabioenergy.com.

And while you are visiting our website you might want to test our brand new PyNe article database: Alex has made an incredible effort to include all published PyNe articles so far. We expect that this will ease the search for specific articles and topics in addition to the existing capability of browsing previous PyNe issues.

In this newsletter, CanmetENERGY-Ottawa/ Canada presents interesting results from their experiences with combined removal of solids and ash from FPBO in a cross-flow microfiltration system.

Ricardo Soares and co-workers summarize several studies from their BioValue consortium conducted around basing a biorefinery on autothermal pyrolysis, i.e. pyrolysis with minor amount of oxygen added to the reactor to supply the energy needed for pyrolysis.

Another R&D project, the European H2020 project Residue2Heat, has been presented in a previous issue already. This project has been finished now and the results around developing a burner for residential heating boilers are showcased in this PyNe issue.

Since we do observe quite some HTL commercialization emerging we are also glad to have one of the actors in the field, Australian based Southern Oil Refining, presenting their activities in the field.

VTT presents their experiences from processing lignin in fluidized bed fast pyrolysis, with interesting differences in bubbling and circulating fluidized bed operation.

And last but not least, the Green Chemical Reaction Engineering group at University of Groningen/ The Netherlands presents their strategy for valorizing pyrolytic lignin obtained from water extraction of FPBO.

Again, we are having a look at what happened twenty years ago: Tom Milne and Bob Evans gave a review in PyNe no 9 on terms around organic products from pyrolysis. Certainly, this short overview is worth having a look at even today – and most likely for the upcoming years, too.

One cannot grow wary of wishing all the best these days and to hope that we can overcome the pandemic with joint efforts. Task 34 is continuing its effort to supply you with relevant DTL information and keep up the work to advance sustainable DTL applications.

Yours sincerely,

Axel Funke
Task lead and NTL German

Residential heating with fast pyrolysis bio-oil

Bert van de Beld, Evert Leijenhorst - BTG Biomass Technology Group BV, Dirk Möntmann, Melanie Grote - OWI Science for Fuels GmbH, Thomas Rütten - *MEKU* Metal Processing GmbH

Residential heating systems have the potential to contribute significantly in the challenges the world faces to make its energy system clean, secure and efficient. For residential heating systems it is vitally important to use a standardized fuel, to allow optimization of the heating systems and create an economically viable value chain. To meet the fluctuating heat demand encountered in residential heating it is advantageous if the fuel load can be rapidly adjusted, which is easily achievable with liquid or gaseous fuels.

A main activity of the *Residue2Heat* project concerned the development of stand-alone, small scale residential boilers in the range of 20 - 200 kW_{th} fuelled with FPBO. Because the properties of the FPBO deviate from conventional fuels, available systems needed to be modified to deal with this type of biofuel. To enable this, a dedicated burner concept has been made by MEKU and, in cooperation with OWI, tested and further optimized. The Residue2Heat project was explained in a previous Pyne contribution (Issue 39, 2016, p 11-13)

In contrast to the combustion of gaseous fuels, liquid fuels must be transferred into the gaseous phase before mixing with combustion air. The combustion process can be divided into two regimes: i) fuel vaporization and mixture formation, and ii) combustion of the fuel-air mixture. Ideally, a homogeneous fuel vapor-air-mixture is generated before entering the combustion zone. It is called premixed combustion. The burner head with baffle plate or swirler has to ensure intensive mixing of combustion air and fuel, and has a major impact on flame stabilization and pollutant formation. Typically a liquid fuel combustion process operates in a yellow flame mode, or in case of premix in a blue flame mode. When yellow flames are applied mixture formation is not fully completed. Fuel droplets reach the combustion zone and vaporize. Hence, fuel rich zones occur, in which the oxygen enters by diffusion. This combustion process induce high local flame temperatures leading to an increased pollutant generation. State of the art liquid fuel combustion systems use a partially premixed flame. The blue-flame is nowadays state of the art for low emission combustion of liquid fuel in residential heating systems.

In *Residue2Heat* the work started with lab scale burner development. Due to its composition it is questionable whether FPBO can be really vaporized, and probably atomization is a better description. In the latter case very fine droplets are needed to ensure fast and complete combustion. Initial experiments with the standard blue-flame burner showed that this is not the case, and FPBO droplets partly leave the flame tube environment.

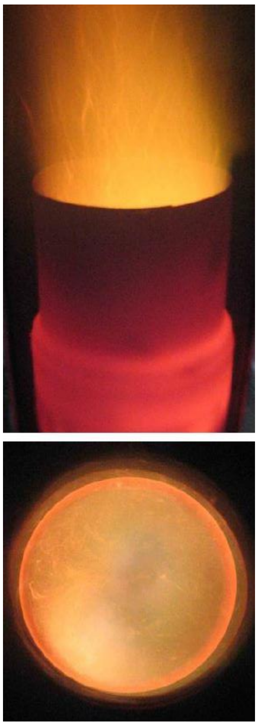


Figure 1: FPBO flame

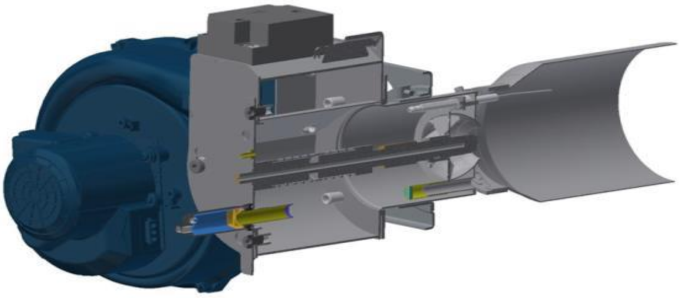


Fig.2: Illustration of the final burner design

Extension of the flame tube improved the combustion performance, but still some droplets were observed leaving the flame tube. To further improve combustion, a reversion cup was installed to increase the temperature of the recirculation flue gas and maintain a higher temperature for a longer time to ensure full combustion of the FPBO. Testing with this system showed good results: i) no streams of droplets leaving the reversion cup are visible, and ii) no deposit formation is observed inside the system. Regretfully, flame stability is difficult to assess since the flame was not visual accessible.

A FPBO boiler category is not present in existing regulations. An alternative for the FPBO boiler would be a biomass pellet boilers, and these emission limits could be considered. In Germany, these limits are 563 ppm CO and 350 ppm NO$_x$ for systems > 100 KW$_{th}$, and the emission measured with the FPBO boiler are well within the limits.

Burner prototype

The lab-scale burner was further optimized and -supported by CFD modelling- a demonstrator burner unit (60-75 kW$_{th}$) was designed by MEKU. The burner has been installed on a Bosch (Buderus)-boiler by OWI. With the demonstrator burner, several long duration tests were performed to demonstrate the stable combustion and intermittent operation of the system. The gas composition with a run using 80% FPBO-20% ethanol blend is shown in Fig. 3

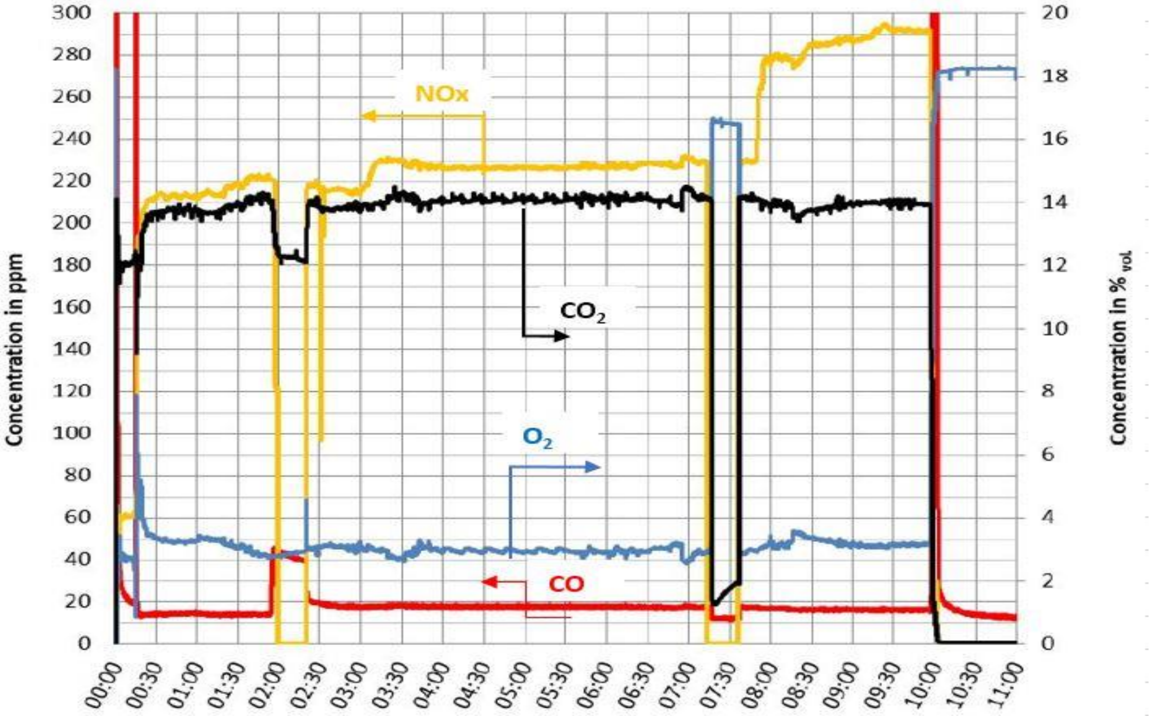


Fig. 3: Flue gas composition of the demonstrator unit firing 80% FPBO- 20% EtOH blend

Fig. 4: FPBO boiler system (right side) integrated with the existing natural gas fired boilers (left side)

The total runtime was about 12 hours and the emissions were comparable to the lab-scale unit. The operation was fairly stable with limited variations in O2, CO2 and CO content. The NO_x content in the flue gas seems more sensitive, and a further reduction in absolute concentration would also be preferred.

Prototype demonstrator

After successful testing of the burner by OWI it was decided to implement a prototype demonstrator at BTG. This demonstrator is integrated with an existing natural gas based heating system (Fig. 4). The latter one already existed and used to heat the BTG laboratory. The FPBO boiler is a condensing boiler provided by Bosch (Buderus-G125B). Besides the MEKU burner a dedicated FPBO feeding skid was developed and implemented (Fig 5). The FPBO storage capacity is about 1,100 liter, and from this skid a small intermediate vessel (8 L) is filled automatically. The fuel for the burner is taken from this small vessel and if needed the oil can be preheated to around 40 °C.

The implementation of the demonstrator has been completed, and recently taken successfully into operation. The *Residue2Heat* project was completed by the end of 2019, but testing and monitoring of the demonstrator will be continued. The focus is on continuous operation, performance monitoring, start-stop behaviour and reliability of the system. A short movie on the *Residue2Heat* project is available via PyroMovie (www.pyroknown.eu).

Fig. 5: FPBO fuel storage and feeding system.

Acknowledgement

The Residue2Heat project has received funding from the European Union's Horizon 2020 Research and Innovation programme under Grant Agreement No. 654650. Bosch-Buderus is gratefully acknowledged for providing the boilers.

Residue2Heat

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Denmark joins IEA Task 34 Direct Thermal Liquefaction

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Denmark joined IEA Task 34 Direct Thermal Liquefaction in 2019. Denmark aims to reduce green house gas emissions by 70% compared to 1990 before 2030 [1]. The transport sector is among the main sources of green house gas emissions in Denmark representing around 30% of the Danish green house gas emissions in CO2 equivalents [2].

The Danish government relies heavily on an increase of the share of electrical cars to help reduce the emissions from transport. However, heavy transport and airplanes will rely on liquid fuels for many years to come. This means that advanced biofuels play a central part in reducing emissions in the transport sector, although the recent focus on Power-to-X and synthetic fuels is also seen as a major contributor to reaching the targets. Currently, it is mandatory to blend 7.6% biofuels in 2020 gasoline, diesel and gas for ground transportation in Denmark. Additionally, it is mandatory that a share of at least 0.15% advanced biofuels is in the fuel delivered for transport in 2020, with an increase to 0.75% in 2021. The demands can only be fulfilled by biofuels living up to the European Union sustainability criteria for biofuels.

The Danish Energy Agency has made a list of raw materials which can be applied to produce advanced biofuels which will count double to the demand of blending in 7.6% biofuels [3]. The Danish-Canadian company Steeper Energy is currently commercializing the Hydrofaction^{TM} process, which is Steeper Energy's implementation of hydrothermal liquefaction.

Fig. 1: Task 34 visiting Aalborg University in October 2019

Since 2013, Steeper Energy has been testing different feeds and process conditions in a bench scale continuous unit of 25-30 kg/h of slurry located at Aalborg University.

Initially lignocellulosic biomass such as straw and miscanthus was used as feed, and more recently, urban waste and algae has been tested in the bench scale unit. Currently Steeper Energy is supplying the technology to establish larger scale production of Advanced Biofuels on a forest-based feedstock in Norway in cooperation with Silva Green Fuel and has recently announced the signing of a Memorandum of Understanding with the City of Calgary, Canada, to develop hydrothermal liquefaction capacity to process sewage sludge from the city waste water treatment facilities.Bio2Oil IVS was founded in 2014 and specializes in developing the hydrothermal liquefaction process. Currently, the company is involved with a pilot plant of 100 L/h at Aarhus University designed by Bio2Oil IVS founder Ib Johannsen [4].

The company intends to construct a larger pilot facility in India, which should form the basis for a full-scale plant design.
MASH Energy was founded in 2015 and is a spin-out company from the Technical University of Denmark (DTU) that incorporates pyrolysis into its technology base. MASH Energy specializes in two processes. Firstly, in converting agricultural waste into fuel products and secondly in converting different types of waste fractions into sustainable electricity and fertilizers. Various feedstocks such as woody biomass, waste plastics, municipal solid waste and used car tyres have been used for these processes.

The National Technology Lead (NTL) for Denmark in IEA Task 34 Direct Thermal Liquefaction is Prof. Lasse Rosendahl, Head of Department of Energy Technology at Aalborg University, Denmark. The department is leading in the field of Hydrothermal Liquefaction with the research programme in Advanced Biofuels. Professor Rosendahl has been active in liquefaction for almost two decades. The NTL represents the country in the Task and is responsible for collecting information on national activities and disseminating information to interested organizations and persons in their country.

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Key Observations from Fast Pyrolysis Bio-Oil Cross-Flow Microfiltration

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The importance of solids/ash removal from fast pyrolysis bio-oils (**FPBO**s) is well documented [1], as there exists a list of technical issues that these contaminants create during upgrading and/or utilization of the fuel including nozzle plugging, erosion, increased particulate emissions, catalyst deactivation, etc. It is acknowledged that commercial producers of FPBO have implemented their own strategies for quality control of solids and ash prior to sale of fuel. However, technical data on these pathways is often limited or restricted.

A Master's research project was initiated to generate publishable data on the topic and to engineer a continuous pilot scale treatment system for solids and ash removal from FPBOs produced from low quality biomass residues.

Treatment pathways that were initially considered for further research included hot vapor filtration, centrifugation, distillation, staged condensation, phase separation and emulsification [2]. Ultimately, the use of membrane separation technologies, and more specifically, cross-flow microfiltration (**CFM**) was selected for further investigation. This concept is illustrated in Figure 1. Vacuum filtration (and other dead-end filtration techniques) are commonly employed for solids removal from laboratory quantities of FPBOs. However, scale-up challenges exist when applying these methods to pilot scale quantities of FPBO. The use of CFM for treatment of FPBO could at first glance be considered a challenging endeavour. Higher relative kinematic viscosities, the presence of hydrophilic and lipohilic phases in FPBO, in which solids and ash species preferentially report, and the additional filtration resistances that develop over time due to "fouling" on the filtration surface are among several considerations. However, the use of CFM for solids/ash removal in FPBO offers some advantages which have not been thoroughly explored in the field of biomass liquefaction: a theoretically continuous treatment process with few additional unit operations that can be scaled up with relative ease by increasing the active filtration surface area

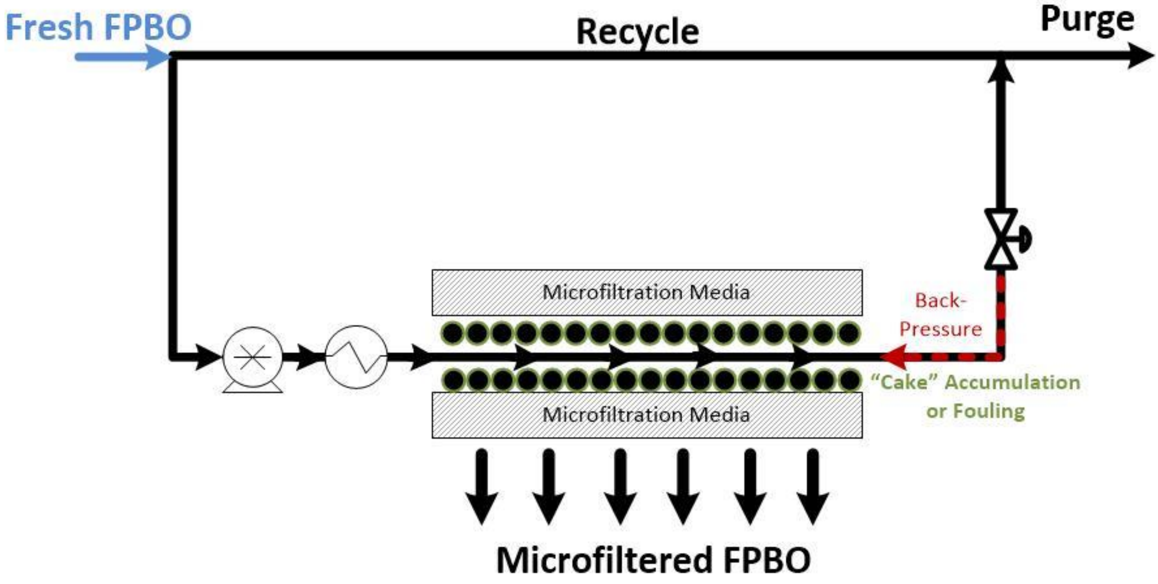

Figure 1: Concept sketch of FPBO cross-flow microfiltration

Figure 2: Bench scale cross-flow microfiltration system designed for solids/ash removal of FPBOs at CanmetENERGY

Altogether, in the completion of a thesis [3], an experimental microfiltration system was designed (Figure 2) and a series of targeted experiments were performed to generate data with the goal of producing cost estimation tools for CFM as an approach for solids/ash removal of FPBO. Uniform FPBOs produced from mill and harvest residues using CanmetENERGY-Ottawa’s 10 kg/hr bubbling fluidized bed pyrolysis system were used to accomplish this project. The experimental system has been detailed elsewhere [4].

Key Observations from Cross-flow Microfiltration of FPBO

The solids removal efficiency by CFM was substantially larger than the ash removal efficiency under the same conditions in this work. While solids rejection from CFM using filtration media with pore sizes of 1-40µm typically ranged from 80-95%, ash rejection only ranged from 5-45%. Figure 3 demonstrates that the correlation between solids rejection and ash rejection was poor. Due to the nature of the ash contained in the FPBOs from sawmill and harvest residues, higher concentrations of soluble ash species were present relative to FPBO produced from clean stem wood.

Thus, although the majority of the suspended solid particulate were separated via size exclusion, this was not found to be the case for total ash content.

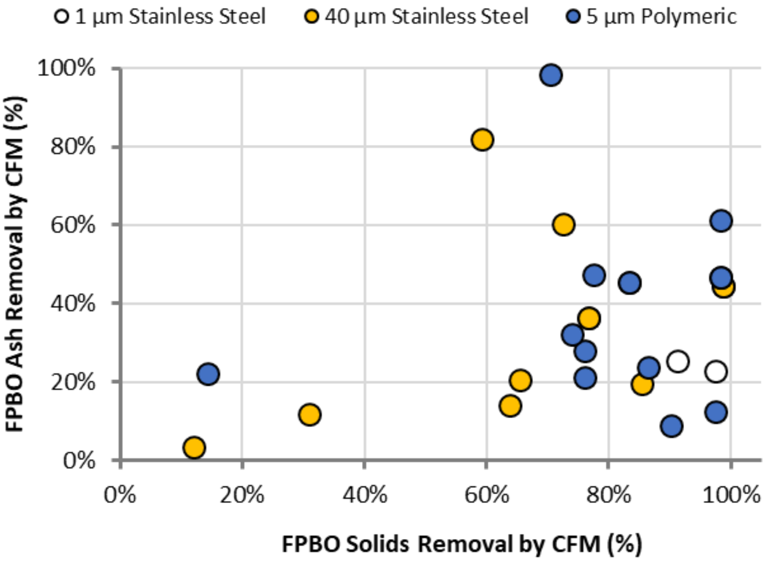

Figure 3: Solids removal vs. ash removal of microfiltered FPBO by cross-flow microfiltration at fluid temperatures ranging from 40-50°C and transmembrane pressures of 5- 45 psig

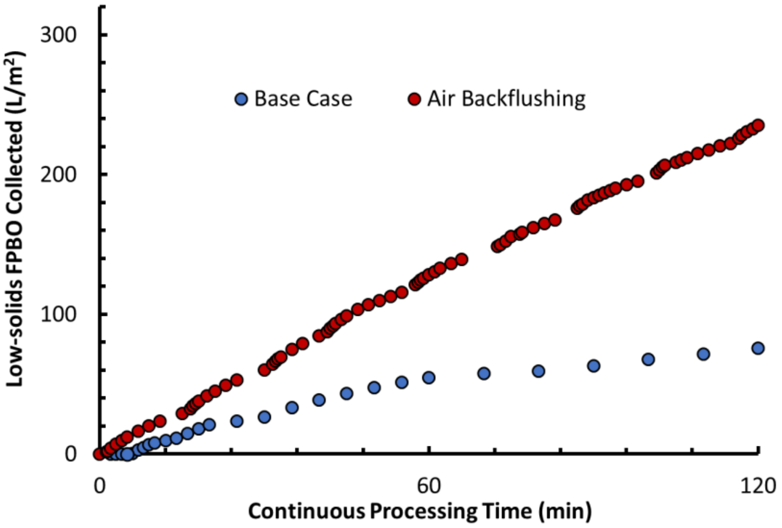

Figure 4: Low-solids FPBO collected vs. continuous processing time in cross-flow microfiltration with/without intermittent air backflushing

CFM operating conditions that led to increased throughput[1] of microfiltered FPBO included higher fluid temperatures, low to moderate transmembrane pressures, and lower FPBO solids content.

The throughput of microfiltered FPBO was increased as the fluid pre-heat temperature increased up to 60°C. There may be an optimal fluid pre-heat temperature above this where incremental benefits to microfiltration throughput are observed while managing the negative impacts of FPBO ageing for end-use or upgrading.

Additionally, higher pressure operation was found to be linked with lower throughputs for operating times longer than a few minutes. It was found that ~10 psi transmembrane pressure provided the best throughput of microfiltered FPBO for continuous operating times exceeding one hour, due to the trade-off between the pressure driving force of the size exclusion process and compaction of the fouling layer on the filtration surface. Furthermore, it was found that FPBO samples with increased solids content experienced more resistance to microfiltration and led to significant decreases in throughput. As a result, for higher solids-containing FPBOs, it would be worth considering the use of a pre-clarification step or other initial solids reduction strategies in combination with CFM as a final treatment step for applications requiring FPBOs with very low solids content.

Figure 5: Filter "cake" leftover after dead-end microfiltration of FPBO (left) and FPBO + 5 wt% solid phase adsorbent (right) from testing combined solids/ash removal strategies

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[1] Throughput, in the context of this work, is defined as the time-averaged collection rate of the microfiltered FPBO normalized by the filtration active area.

The use of backflushing significantly improved the throughput in the CFM configuration. Due to the development of fouling on the active filtration surface, constant throughput of low-solids FPBO is achieved once the fouling layer thickness on the active filtration surface stabilizes. Typical throughputs of low-solids FPBO in the "steady-state" operating regime ranged from 20-50 L/m^{2}h. Increases in throughput up to 100% were observed by activating an intermittent on-line backflushing technique using compressed air, solvents or permeated FPBO. Figure 4 exemplifies this concept. The processing downtime required to perform an individual backflush in the experimental system was on the order of seconds.

Combining the use of solid-phase adsorbents (SPAs) and microfiltration can help meet both solids and ash reduction targets in FPBOs produced from lower quality biomass feedstocks**.** There was evidence that performing solids/ash removal in two microfiltration steps (a first microfiltration step followed by mixing of the low-solids FPBO with SPAs, then a second microfiltration step of this mixture) can lead to increases in the overall throughput of the process. This observation was largely attributed to the changes in the fouling layer properties due to the interaction between the suspended solid particulate and the SPA.

Figure 5 5 demonstrates the different filter cakes after microfiltration in both cases. Practically speaking, it took less time to pre-filter the FPBO and undergo a secondary filtration after contact with SPAs compared to the base case scenario of a single step approach. This result has interesting implications related to the use of ion exchange columns, or alternatively, the use of ion exchange membranes for superior solids/ash removal from FPBOs derived from high ash biomass feedstocks.

Additional information contained within the thesis includes the description and use of an empirical modelling approach to predict CFM performance compared to experimental data, the use of a low-cost settling apparatus to monitor suspended solid dispersion after FPBO standing tests, procedures on the use of optical microscopy for qualitative evaluation of FPBO, and highlighting an acid-leaching procedure for ash reduction in a hog fuel prior to fast pyrolysis liquefaction. The reader can refer to the following link to access the full thesis, in which the topics in this newsletter are explored and discussed in more detail [3].

http://dx.doi.org/10.20381/ruor-24122

Acknowledgements
The contributions of Benjamin Bronson, Dr. Boguslaw Kruczek, Dr. Fernando Preto, Dr. Sebnem Madrali and many others, along with funding from Natural Resources Canada's Office of Energy Research and Development is acknowledged for the completion of this work.

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Hydrothermal Liquefaction for the sustainable management of municipal wastewater sludge

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Southern Oil Refining Pty Ltd (SOR) is a private, 100% Australian owned company, based in Wagga Wagga, New South Wales, which has been re-refining waste oil since 2001. SOR re-refines waste lube oil for reuse as lube oil – its best and highest use and a cradle-to-cradle solution.

SOR produces no waste, reduces the need for oil imports and its product has a significantly smaller carbon footprint than crude base oils – making SOR a natural partner for organisations that are committed to protecting and enhancing their environmental credentials and reputation. SOR's Wagga Wagga plant and Northern Oil Refinery (NOR) at Gladstone, Queensland, are the only facilities in Australia producing fully re-refined lube oil accredited for use by a major international oil company for global applications.

These re-refineries give SOR the capacity to process 38% of Australia's annual waste lube oil production (including 100% of Queensland's waste lube oil). The NOR brings together the re-refining expertise of SOR with the established waste collection knowledge and geographical coverage of J.J. Richards & Sons to provide a long-term, environmentally sustainable waste oil recycling option for truck fleets, heavy vehicle operators, mines and local governments. The Northern Oil Advanced Biofuels Pilot Plant (NOABPP) is a $16 million renewable fuel facility being developed by SOR at the NOR. Opened in June 2017, the pilot plant will use organically rich material such as sugarcane bagasse, prickly acacia, and municipal wastewater sludge/biosolids as feedstock for the production of renewable crude oil, which will be refined into saleable renewable kerosene and diesel products.

Within three years of opening, the NOABPP aims to have produced one million litres of fuel for use by Australian heavy road transport operators and possibly for the aviation sector. The pilot plant aligns with the objectives of the Queensland Government's Biofutures Roadmap and Action Plan; stimulating an industrial biotechnology revolution in the state

SOR continues to drive innovation in recycling and refining oil and will assess scalable hydrothermal liquefaction (HTL) as part of a suite of technologies for biofuel production. HTL is an emerging technology that has enormous potential to be exploited for the management of municipal wastewater sludge/biosolids, providing a sustainable waste management solution for Australia's municipal wastewater industry and a reliable source of renewable crude oil for biofuel production. Currently SOR is the industry partner on an AustralianResearch Council Linkage Project (LP150101241) titled '*Commercial scale production of biocrude by hydrothermal liquefaction*'. In this ARC project trials of HTL for various feedstocks undertaken at the University of Adelaide in the School of Chemical Engineering & Advanced Materials, have demonstrated the great potential for sustainable production of renewable crude oil. However most reported work has been at lab to pilot scale without addressing the issue of scale and commercialisation. Preliminary investigation on the valorisation of municipal wastewater sludge (bio-solids) sourced from an advanced municipal wastewater treatment plant using a proprietary pilot-scale semi-continuously operated hydrothermal liquefaction (HTL) reactor was investigated.

The targeted product was renewable crude oil for fractionation to renewable diesel. The trials were carried out with a ~25$_{w/w}$% bio-solids slurry feed, that was reacted at 350°C, 330°C, and 310°C, 40-minute and 20-minute retention times (RT); at ~200bar, respectively. The renewable crude oil yields ranged from 46-52wt% on an ash free basis (afb) or 16-19wt% on a dry basis (db).

The highest renewable crude oil yields were obtained at 350°C (52wt% afb / 19wt% db), and at 330°C (50wt% afb / 19wt% db) for 20-minute RT. The 330°C/20-minute reaction condition favoured the formation of diesel range equivalent hydrocarbons (C10-C24). Simultaneously, the 330°C/20-minute reaction generated the highest non-extracted C10-C24 compounds that remained in the aqueous fraction and in the residual-solids fraction (after renewable crude oil solvent extraction process) than the other reaction conditions.

Further investigation is being undertaken to limit the mass transfer of C10-C24 to the aqueous fraction and to improve the extraction of renewable crude foil from the residual-solids fraction. Valorisation of the aqueous fraction to produce a slow-release fertiliser and CH_4 production was determined to be feasible due to the significant concentration of TKN (11g/L) and volatile fatty acids (13/g/L) present. A broad range of construction materials could enable the valorisation of residual-solids fraction; however, the presence of clay and heavy metals need to be addressed.

In 2019 SOR commenced a pre-commercial deployment Project to design, build and operate a proprietary designed and commercially relevant fully integrated and continuously operated sub-critical water reactor process (herein referred to as HTL technology) taking raw feedstock to product fractionation for the production of renewable crude oil.

The design basis for the proposed system is for continuous operation with each reactor tube processing up to 1 tonne of feedstock per hour, producing ~1ML per annum of renewable crude oil per reactor vessel, a first-of-a-kind renewable energy solution and hybrid enabling technology linking the emerging biofuel industry and established municipal wastewater treatment utilities.

SOR has obtained financial support from the Australian Renewable Energy Agency (ARENA) Advancing Renewables Program to advance the technology readiness and commercial readiness of HTL technology for renewable energy production to 9 and 2 respectively

Support from ARENA will help bridge the gap between innovative HTL technology and commercialisation and deployment of this sustainable renewable energy solution.
The ARENA project is titled '*Commercialisation of Renewable Crude Oil Production*'.
Melbourne Water Corporation (MWC) and Urban Utilities (UU) are interested in the research and development of HTL technology for the sustainable management of wastewater sludge, which has the potential to assist their respective businesses in their sustainable approach for innovative resource recovery and reduction of emissions.
Successful completion of this Project will position SOR for full-scale commercialisation of HTL technology, in particular UU will participate in the Project as a feedstock supplier and potential early adopter of HTL technology, providing an initial commercialisation pathway for the Project, which will be replicable at wastewater utilities across the globe.

Commercialisation of HTL technology for management of municipal wastewater sludge will enable the production of renewable crude oil can be upgraded to biofuels providing an indirect reduction in global carbon emissions contributing to the IEA 2DS trajectory [8]. The HTL technology can be applied to wet and organically rich waste feedstocks. SOR is developing a biofuel business that requires multiple technologies to be distributed around Australia to process dry and wet organically rich feedstocks, providing sustainable waste management solutions and production of renewable crude oils.

SORs innovative HTL Project will provide a pathway to commercialisation for production of renewable crude oil with both national and international implications; and unlock future investment from the municipal wastewater industry. Emissions savings will be realised both in reduction of municipal wastewater treatment unit operations, end of life disposal of sludge/biosolids (e.g. land applied biosolids, landfill emissions etc), and improved life cycle efficiencies with the production of renewable crude oil. New business opportunities will develop as other sustainable organically based feedstocks and wastes are diverted to SORs HTL technology platform.

The subsequent development SORs biofuel refinery/s will produce liquid transportation fuels including renewable kerosene (aviation) and diesel (heavy transportation) products that can be used locally and exported around the World. The HTL Project forms part of a complex suite of projects at various stages that address the biofuel supply chain. SOR has developed the Northern Oil Advanced Renewable Fuels Roadmap which addresses the processing requirements from feedstock to fuel using innovative technologies that will provide new opportunities for economic prosperity.

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David M. Lewi

Towards a pyrolysis biorefinery: Valorization strategies for the pyrolytic lignin fraction (part I)

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The raw pyrolysis liquids obtained via fast pyrolysis have the advantage of being pumpable and of increased energy-density, yet they are acidic, unstable and prone to repolymerization upon storage. As such, efficient upgrading strategies must be applied to further convert these chemically heterogeneous mixtures into valuable products. [1-3] Raw pyrolysis liquids can be easily separated by a straightforward water fractionation into an aqueous sugar-rich (pyrolytic sugar – PS) fraction and a hydrophobic mostly lignin-derived (pyrolytic lignin – PL) fraction.

The two fractions, possible intermediates in a so-called pyrolysis biorefinery (Figure 1), can be processed independently into a wide range of valuable products by strategies tailored to their nature and inherent properties, or alternatively serve as feedstocks suitable for co-feeding in traditional refineries. [4]

Various upgrading technologies have been applied to biobased sugars such as PS (*e.g.* hydrolysis and fermentation) [5,6], however, the valorization of the PL fraction remains relatively unexplored due to its complex structure. Our ambition is to demonstrate the untapped potential of PL as a biobased source of valuable chemicals in the context of sustainable pyrolysis-based biorefineries. An in-depth structural characterization of a typical PL using advanced techniques was recently performed by our research group, *Green Chemical Reaction Engineering (University of Groningen)*, in collaboration with BTG, to better understand its chemical features both qualitatively and quantitatively.

Our results showed that PL is a mixture of lignin-derived oligomers (around 85 wt%) and monomers (around 15 wt%, mostly phenolics), comprised of (methoxy substituted) phenolic subunits linked by alkyl, ether, ester and carbonyl groups, without the typical native lignin linkages (β-O-4, β-β, β-5). [7]

Due to the low amount of monomers and chemical heterogeneity, PL requires further depolymerization before it can be effectively used as a source of low molecular weight biobased chemicals and fuels. Strategies for PL valorization have been also explored in detail by our research group, particularly catalytic hydrotreatment, which is known in the scientific literature as a way to depolymerize and deoxygenate other technical lignins (such as Kraft) and whole pyrolysis liquids. [8,9] For instance, carbon-supported (Ru/C, Pd/C, Pt/C and Rh/C) and alumina-supported (sulphided NiMo/Al_2O_3 and CoMo/Al_2O_3) commercial heterogeneous catalysts were used in the catalytic hydrotreatment of a pine-derived PL (4 h, 100 bar of H_2, 350 – 400 °C). [10] The results showed a wide variability in the yields of deoxygenated organic product (41.6 – 63.1 wt% based on PL intake) depending on the catalyst and an overall low solid formation.

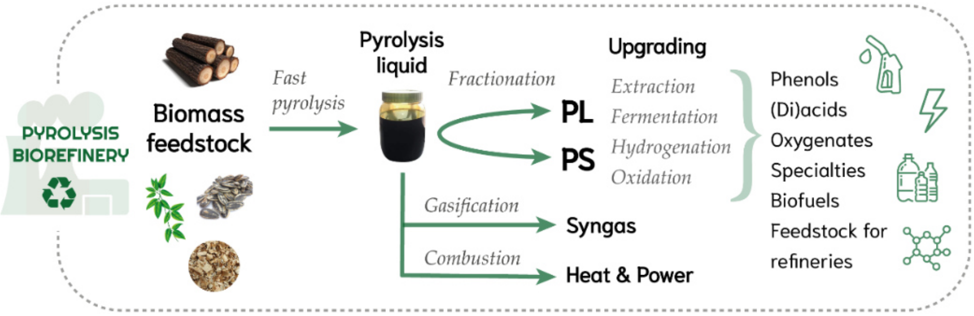

Figure 1: The pyrolysis-based biorefinery

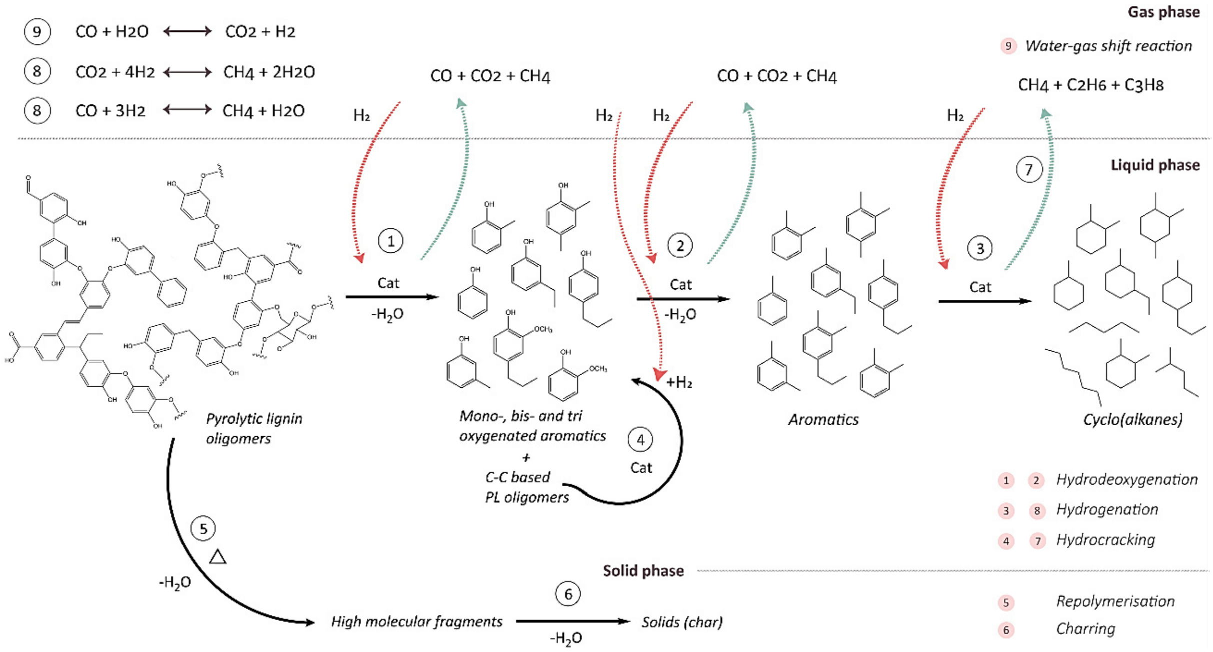

Figure 2: Proposed global network for the catalytic hydrotreatment of PL [10]

In the reactions catalyzed by Pd/C (the catalyst of best performance), the monomer yields as estimated by GCxGC-FID reached around 60 wt% of the organic product (33 wt% based on PL intake), and a high carbon retention of 80% was observed in the organic product. Most of the monomers (19 wt% based on PL intake) were in the class of aromatics and phenolics. The overall hydrocracking efficiency and carbon yields were also shown to be strongly dependent on the reaction temperature, and a global reaction network was proposed for the catalytic hydrotreatment of PL (Figure 2).

Interestingly, Ru/C, a benchmark for pyrolysis liquids [11], performs less with PL when compared to Pd/C due to its high methanation activity. Furthermore, sulphided catalysts seem to favor dehydrogenation reactions, leading to a relatively higher aromatic content in the organic products than found for the non-sulphided, noble metal catalysts. This exploratory study using different catalysts showed the potential of catalytic hydrotreatment for upgrading PL into valuable monomers like alkyl phenolics and aromatics. Inspired by the results and knowing that the (limited) existing literature mainly used PLs obtained from wood, we decided to explore PL from different biomass sources in a second study, using Pd/C as catalyst. [12] The PLs were extracted by adding water to six different pyrolysis liquids (obtained from the fast pyrolysis of pine wood, prunings, verge grass, miscanthus and sunflower seed peel), which were then characterized in detail and hydrotreated at set conditions (1 – 4 h, 100 bar of H_2, 350 – 435 °C). Results showed that both the PL yields and product distribution after hydrotreatment vary substantially depending on the biomass source - for instance, the organic product yields varied from 42.9 wt% up to 71.9 wt%. Furthermore, the molecular composition of the organic products was shown to be a strong function of the PL feed and reaction conditions. Higher monomer yields (up to 39 wt% based on PL intake) were achieved for the PLs derived from pine wood and sunflower seed peel. The large dataset obtained was further used as input in statistical analyses to identify the specific structural features in the PL feeds influencing the formation of aromatics and phenolics. A surprisingly simple mathematical model based on only a few feedstock characteristics (from GPC and ^{13}C-NMR).

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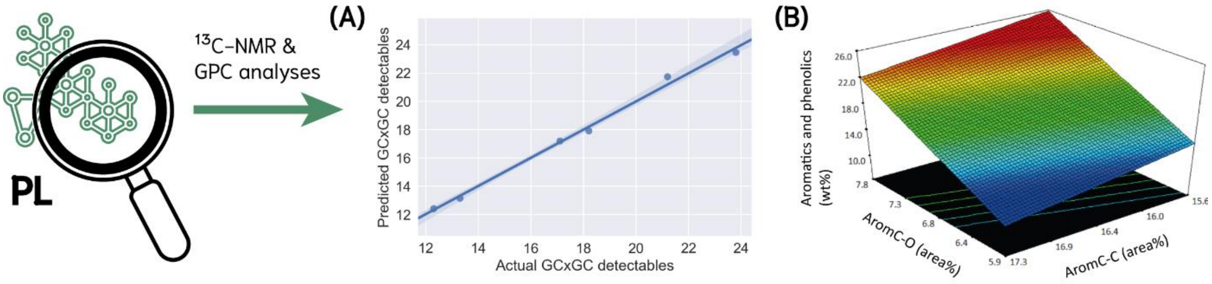

$$GCxGC_{(arom+phe)} = -8.97 + 0.02 \times MW_{avg} - 2.15 \times AromC\text{-}C + 5.99 \times AromC\text{-}O$$

Figure 3: (A) Model prediction ($R^2 = 0.9944$) of the monomer yields (aromatics and phenolics) after PL hydrotreatment (4h, 100 bar H_2, 350 °C). (B) Surface plot based on the weight averaged MW (GPC), AromC-C area% and AromC-O area% (^{13}C-NMR) of the PL feed. The model equation obtained is also shown [12]

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Acknowledgements

We thank BTG for providing the pyrolysis oils and for all the stimulating discussions. Financial support from the Science without Borders program (CNPq, Brazil) for the PhD project of M.B.F. is gratefully acknowledged. We also thank Erwin Wilbers, Marcel de Vries, Léon Rohrbach and Jan Henk Marsman for technical support.

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Fast pyrolysis of hydrolysis lignin in fluidized bed

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Lignin is the only renewable aromatic source in nature, and therefore a lot of research has been done to convert the lignin in wood to higher value products. Lignin is a side product both in chemical pulping and in the production of ethanol by enzymatic hydrolysis.[1,2]A lot of efforts have been made to convert the solid lignin into liquid product with fast pyrolysis. Upon heating, lignin undergoes softening overlapped with depolymerization followed by solidification of the softened material. Due to this phenomenon, lignin is difficult to feed into a fluidized bed with a screw feeder. In the reactor, foam is formed from the melted lignin which leads to defluidization and cyclone failure.[3]The severity of the operational problems are dependent on how much carbohydrates are left with the lignin and increase with decreasing carbohydrate content of the feedstock. The use of right reactor technology for lignin pyrolysis affects also how well the lignin is converted. A CFB reactor is probably more suitable for lignin pyrolysis compared to BFB reactor.[4] Both lignin types, Kraft lignin from chemical pulping and hydrolysis lignin from enzymatic hydrolysis has been previously tested at VTT. However, emphasis in this work was on hydrolysis lignin and a concept to valorize hydrolysis lignin from ST1's lignocellulosic ethanol production process (Cellulonix®), as a refinery feed via fast pyrolysis was developed. Feedstock was processed in VTT's 1 kg/h bench scale bubbling fludized bed (BFB) and 20 kg/h pilot scale circulating fluidized bed (CFB) units. The effect of steam and ethanol as additives in the bench scale unit was also tested.

To overcome the bed agglomeration and defluidization problem, a mechanical mixer was attached in the bubbling fluidized bed to break the agglomerates in the bed (Figure 1). In addition, the feed capacity in the both units were decreased (bench scale 0.5 kg/h and pilot 15 kg/h) to minimize the risk for blockage. In the bench scale unit the feeding screw was covered with a water cooled jacket to avoid the melting of the lignin on the feeding screw. In CFB unit, melting problem was avoided by feeding the raw material in the cold section of reactor before the contact with the heat carrier sand. Although the lignin could be processed with both units, many challenges were identified. In both units a rapid deposit formation in product gas lines was observed, which resulted in increased pressure build-up and shorter operational periods. In pilot test run, several maintenance breaks were needed to burn the carbon deposits from the product gas lines to avoid the extensive rise of pressure

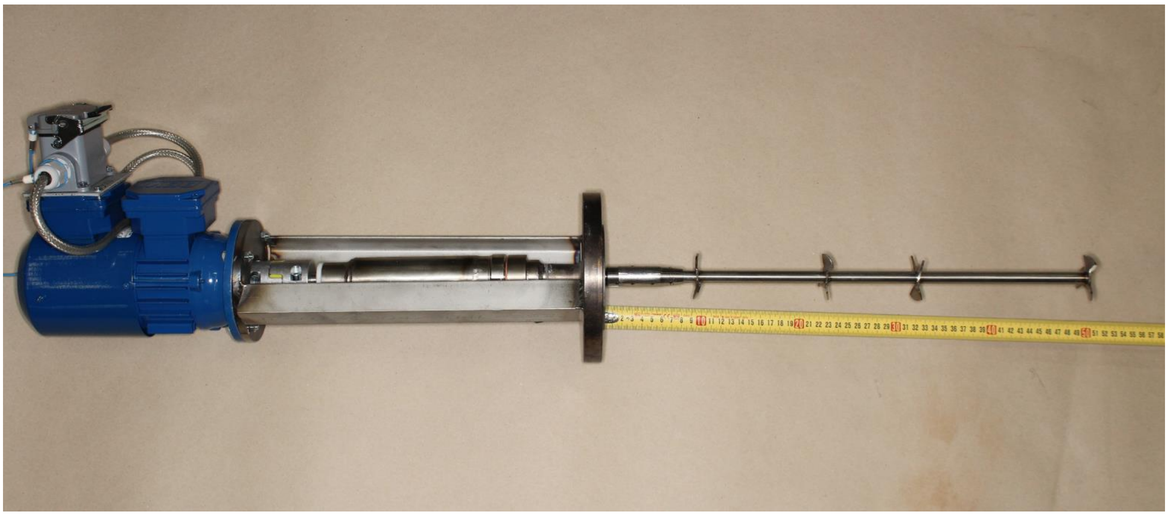

Figure 1: Mechanical mixer used in VTT's bench scale BFB reactor.

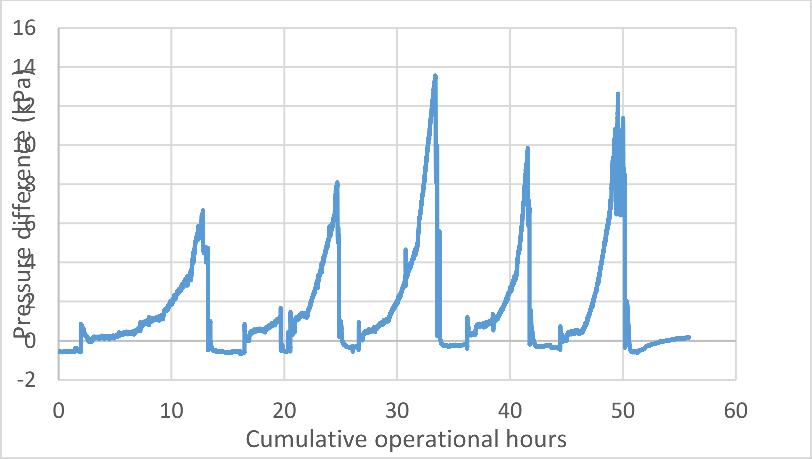

Figure 2: Pressure difference over the second cyclone and deposit burning cycles during the pilot test run.

In the system (Figure 2). The longest continuing operational period reached was a bit over ten hours at the beginning of the test run. Measured organic liquid yield for lignin pyrolysis was between 35 and 44 wt%, while around 10 wt% of gases, 5-10 wt% of water and 40 wt% of char was produced.

As predicted, the bed agglomeration was not a problem with hydrolysis lignin in the CFB unit due to the high gas and particle velocity. On the other hand, bed agglomeration took place in the bench BFB reactor even if the mixer was used. Carbohydrate content of the feedstock was changing within the lignin batches received due to the changes in the operational parameters of Cellunolix® process (Figure 3).

This had a direct impact on how successfully the lignin was processed in the BFB reactor. More of the above mention problems were present when the lignin content of the feedstock was higher.

However, compared to separate and previous experiments with Kraft lignin, problems with hydrolysis lignin were much less severe. Partial explanation to this might be that the residual carbohydrate content of Kraft lignin is typically much lower than with hydrolysis lignin, but different molecular structures of these lignins will most likely have also an effect.[5] In the tests with additives in the BFB unit, roughly, 15 vol-% of fluidization nitrogen was replaced with steam and ethanol, separately, to provide excess hydrogen into the system. Regarding to the liquid quality no major differences were seen (Figure 4), but slight increase in the liquid yield was observed with both additives.

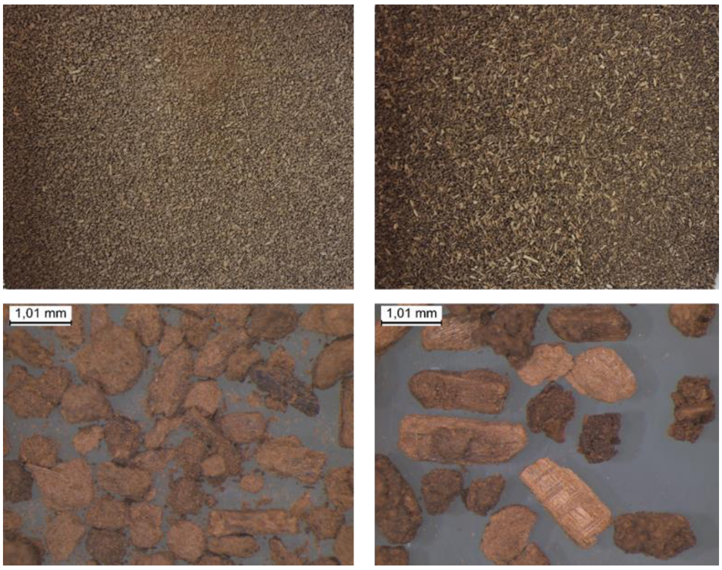

Figure 3: Variation in hydrolysis lignin quality is observable already visually in the colors of the particles. Pictures on the left side are from the first feedstock batch and pictures on right side form the second batch.

Interestingly, the rate of pressure build up was reduced when additives were used, indicating that additives may have stabilized the pyrolytic vapors to some degree. However, this observation needs to be still confirmed and studied more thoroughly. Problems with the deposit formation seems to be the major issues to be solved before scale-up of the process. Success in the development work with hydrolysis lignin would also be one step forward to overcome the issues with the more challenging, but also more abundant, Kraft lignin.

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Autothermal oxidative pyrolysis pilot plant in BioValue

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Recently, a Brazilian consortium named BioValue has initiated its activities, which are completely aligned with the European H2020 project BECOOL. It gives the opportunity to explore the Brazilian and European synergies in relation to biomasses production, diversification and logistics of defined value chains for the developing and deploying process technologies for advanced biofuels (with a special focus on aviation biofuels) via thermochemical routes.

The goals of the BioValue proposal are: (i) the development of new agricultural systems, crop diversification considering integrated food/feed and lignocellulosic crops for advanced biofuels production; (ii) biomasses logistics and efficient conversion processes, including biochemical and thermochemical routes; (iii) integrated technical, economic, environmental and social sustainability assessments of the whole value chains.

In this project, advanced biofuels production will be focused on the gasification of agroforestry industries residues (sugar cane bagasse and straw, eucalyptus and pine) and intermediate energy carriers obtained from technologies as pyrolysis and hydrothermal liquefaction (allowing the biomasses decentralization in energy densification units).

In BioValue, the pyrolysis process under development is the oxidative fast pyrolysis, which involves the addition of low concentrations of oxygen and prevents significant effects on combustion reactions. It is a breakthrough in the pyrolysis process, since the energy required for the process is supplied by combustion of the pyrolytic products, resulting in an autothermal operation; this facilitates the energy optimization and operational feasibility of the system [1]. The oxidative pyrolysis mechanism can be expressed by two stages: a combination of total decomposition of hemicellulose and cellulose and partial decomposition of lignin and a second stage, related to the decomposition of lignin and combustion of char residues. Ferreira *et al.* [2] used 0, 3, and 20% of O_2 to simulate the oxidative pyrolysis atmosphere by using sugar cane straw. The authors assessed the activation energy and heat required for the pyrolysis process. The best results observed were for the atmosphere with 3% O_2, which corresponded with the lowest values of activation energy: 101–130 kJ/mol and 96–137 kJ/mol. More recently, Ferreira *et al.* [3] have reported that the optimal conditions for the whole oxidative pyrolysis process, are carrying out at oxygen concentrations and heating rates around the central level of 10%, and 298 K/min, respectively. This condition resulted in approximate values of required heat and percent residual residue of 181.74 kJ/kg and 9.89%, respectively. In BioValue, the oxidative fast pyrolysis reactions have been conducted in a fluidized bubbling reactor (10-30 $Kg.h^{-1}$ dry biomass) with air flow and recycling of the non-condensable gases (NCG). The bio-oils are collected into 3 fractions: acid extract (AE), light bio-oil (LB) and heavy bio-oil (HB), where the ratios will depend on the biomass nature and the pyrolysis condition.

For example, an oxidative fast pyrolysis of eucalyptus residue at 500 ± 5°C, with 11.1 ± 0.01 m^3/h of fluidization air flow, recycling ratio 1:1 and 14.6 ± 0.01 kg/h of mass flow rate can produce 23.83 wt. % of AE, 15.21 wt. % of LB and 18.63 wt. % of HB, totalizing 57.67 wt. % for the condensable products yield. For the pyrolysis solid product, biochar (B), the

Table 1: Chemical composition of the bio-oil fractions (BF: AE,LB,HB)

BF	Chemical composition of the bio-oil fractions (wt. %)														
	GL	XY	AR	LA	FA	AA	HM	FU	AA*	PH	GU	SYR	HC	O	PL
AE	1.1	0.7	**4.6**	**6.2**	**3.6**	**3.9**	0.2	0.2	0.1	0.1	0.4	1.0	0.1	0.1	1.6
LB	**2.4**	0.1	0.2	1.9	**4.8**	1.4	0.1	0.2	0.0	0.1	0.9	1.7	0.1	0.2	1.1
HB	0.0	0.0	0.1	-	-	0.2	0.1	0.2	0.6	0.2	**3.5**	**9.8**	0.9	**2.8**	0.2

Analyzed by HPLC: **GL**-Glucose, **XY**–Xylose, **AR**–Arabinose, **LA**-Latic acid, **FA**-Formic acid, **AA**-Acetic acid, **HM**–Hydroxymethylfurfural, **FU**-Furfural; **Analyzed by CG/MS**: **AA***-Acetic acid, **PH**-Phenil group; **GU**–Guaiacyl group; **SYR**–Syringyl group; **HC**-Hidrocarbons; **Others**-Carbohydrates, aldehydes, ketones and esthers, **PL** – Polymeric Lignin.

yield was around 11.64 wt. % and the yield for pyrolysis non-condensable vapors were less than 30.0 wt. %. The chemical composition of the bio-oil fractions are exhibited in Table 1. We have been developing bio-oil upgrading processes in order to adjusting the oxidative fast pyrolysis process into different integrated biorefinery scenarios.

For example, we have taken advantage [4-6] f the oxygen and acidic properties of bio-oil, (EA) to extract iron from mining tailings to produce different materials and fuels [4] and derivatization of esterification reactions.

Moreover, the reactivity of the oxygen groups of bio-oil have also been used to produce carbon nanostructures such as graphene, nongraphite, nanotubes and nanoparticles by the simple reaction with H_2SO_4 [5].

The BioValue oxidative pyrolysis pilot plant can also operate in conditions to enhance the biochar production, 30 wt. % (bio-oil/NCG = 40/30, wt.), when it has a high value.

By operating at 400 °C with a recycling ratio of 0.3, 20 Kg.h^{-1} of chicken litter can convert toward around 8 Kg.h^{-1} of organomineral fertilizer. In conclusion, the oxidative pyrolysis pilot plant in BioValue is well flexible and adaptable in order to tuning in the process operation toward target products in different integrated biorefineries scenarios.

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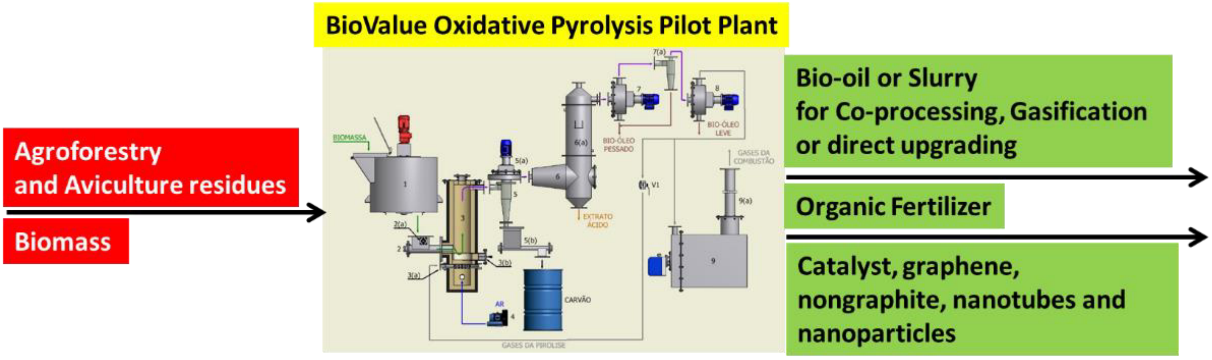

Figure 1: Biovalue Oxidative Pyrolysis Pilot Plant

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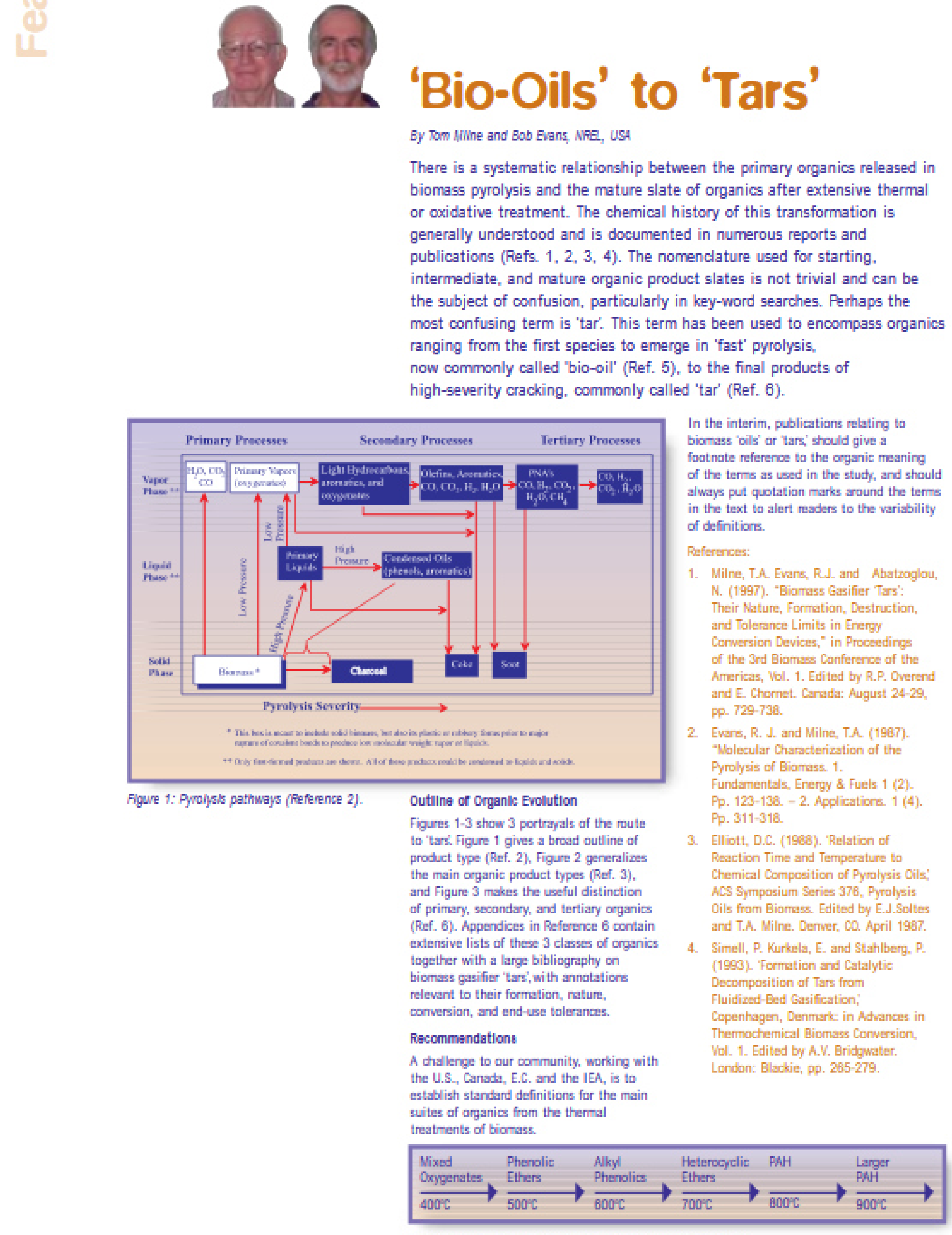
What happened 20 years ago?

It is interesting to see how the field of direct thermochemical liquefaction developed over the years. We are thus presenting one example highlight from the PyNe newsletter twenty years ago in this regular feature...:



'Bio-Oils' to 'Tars'

By Tom Milne and Bob Evans, NREL, USA

There is a systematic relationship between the primary organics released in biomass pyrolysis and the mature slate of organics after extensive thermal or oxidative treatment. The chemical history of this transformation is generally understood and is documented in numerous reports and publications (Refs. 1, 2, 3, 4). The nomenclature used for starting, intermediate, and mature organic product slates is not trivial and can be the subject of confusion, particularly in key-word searches. Perhaps the most confusing term is 'tar'. This term has been used to encompass organics ranging from the first species to emerge in 'fast' pyrolysis, now commonly called 'bio-oil' (Ref. 5), to the final products of high-severity cracking, commonly called 'tar' (Ref. 6).

Figure 1: Pyrolysis pathways (Reference 2).

Outline of Organic Evolution

Figures 1-3 show 3 portrayals of the route to 'tars'. Figure 1 gives a broad outline of product type (Ref. 2), Figure 2 generalizes the main organic product types (Ref. 3), and Figure 3 makes the useful distinction of primary, secondary, and tertiary organics (Ref. 6). Appendices in Reference 6 contain extensive lists of these 3 classes of organics together with a large bibliography on biomass gasifier 'tars', with annotations relevant to their formation, nature, conversion, and end-use tolerances.

Recommendations

A challenge to our community, working with the U.S., Canada, E.C. and the IEA, is to establish standard definitions for the main suites of organics from the thermal treatments of biomass.

In the interim, publications relating to biomass 'oils' or 'tars,' should give a footnote reference to the organic meaning of the terms as used in the study, and should always put quotation marks around the terms in the text to alert readers to the variability of definitions.

Figure 2: 'Tar' maturation scheme proposed by Elliott (Ref. 3)

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TCS 2020

2020 Thermal & Catalytic Sciences Symposium

5h Oct. 2020 – 7th Oct. 2020, Kennewick, USA

https://web.cvent.com/event/f36c8689-c576-4186-a488-fcd692d86a58/summary?RefId=TCS2020


2nd International Conference on
Biofuels, Bioenergy and Bioeconomy
THEME: "Accelerating Advancements and Frontiers in Biofuels, Bioenergy & Bioeconomy"
Second Edition | Oct 19-21, 2020 | Vancouver, Canada

19th Oct. 2020 – 21th Oct. 2020, Vancouver, Canada

https://frontiersmeetings.com/conferences/biofuels/


PYRO 2020
GHENT
29 NOVEMBER - 4 DECEMBER
Het Pand, Ghent, Belgium

29th Nov. 2020 - 4th Dec. 2020, Ghent, Belgium

http://www.pyro2020.org

biofuture SUMMIT II
BBEST 2020
BRAZILIAN BIOENERGY SCIENCE & TECHNOLOGY CONFERENCE

30th Nov. 2020 - 2nd Dec. 2020, Sao Paulo, Brazil

http://bbest-biofuture.org/v2/

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How To Become a Member
Contact your national representative in the IEA Bioenergy ExCo to assess the benefits of joining Task 34.
https://www.ieabioenergy.com/directory/executive-committee

For more information

IEA Bioenergy Task 34 Website

www.task34.ieabioenergy.com

IEA Bioenergy

www.ieabioenergy.com

Past Issues of the Task 34 Newsletters

http://task34.ieabioenergy.com/iea-publications/newsletters/

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

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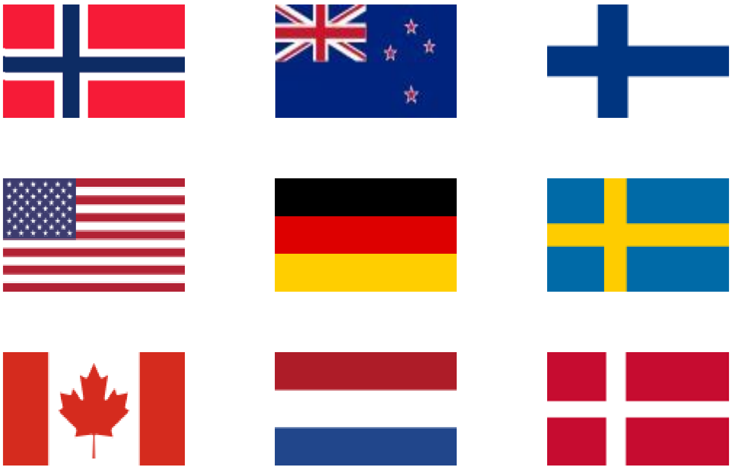
Task 34: Direct Thermochemical Liquefaction



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