IEA Bioenergy
Task 34
Direct Thermochemical Liquefaction
PyNe 45
December 2019

New member Denmark to host Task 34

Figure 1: Task 34 at University of Aalborg, Denmark

There was a tremendous increase in industrial DTL activities this year, particularly in Northern Europe. It is surely an exciting time to see these developments and how the topics Task 34 has been working on for so many years is experiencing such an increase in market interest!

(Continued on page. 2)

Inside this Issue:

Within this PyNe newsletter we are presenting articles from two companies involved in the field of biomass pyrolysis: Envigas and Mainstream Engineering. Canmet is sharing their experiences with an immiscible fluid in quenching. Hydrothermal liquefaction will not be missing in this newsletter, either: KIT is presenting work on HTL of microalgae under consideration of latest pretreatment developments and there will be a summary of the HTL workshop held in November this year. Last but not least, Norway is being presented as the newest Task 34 member and the European H2020 project 'Brisk 2' is featured representing interesting collaboration opportunities for the global DTL community.

The second Task 34 meeting of this triennium took place in Aalborg/ Denmark in October. We started with a visit of the local plastic sorting facility, which proved to be extremely fascinating for all of us. It seems a bit off-topic at first glance, but most of you are aware of how (chemical) recycling of plastic waste is becoming an increasingly important issue and thermochemical liquefaction is one of the key processes investigated. We as Task 34 do see the necessity to follow developments in this field and to get active once opportunities evolve in connection with biomass conversion.

We had a fascinating session with Steen Iversen from Steeper Energy and visited their pilot unit that is operated at Aalborg University in cooperation with Lasse Rosendahl. The discussions that evolved during this meeting as well as the lab-tour with Lasse impressively showed where the concepts, challenges, and opportunities of the different DTL technologies overlap.

The internal Task meeting focused on this year's work packages. We also created additional work packages e.g. DTL commercialization and safety assessment of DTL condensates. There is also great interest among Task 34 members to join other.

Personally, I am very excited about a workshop that is planned for late 2020 for experts to discuss material issues around DTL technologies. There are plenty of projects to follow up on over the next two years and we are going to make sure to keep you updated!

Yours sincerely,
Axel Funke
Task lead and NTL Germany

Figure 2: Task 34 Members at the local plastic sorting facility

Consequences of using an immiscible quench fluid for engineering scale R&D in fast pyrolysis

Benjamin Bronson, Dillon Mazerolle, Travis Robinson
Natural Resources Canada, CanmetENERGY-Ottawa

Experimental fast pyrolysis systems help to advance the science of the direct thermochemical liquefaction of biomass. They provide fast pyrolysis bio-oil (FPBO) and fast pyrolysis bio-char, made under controlled conditions and derived from specific feedstocks. Ideally, these products mirror those produced in full-scale commercial systems allowing researchers to gather process data at a reasonable cost. However, for a variety of reasons the design of experimental systems may incorporate features that are not present in commercial systems. CanmetENERGY-Ottawa (CE-O) has incorporated a closed-loop immiscible hydrocarbon spray quench system into its fast pyrolysis pilot plants. This note describes some of the challenges and observations made with this quench strategy.

One major experimental convenience this approach provides is that freshly-produced FPBO is never mixed or contaminated with previously-produced FPBO in the condensation system. Unlike indirect cooling approaches, the hydrocarbon quench approach retains the rapid quenching characteristics of an FPBO quench strategy. However, if a FPBO quench were used, it would take much longer to produce FPBO that is representative of the current experimental conditions. The use of an immiscible hydrocarbon quench system also eliminates the thermal aging that would occur if the FPBO were recirculated. This can simplify interpretation and comparison of results.

Engineering scale fast pyrolysis systems at CE-O

CE-O maintains a bubbling fluidized bed fast pyrolysis system (Figure 1) and a centrifugal ablative fast pyrolysis system (Figure 2). Both systems have a capacity up to 10 kg/h and both systems employ closed loop isoparaffin spray quenching to accomplish product condensation. The selected quench fluid is an isoparaffin composed of C14-C19 isoparaffinic hydrocarbons boiling between 250 and 350°C. This isoparaffin was selected based on its low vapour pressure, thermal stability, and presumed immiscibility with bio-oil.

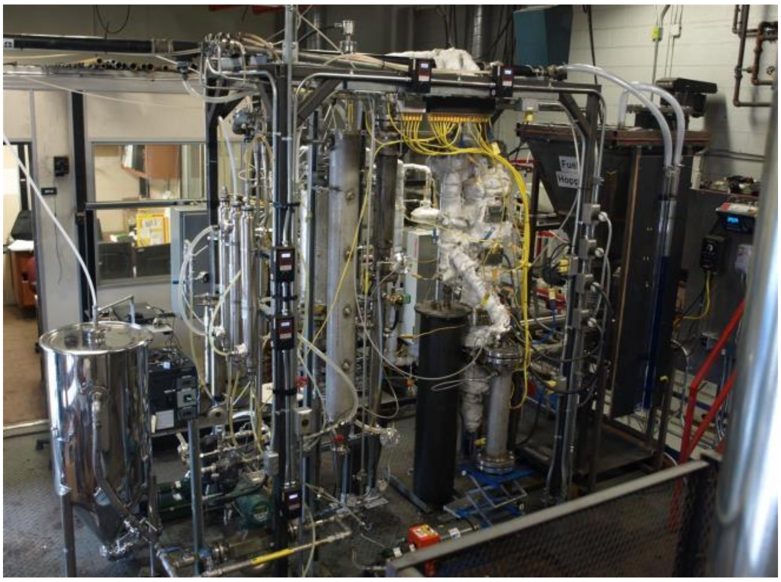


Figure 1: Image of CE-O's bubbling fluidized bed fast pyrolysis system

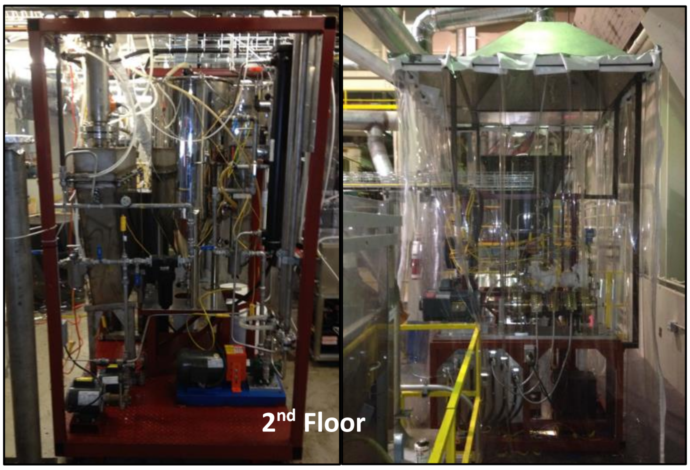


Figure 2: Images of CE-O's centrifugal ablative pyrolysis reactor

Dissolution of biogenic components

While FPBO and isoparaffin are immiscible, in the sense that they cannot be mixed to form a homogenous liquid, contact between the two fluids does result in mass transfer. Ideally, this mass transfer would be negligible but this may not be the case for some bio-oil components. Although this may seem obvious, the magnitude of this effect can easily be overlooked.

Some fractions or components within FPBO are much more amenable to being leached out of the FPBO and into the isoparaffin. Figure 3 is an overlay of the chromatograms from analysis of fresh and used isoparaffin. The broad elution of the quench fluid between 60 and 140 min elution time prevents a clear interpretation of this region of the chromatogram. However, from 0-60 min and 140 – 190 min, the presence of compounds not native to the isoparaffin is readily apparent. FPBO components detected in the isoparaffin include lipids, terpenoids, and methoxyphenols.

The concentrations of some of the identified compounds are estimated to be in the range of 0.01 – 0.1 % (by mass). This may not seem like much, but the concentration of individual methoxyphenols in FPBO is often only 0.1 – 1.0 % (by mass) and there is a much greater inventory of quench fluid in the system than bio-oil, so for some components the amount of mass transfer from the FPBO to the isoparaffin may be significant.

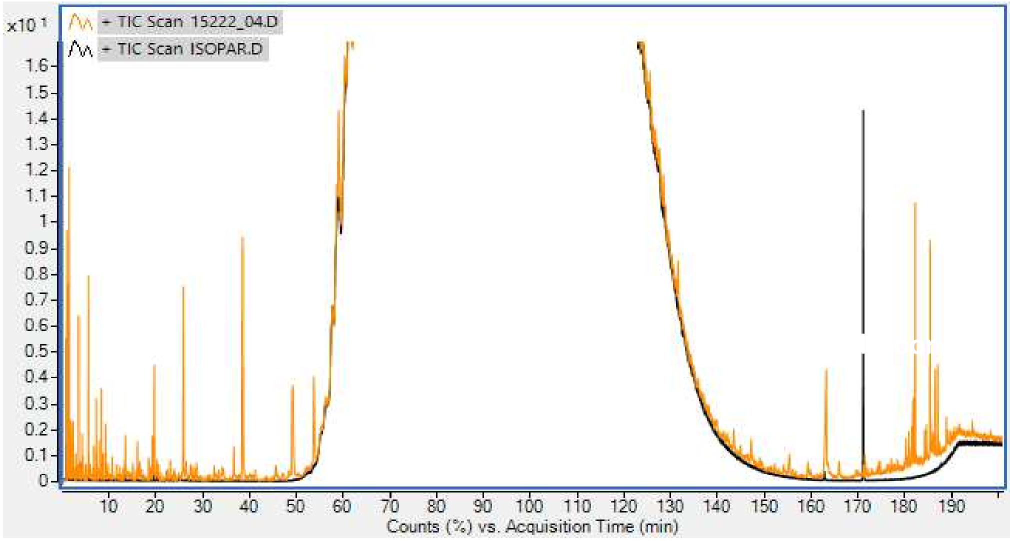


Figure 3: GC Chromatogram comparing fresh quench fluid (black data trace) and used quench fluid (orange data trace).

Table 1: Measured concentrations after mixing unused isoparaffin with bio-oil at room temperature. Approximately 50 mg/mL of the highlighted compounds were added to the bio-oil in order to augment their concentration. <LOQ signifies less than limit of quantification.

Component	**Isoparaffin after** (mg/mL)	**Bio-oil after** (mg/mL)	**Partition coefficient** C_{quench}/C_{FPBO}
glycolaldehyde	<LOQ	34.18	
acetic acid	<LOQ	50.70	
1-hydroxypropan-2-one	0.10	55.07	0.002
furfural	0.24	4.27	0.056
2(5H)-furanone	<LOQ	6.36	
phenol	<LOQ	2.09	
2-methoxyphenol (Guaiacol)	5.76	58.70	0.098
creosol	0.04	2.05	0.020
5-hydroxymethylfurfural	<LOQ	2.48	
2,6-dimethoxyphenol (Syringol)	0.82	87.71	0.009
levoglucosan	<LOQ	99.66	
4-hydroxy-3,5-dimethoxybenzaldehyde	<LOQ	3.34	

CE-O has estimated partition coefficients for FPBO components in an isoparaffin-FPBO system (Table 1). A FPBO sample produced from hardwood flooring sawdust residue at CE-O was spiked with approximately 50 mg/mL of 2-methoxyphenol (guaiacol) and 2,6-dimethoxyphenol (syringol) and then mixed at room temperature with used isoparaffin at a ratio of 1:1 FPBO:isoparaffin.

GC-MS and GCxGC-FID was used to measure the concentration of these components in the isoparaffin and FPBO before and after mixing. Table 1 shows selected results from the GC-MS analysis. Some components, such as acetic acid, glycoladehyde, and levoglucosan were not detected in the isoparaffin after the mixing, some were.

The work demonstrated that although the quench fluid had a much lower concentration of the measured compounds than the bio-oil, there was still a quantifiable transfer of some components from the bio-oil to the quench fluid. Guaiacol was found to have a much greater partition coefficient than syringol, and it was apparent that the extra methoxy group of the syringol molecule has a marked impact on its solubility in isoparaffin.

Figure 4 compares the region of a GCxGC-FID chromatogram for fresh isoparaffin to the same region after exposing the isoparaffin to FPBO. This region of the 2D chromatogram was essentially empty for fresh quench fluid. This region of the chromatogram should contain components, which boil in the same range as isoparaffin, but contain polar moieties. After mixing the isoparaffin with FPBO, this region was populated with FPBO components including guaiacol and syringol (circled peaks).

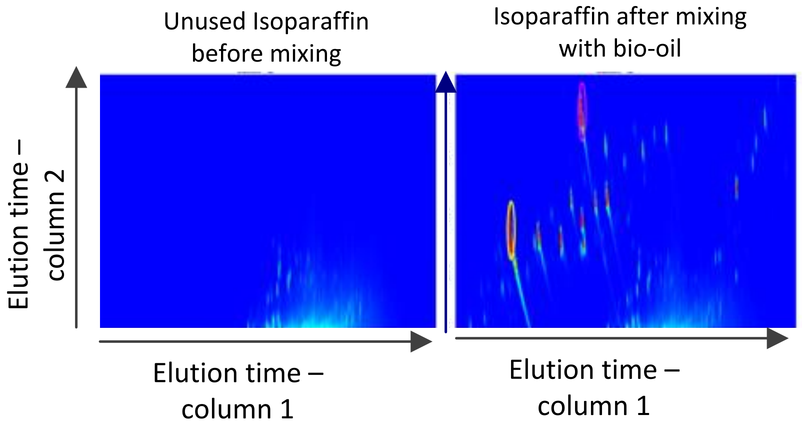


Figure 4: GCxGC-FID analysis of isoparaffin before (left) and after room temperature mixing with FPBO (right).

The large number of components involved makes it difficult to estimate the total amount of biogenic material transferred to the isoparaffin using chromatographic methods. 14C analysis was conducted on a sample of isoparaffin, which over the course of 71 pyrolysis experiments had been exposed to roughly 9-10 times its own weight in FPBO vapours. This sample was found to contain 6% biogenic carbon. Since the maximum oxygen content ever measured in the used quench fluid had been 1.2 % (by mass), it is believed that most of this biogenic material must result from compounds with O/C ratios lower than that of guaiacol. A considerable amount of the biogenic carbon is likely attributable to low polarity compounds such as lipids and other biomass extractives that were not considered at the time of the partition coefficient approximation experiments. Considering that at the time of those 71 experiments, the system contained roughly 5-10 times more isoparaffin quench fluid inventory than the amount of bio-oil yielded in a single experiment, the potential for exchange of these compounds between the FPBO and the isoparaffin should be considered in the interpretation of the results from those experiments.

The ratio of quench fluid to FPBO used during an experimental trial is an important factor in determining the impact that mass transfer to the quench fluid has on experimental results. The quench fluid circulation rate is largely determined by the heat balance. To keep the condensation temperature low, it is necessary to circulate a large quantity of the quench fluid. When gravitational separation, which is rather sluggish, is used to separate the quench fluid from the FPBO, large inventories of quench fluid are required to ensure FPBO is adequately separated from the quench fluid before the quench fluid is recirculated.

Illustrative Example

Assume an experiment that:

consumes 25 kg of dry feedstock per experiment,

uses an inventory of 100 kg of quench fluid,

and results in a change of 1% biogenic concentration (1 kg) in the quench fluid.

Under these assumptions, the transfer of biogenic components from the FPBO to the quench fluid would account for 4% of the total mass balance (1/25).

Property changes of the quench fluid over time

Another consequence of mass transfer from the FPBO to the quench fluid is unintended changes in the properties of the quench fluid. Some of these changes are inconsequential but others have caused operational difficulties. Over the course of operation of CE-O's systems, the density of the quench fluid has ranged from 0.81 kg/L (fresh) to as high as 0.85 kg/L. This has not had any substantial impact on the operation of the

Figure 5: Precipitated wax on strainer element used in the quench fluid circulation system

quench system. A more impactful change has been the change in cold flow properties. In order to measure changes in the cold flow properties, the cloud point temperature of fresh isoparaffin was compared to some exemplary used isoparaffin samples. The fresh isoparaffin has a cloud point below -60°C and there is no difficulty in pumping it through screens and filters. In one case, four hours of operation using an extractives-rich forestry residue was enough to raise the cloud point of fresh isoparaffin to 1°C. Another sample, collected after the course of 71 experiments, the cloud point rose to 12°C. In the case of the latter sample, the pyrolysis system was rendered inoperable due to the precipitation of a waxy substance (Figure) in the quench fluid cooling system.

Additionally, the distillation behavior of the quench fluid after exposure also changed as would be expected based on the chromatogram shown in Figure 3. Some of the leached components contributed to a reduced initial boiling point of the quench fluid. As Figure 6 shows, after use, the initial boiling point of the quench fluid decreases while there is also the presence of new high boiling point material in the quench fluid. The presence of these more volatile components has caused odour abatement issues.

Separation of bio-oil and quench fluid

Normally the separation of the quench fluid from the FPBO has been easy due the presence of a distinct interface between the two liquids. However, for some feedstocks, especially bark-rich and construction and demolition waste, separation has been challenging. Instead of a distinct interface at the boundary between the two fluids, there has been a cloudy transitional layer in between the two fluids. (Figure 7) CE-O is working to better understand this phenomenon as part of our focus on lower cost residual feedstocks.

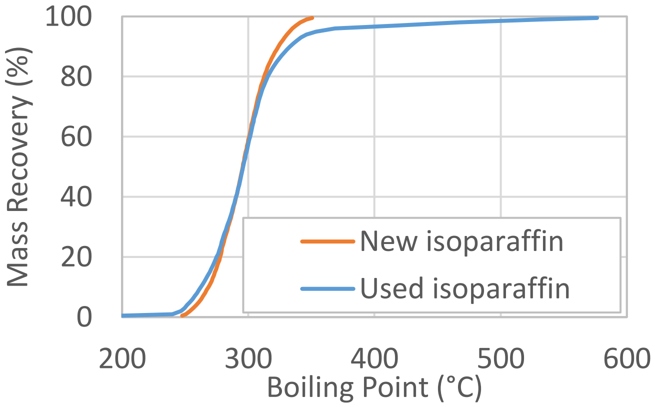


Figure 6: Distillation curves of fresh (new) and used isoparaffin quench fluid

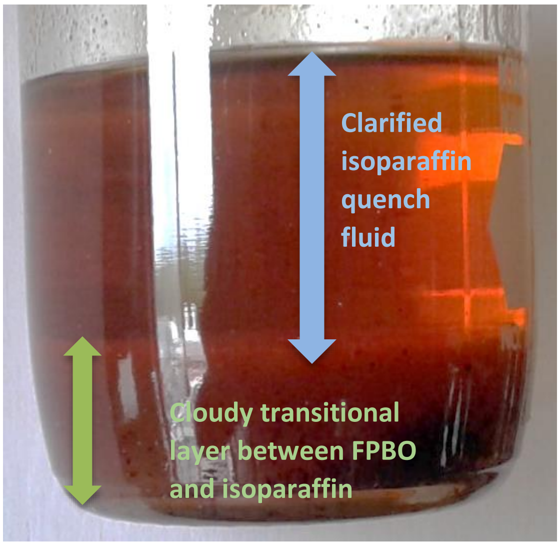


Figure 7: Image of quench fluid with transitional layer following fast pyrolysis of poplar bark

Emulsification of quench fluid in bio-oil

An important challenge when using isoparaffin as a quench fluid is the presence of a small amount of isoparaffin in the FPBO. Components of the isoparaffin have not been found to dissolve in the FPBO. Rather, droplets of isoparaffin have been found suspended in the FPBO as a coarse emulsion.

Quench fluid droplets are readily observed in microscope images of FPBO produced using the isoparaffin quench system. The droplets span a range of sizes up to about 100 µm (Figure 8 and Figure 9). Despite their large size, they have proven quite stable under a variety of conditions. In FPBOs produced from dry, low ash, woody feedstocks, which have not separated into an aqueous and an organic phase, suspended char particles often collect at the interface of the quench fluid droplets and the FPBO (Figure 8).

For phase separated FPBOs, which often result from the pyrolysis of high ash or wet feedstocks, the quench fluid has been observed to report almost entirely to the organic-rich phase (Figure 9). Centrifugation can be used to separate the emulsified

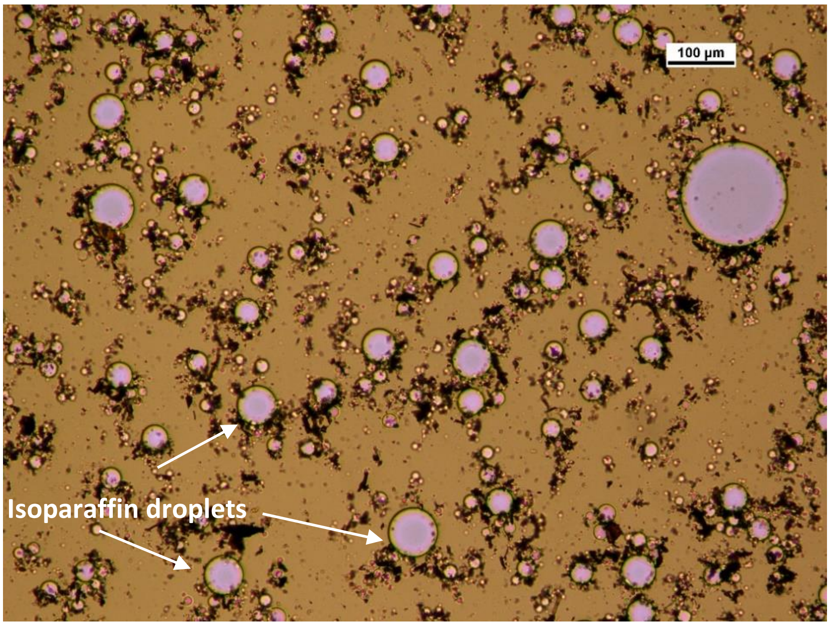


Figure 8: Microscopic image of fast pyrolysis bio-oil produced at CE-O from a dry, flooring residue

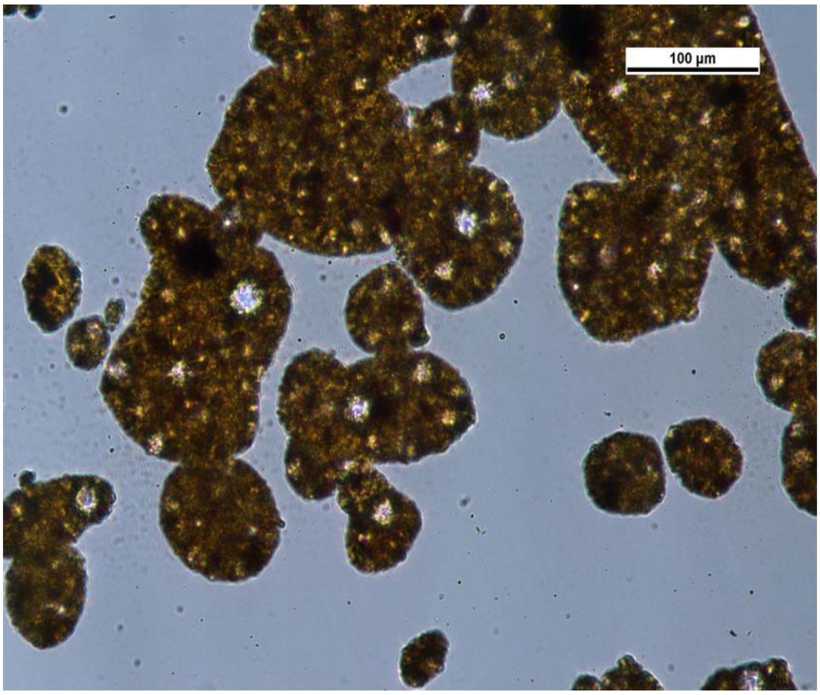


Figure 9: Microscopic image of a two-phase fast pyrolysis bio-oil, produced from a salt-laden forestry residue

isoparaffin quench from the bio-oil but careful sampling is required to ensure a representative sample is obtained. The concentration of emulsified isoparaffin quench fluid can vary with height in the FPBO for stagnant samples. Generally, the level of this contamination has been found to be about 2 – 5% (by mass) of the liquid recovered product. Experience has also shown that certain manipulations of the FPBO can cause (or at least significantly accelerate) separation of the quench fluid from the FPBOs. Two significant examples have been the addition of salts (e.g. KCl) and heating the FPBO to above 60°C.

Material compatibility issues

FPBO itself can present challenges for selection of materials, especially when using elastomeric components. Unfortunately, some of the better performing, common elastomers for FPBO tend to be elastomers that are not well suited for hydrocarbon oils. The fact that the quench circulation system sees a mixture of bio-oil and quench fluid means that components need to be specified which are suitable for both isoparaffin and FPBOs. This has made selection of low-cost materials for flexible gaskets, mechanical seals and other fluid handling components difficult. For experimental purposes, the most cost effective option has been to treat many of these seals and components as consumables that are periodically replaced. This material compatibility challenge has practically ruled out some equipment options where it would be impractical to replace regularly a critical elastomeric component (e.g. progressive cavity pumps).

Conclusions

The use of an immiscible quench fluid for condensation in fast pyrolysis has been an instrumental approach in achieving CE-O’s research objectives, particularly when studying the impact of feedstock properties and operating conditions on conversion performance and product properties. However, the approach has introduced new, unforeseen challenges some of which introduce new uncertainties in the interpretation of data. Firstly, there needs to be the expectation of transfer of some components back and forth between bio-oil and the quench fluid. The types of components that the quench fluid absorbs will affect the properties of the quench fluid thus affecting its behaviour. This includes decreasing the initial boiling point of the liquid and negatively affecting cold flow properties. Secondly, the easy separation of bio-oil and quench fluid is not guaranteed. Thirdly, we have observed that our bio-oils contain a small amount of coarsely emulsified quench fluid. Finally, the differences between bio-oil and the quench fluid can make specification of suitable equipment and materials challenging.

Acknowledgments
The authors would like to thank Fernando Preto, Frank Leclair, Leslie Nguyen, and Andrew Jewlal for their contributions to this work. The authors gratefully acknowledge the Program of Energy Research and Development, the Energy Innovation Program, and the Forest Innovation Program all of which have been administered and operated by Natural Resources Canada. The compilation of this data specifically has been supported by the Program of Energy Research and Development's Development and Optimization of Multi-product Bio-refinery Processes as operated and administered by Natural Resources Canada. The authors also wish to thank the characterization laboratory staff, in particular Phil Bulsink and Ajae Hall, at CanmetENERGY-Ottawa and CanmetENERGY-Devon.

Benjamin Bronson

Dillon Mazerolle

Travis Robinson

CanmetENERGY
Leadership in ecoInnovation

CanmetENERGY
Natural Resources Canada
Government of Canada
1 Haanel Dr Ottawa ON, K1A 1M1
Tel: +1-613-797-3097
benjamin.bronson@canada.ca

Norway joins IEA Task 34 - Direct Thermal Liquefaction

Kai Toven
Rise PFI, Trondheim, Norway

Norway has decided to participate in IEA Task 34 Direct Thermal Liquefaction. Key factors for the decision are strong national policy incentives for promoting increased use of advanced biofuels in transportation as well as national industrial initiatives related to initiating production of advanced biofuels based on novel thermochemical liquefaction technologies.

The Norwegian government has set targets to halve the emissions from transport sector by 2030 and obtain at least 30% biofuel share in sold aviation fuels by 2030. The transport sector generates 30% of the national CO_2 emissions in Norway. Norway aims to reduce total CO_2 emissions by at least 40 percent in 2030, compared to 1990 level. In Norway, there are two main policy incentives to increase use of biofuels in transport. These are mandatory sales requirement of biofuels as a percentage of total fuel sales and exemption for so-called “road tax” for any biofuels sold on top of the mandatory sales requirement. Here, the biofuels sold under the mandatory sales requirement must lead to a reduction in fossil fuel CO_2 emissions equal to at least 50%. In road transport, minimum 20% of fuel sales by 2020 must be biofuels and minimum 8% of these must be advanced biofuels. In aviation, the Norwegian government recently announced that all aviation fuels must contain 0.5% advanced biofuels from 2020. For both road transport and aviation, the sales of advanced biofuels count double to further promote production of more sustainable advanced biofuel by novel technologies.

Strong policy incentives for advanced biofuel have led to several industrial initiatives for producing advanced biofuels in Norway. Most initiatives focus on utilizing lignocellulosic feedstocks like forest residues. Two industrial initiatives related to novel thermochemical liquefaction technologies are led by the companies Silva Green Fuel and Biozin.

.

Figure 1: Norway has decided to participate in IEA Task 34 Direct Thermal Liquefaction. Dr. Kai Toven, Lead Scientist in Biorefining and Bioenergy at RISE PFI is the National Team Leader (NTL) for Norway in IEA Task 34. RISE PFI is a research institute with leading expertise in pyrolysis technology in Norway.

Silva Green Fuel aims to establish production of advanced biofuel based on forest-based feedstock at the industrial site of the former Tofte pulp mill in Hurum, Norway. Initially a demonstration plant will be built in cooperation with the Danish-Canadian company Steeper Energy as technology supplier. The technology is based on hydrothermal liquefaction of slurries at super-critical condition, also termed "hydrofaction". Silva Green Fuels is a joint venture between the Norwegian company Statkraft and the Swedish company Södra. Statkraft is a leading company in hydropower internationally and Europe's largest generator of renewable energy, whereas Södra is a cooperative of 50,000 forest owners with extensive forestry operations and a leading producer of paper pulp, sawn timber and bioenergy

Biozin Holding aims to establish production of renewable fuels from Norwegian sawmills and forestry residues based on the Integrated Hydropyrolysis and Hydroconversion (IH2®) process. The IH2® process was invented by the Gas Technology Institute (GTI) and has been licensed to Shell-owned CRI Catalyst Company for exclusive worldwide deployment. Biozin Holding is owned by Bergene Holm AS, the second largest sawmill company in Norway, and Preem AB, Sweden's largest refinery and fuel company, with oil refineries in Lysekil and Gothenburg. Biozin Holding intend to realize full scale biofuel production sites in Norway. The initial production facility shall be located adjacent to the Bergene Holm sawmill in Åmli in southern Norway.

The National Team Leader (NTL) for Norway in IEA Task 34 Direct Thermal Liquefaction is Dr. Kai Toven, Lead Scientist in Biorefining and Bioenergy at RISE PFI. RISE PFI is a research institute with leading expertise within pyrolysis technology in Norway and Dr. Toven has more than ten years' experience in the field. 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.

Kai Toven

PFI
PART OF RI.SE

RISE PFI

Høgskoleringen 6b
NO-7491 Trondheim, NORWAY

Tel: +47 952 11 704

Email: kai.toven@rise-pfi.no

Web: www.rise-pfi.no

Biocarbon for metallurgical applications: An overview

Nanta Sophonrat, Tobias Brink, Kurt Sjöblom
Envigas Technology AB

According to the report from the Swedish Environmental Protection Agency [1], in 2017, Greenhouse gas (GHG) emission in Sweden amounted to 52.7 million tons CO_2-eq. Although living trees in forests of Sweden have helped removing approximately 44 million tons of CO_2, more effort is needed to reduce the emission to meet the net-zero emission goal of Sweden by 2045.

Metal industry is one of the major emitters in industrial processes sector with 9.4 % of the total emission or 4.9 million tons of CO_2 generated by iron and steel production process [1]. The CO_2 is produced by the utilization of coke, coal, LPG, and fossil oil in the process and in the energy production for the process. The replacement of the fossil carbons such as coke and coal by bio-carbon derived from wood pyrolysis is one of the promising ways to help reduce CO_2 emission.

At Envigas AB, we are proud to be a part of the solutions to reducing GHG emission in Sweden. Envigas AB is a privately-owned Group with a headquarter in Stockholm. The fully owned subsidiary Envigas Technology AB, located in Bureå, Skellefteå, is focusing on R&D with a strategy to optimize yields, quality and value of the commodities produced as well as performing project engineering and operational support functions. Our process produces charcoal or biocarbon by slow-to-intermediate pyrolysis with the aim to reach similar quality of the carbons used in metallurgical process. Bio-oil and syngas is also produced and can be used in many applications such as fuel and chemical synthesis. The pilot plant is currently in operation using sawdust sourced from sawmills near Bureå as a feedstock.

The process uses an electrically heated screw reactor with the production capacity of 150 kg of almost dry feedstock per hour. The pilot plant constitutes an integral part of the company's R&D efforts going forward in cooperation with industries and universities. Through our subsidiary, Skellefteå Carbon AB, we are currently building our first pyrolysis plant on an industrial scale. The factory will be directly linked to the pilot plant in Bureå.

In this newsletter, an overview of properties of cokes used in metallurgical process as compared to those of biocarbon are presented. A short introduction on bio-oil derived from slow pyrolysis as compared to fast pyrolysis bio-oil is also presented.

Coke VS Biocarbon

The properties of charcoal as compared to coke and pulverized coal are shown in Table 1. For proximate analysis, fixed carbon content of coal is in the range of 80 wt%, while that of pulverized coal and charcoal are varied in a wide range. The properties of charcoal can be varied by changing biomass feedstock and pyrolysis conditions. Usually the higher the pyrolysis or carbonization temperature, the higher the fixed carbon content of the charcoal product. Moreover, charcoal generally has lower ash content than coke and coal.

Mechanical strength of charcoal is lower than coke as can be seen from compression strength for cold material and coke strength after reaction (CSR) which is tested after CO_2 reaction at 1100 °C. The CO_2 reactivity of charcoal is usually higher than coke as can be seen from the higher coke reactivity index (CRI) and lower peak temperature during reaction with CO_2 in thermogravimetric analysis (TGA). The high reactivity of charcoal can be attributed to its high surface area in the range of 170-500 m^2/g as compared to 2-15 m^2/g of coke and coal.

The application of charcoal/biocarbon in metallurgical processes is summarized in Table 2. Charcoal can be used in blast furnace as demonstrated in Brazil [2]. However, due to the lower mechanical strength of charcoal, the size of a charcoal blast furnace is limited and much smaller than coke blast furnaces.
Table 3 further elaborates on the difference between charcoal blast furnace and coke blast

furnace. Beside the size of furnace, metal and slag composition, and operating parameters are different. To replace coke in the coke blast furnace by charcoal, mechanical strength (hot and cold) and reactivity of charcoal must be improved.

Charcoal cannot yet replace coke in electric arc furnace due to its low electrical conductivity which results in a lower temperature in the reduction zone. Moreover, the high CO_2 reactivity of charcoal is undesirable due to a higher energy consumption. Although SiO reactivity of charcoal is higher than coke which is attractive for silicomanganese production, with the other undesirable properties of charcoal mentioned above, the target quality of the produced metal was not reached [3].

Table 1: Properties of Charcoal as compared to coke

	Unit	**Charcoal** [2], [4], [5], [7]	**Coke** [2], [5], [7], [8]	**Pulverized coal** [4], [8]	**Envigas biocarbon**
Proximate analysis					
Moisture	wt%	5.6-8.1	~1		4-8
Fixed carbon	wt%DB	65-94	85-88	50-80	86.7-89.6
Volatile matter	wt%DB	5-35	1-3	8-40	8.5-11.4
Ash	wt%DB	0.6-5	10-16	7.5-10.4	1.3-1.4
Ultimate analysis					
C	wt%DB	80-92	80-86	79-83	92.2-93.4
H	wt%DB	0.2-3	0.3-0.5	3.3-5.8	2.0-2.2
O	wt%DB	4.3-15	1.2-1.3	3-13	4.0
N	wt%DB	0.2-0.6	1.1-1.8	0.9-1.6	<0.1
S	wt%DB	0.03-0.10	0.45-0.70	0.3-1.0	
Ash composition					
SiO_2	%DB	5-10	50-55		
CaO	%DB	37-56	4-5		
MgO	%DB	5-7	4-5		
Al_2O_3	%DB	2-12	25-30		
Fe_2O_3	%DB	6-13	5-7		
P_2O_5	%DB	8-12	0.4-0.8		
K_2O	%DB	15-25	2-4		
Na_2O	%DB	2-3	1-3		
Compression strength	kgf/cm^2	10-80	130-160		
Size range	mm	9-100	25-75		
Density	kg/m^3	180-350	550		
Coke Reactivity Index (CRI)†	%	38-47.7 [9]	<23 13.7 [9]		
Coke Strength after Reaction (CSR)‡	%	Low [10]	>65		
CO_2 Reactivity	–	Higher	Lower		
CO_2 Reactivity at TGA Peak temperature (°C) [6]		950-1010	1220		
BET surface area	m^2/g	172.3-495	2.8	1.5-14.0	
Electrical resistance [3], [6]		High	Low		

* DB = Dry basis

† CRI is the percentage of weight loss to the original coke mass after reaction in 100 vol-% CO_2 at 1100 °C for 2 h.

‡ CSR is the percentage of coke particle larger than +10 mm after 600 revolutions in an I-drum, which is performed after gasification in the CRI test. [11]

Pulverized coal injection (PCI) is one of the methods to help reduce coke consumption in blast furnace. Partial replacement of pulverized coal with charcoal is possible [4]. Replacement of coke with charcoal in a sinter plant is possible [5]. It was reported that using charcoal helped reducing sinter time and increasing productivity. Although the quality of the sinters is lower when charcoal is used, e.g., higher glassy phases and lower proportion of ferrites, it is still acceptable. In conclusion, some of the properties of charcoal that should be improved in order to be able to replace coke in metallurgical applications are 1) to increase mechanical strengths (cold and hot), 2) to reduce CO_2 reactivity, and 3) to increase electrical conductivity. These are the topics for future researches. For examples, the production process could be changed by addition of tar during pyrolysis, secondary treatment with high temperature, or using binders for pelletizing [6].

Table 2: Applications of charcoal in metallurgy

Applications	Possibility of replacement	Properties to be improved
1. To replace coke in blast furnace	- Applicable in a small-size blast furnace [2]. - The different of charcoal blast furnace and coke blast furnace is shown in Table 3.	- Need to increase mechanical strength and strength after reaction (CSR) - Need to reduce CO_2 reactivity
2. To replace coke in electric arc furnace	- Not yet applicable. - Show good SiO reactivity for SiMn production [3].	- Need to increase the electrical conductivity - Need to lower CO_2 reactivity
3. To replace pulverized coal	- Coal blend with charcoal up to 50% considered satisfactory for PCI [4].	- Would be good to reduce CO_2 reactivity of charcoal
4. To replace coke in sinter plant	- Able to replace [5]. - Help reduce sinter time, increase productivity - The quality of sinters is lower than using coke but acceptable	- Need to reduce CO_2 reactivity

Table 3: Comparison between charcoal blast furnace and coke blast furnace [2]

	Charcoal blast furnace	Coke blast furnace
Largest size of blast furnace	1200 t/d (Due to low meachanical strength)	~10000 t/d
Hearth diameter (m)	1.5 to 6	8 to 14
Productivity (ton/day.m^3)	1.6 to 2	>2
Amount of slag produced	<150 kg/ton of pig iron (Due to lower ash content)	~300 kg/ton of pig iron
Hot metal composition	% Si variable High phosphorus	% Si < 1 High sulfur
Slag	Charcoal has higher contents of K_2O and Na_2O, and to diminish deleterious effects of these in the operation of charcoal blast furnaces, an acid slag with high SiO_2 content should be preferred.	Coke has high sulphur content and hence, to produce pig iron with low sulphur content, a basic slag is required ($CaO + MgO > SiO_2$).
Metallic burden	It can be 100% lump ore	Sinter and/or pellet
Flux addition	The most commonly used fluxes are lime, quartz, dolomite, and bauxite.	Sinter and pellet are self-fluxing

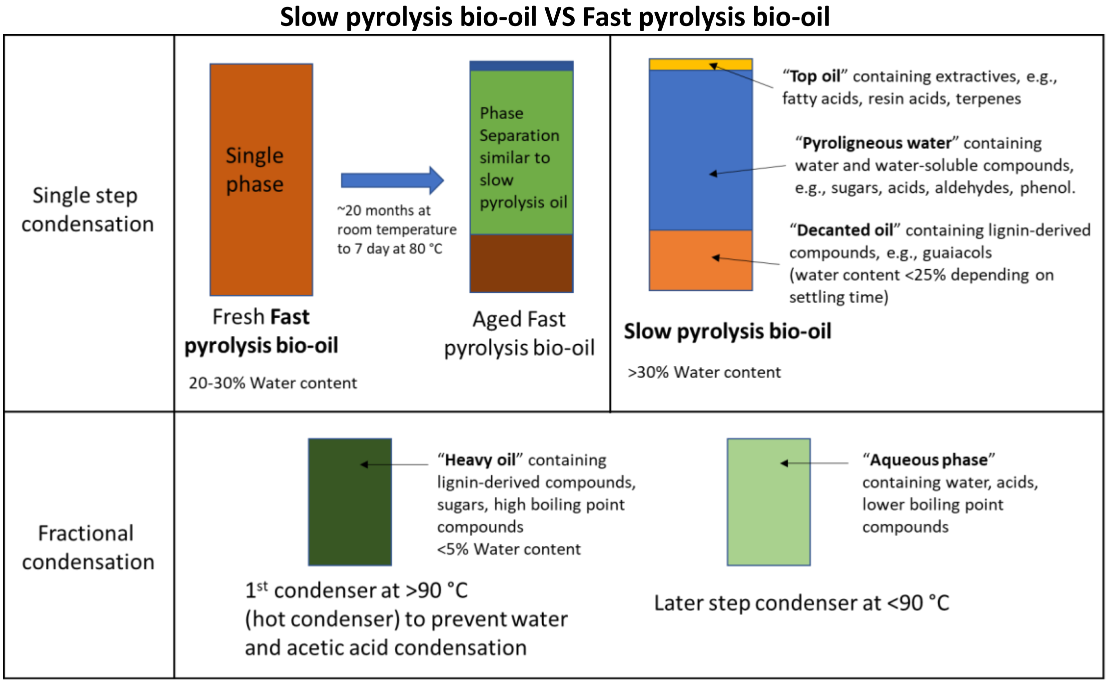


Figure 1 Comparison between fast pyrolysis bio-oil, slow pyrolysis bio-oil, and bio-oil from fractional condensation. (Illustrated from text in [13] and other references [14]–[16])

Another interesting product from slow pyrolysis is the liquid products. The characteristics of the slow and fast pyrolysis bio-oils are different. One of the prominent characters is the phase separation. Phases of fast pyrolysis bio-oil, slow pyrolysis bio-oil and bio-oil from fractional condensation are shown in Figure 1. With single step condensation, phase separation occurs immediately in slow pyrolysis bio-oil.

As the vapor residence time is higher in slow pyrolysis process, a more extensive cracking of the volatile products occurs which results in a lower average molecular weight of compounds in the slow pyrolysis bio-oil as compared to fast pyrolysis bio-oil. At the pyrolysis temperature of 500-600 C, fast pyrolysis bio-oil contains much less methoxyl and carbonyl groups, and much higher aliphatic C-O and aromatic C-C than slow pyrolysis bio-oil [12]. The lower content of carbonyl functional group implies that fast pyrolysis bio-oil is less acidic than slow pyrolysis bio-oil. Another obvious difference in the composition is the higher water content of slow pyrolysis bio-oil which causes the phase separation.

The different phases of slow pyrolysis bio-oil is also shown in Figure 1 (Illustrated from description in [13]). The "Top oil" consist of hydrophobic compounds with lower density than water, e.g., fatty acids, terpenes. The "pyroligneous water" in the middle has high water content together with sugars and other water-soluble compounds. The "decanted oil" at the bottom consist of high molecular weight compounds mostly derived from lignin. This bottom phase has higher density than water and can be separated by decantation.

In case of fractional condensation with the first condenser maintained at higher than 90 °C to prevent water and acetic acid from condensation, the bio-oil condensed in this first stage is called "heavy oil" which contains high boiling point compounds, sugars and lignin derived compounds. The water content in this fraction can be less than 5 %.
Slow pyrolysis bio-oil can be used as fuel, biocides, and wood preservatives.

References

[1] Swedish Environmental Protection Agency,"National Inventory Report Sweden 2019: Greenhouse Gas Emission Inventories 1990-2017," Stockholm, 2019
[2] L. F. A. De Castro, R. P. Tavares, and V. Seshadri, "Process control model for charcoal blast furnaces in Brazil," *Mater. Manuf. Process.*, vol. 20, pp. 287–298, 2005.

[3] B. Monsen, M. Tangstad, and H. Midtgaard, “Use of Charcoal in Silicomanganese Production,” *South Africa ISBN*, vol. 1, no. 2, pp. 392–404, 2004.
[4] C. C. T. Barbieri, E. Osório, and A. C. F. Vilela, “Combustibility and reactivity of coal blends and charcoal fines aiming use in ironmaking,” *Mater. Res.*, vol. 19, no. 3, pp. 594–601, 2016.
[5] R. Lovel, K. Vining, and M.Dell’Amico, “Iron ore sintering with charcoal,” *Miner. Process. Extr. Metall.*, vol. 116, no. 2, pp. 85–92, 2007.
[6] G. Surup, T. Vehus, P. A. Eidem, A. Trubetskaya, and H. K. Nielsen, “Characterization of renewable reductants and charcoal-based pellets for the use in ferroalloy industries,” *Energy*, vol. 167, pp. 337–345, 2019.
[7] G. R. Surup, H. K. Nielsen, M. Heidelmann, and A. Trubetskaya, “Characterization and reactivity of charcoal from high temperature pyrolysis (800–1600 °C),” *Fuel*, vol. 235, no. pril 2018, pp. 1544–1554, 2019.
[8] A. Babich and D. Senk, *Coal use in iron and steel metallurgy*, vol. 2. Woodhead Publishing Limited, 2013.
[9] I. Agirre, T. Griessacher, G. Rösler, and J. Antrekowitsch, “Production of charcoal as an alternative reducing agent from agricultural residues using a semi-continuous semi-pilot scale pyrolysis screw reactor,” *Fuel Process. Technol.*, vol. 106, pp. 114–121, 2013.
[10] H. Suopajärvi, E. Dahl, A. Kemppainen, S. Gornostayev, A. Koskela, and T. Fabritius, “Effect of Charcoal and Kraft-Lignin Addition on Coke Compression Strength and Reactivity,” *Energies*, vol. 10, p. 1850, 2017.
[11] J. Haapakangas, “Coke properties in simulated blast furnace conditions : investigation on hot strength, chemical reactivity and reaction mechanism,” University of Oulu, 2016.
[12] H. Ben and A. J. Ragauskas, “Comparison for the compositions of fast and slow pyrolysis oils by NMR characterization,” *Bioresour. Technol.*, vol. 147, pp. 577–584, 2013.
[13] A. Oasmaa, I. Fonts, M. R. Pelaez Samaniego, M. E. Garcia-Perez, and M. Garcia Perez, “Pyrolysis Oil Multiphase Behavior and Phase Stability: A Review,” *Energy and Fuels*, vol. 30, no. 8, pp. 6179–6200, 2016.
[14] L. Fagernäs, E. Kuoppala, K. Tiilikkala, and A. Oasmaa, “Chemical composition of birch wood slow pyrolysis products,” *Energy and Fuels*, vol. 26, no. 2, pp. 1275–1283, 2012.
[15] B. D. Elliott and T. Leader, “IEA Bioenergy Agreement Task 34 Newsletter — PyNe 38,” 2015.
[16] E. Alsbou and B. Helleur, “Accelerate aging of bio-oil from fast pyrolysis of hardwood,” *Energy and Fuels*, vol. 28, no. 5, pp. 3224–3235, 2014.


Nanta Sophonrat


Tobias Brink


Kurt Sjöblom

envigas
Contact
Envigas AB
Sankt Eriksgatan 117, 11343 Stockholm, Sweden
Website: www.envigas.com
+46 8 121 44 020
Tobias.brink@envigas.com

BRISK2 Project – opening doors worldwide for biofuels scientists

Karola Woods
European Bioenergy Research Institute (EBRI)

We all want to reduce carbon emissions. However, for this to happen, we need changes in law, in science, in industry and in society.

Horizon2020 EU-funded BRISK2 is helping change happen by enabling bioenergy scientists to advance crucial research and development in the world of biofuels. When a bioenergy scientist does not have the expertise, equipment or software at their home research institute, he or she can apply to BRISK2 and visit a centre where the expert, lab, software or machinery already exists.

BRISK2 calls this transnational access. The project started in 2017 and is made up of 15 European bodies who have agreed to work together because they share the common goal of making biofuels more economically viable and more efficiently.

The project is just over half way through its five year lifespan and is still welcoming applications from scientists all around the world who need to access facilities or expertise their home institutes do not have. So far over a hundred scientists have had the chance to visit a centre or institute in this way.

Scientists wishing transnational access need to agree the purpose of their proposed visit with their destination institute first, also checking the availability of their rig or facilities which are listed at www.brisk2.eu. They then make an application to BRISK2 via the same website.

Examples of these collaborative visits include:

1. Dr. Yeshui Zhang (see Figure 1), from University College London, who visited the Energy Department of Politecnico di Torino, Italy, to study carbon’s capabilities in sulphur removal. Her research used three different activated carbons (wood-derived biochar, sludge-derived carbon and ash) as adsorbents for biogas clean-up with the "POL3 test rig" available at POLITO. The activated carbon was used to remove sulphur compounds that are harmful to fuel cells and several tests were carried out.

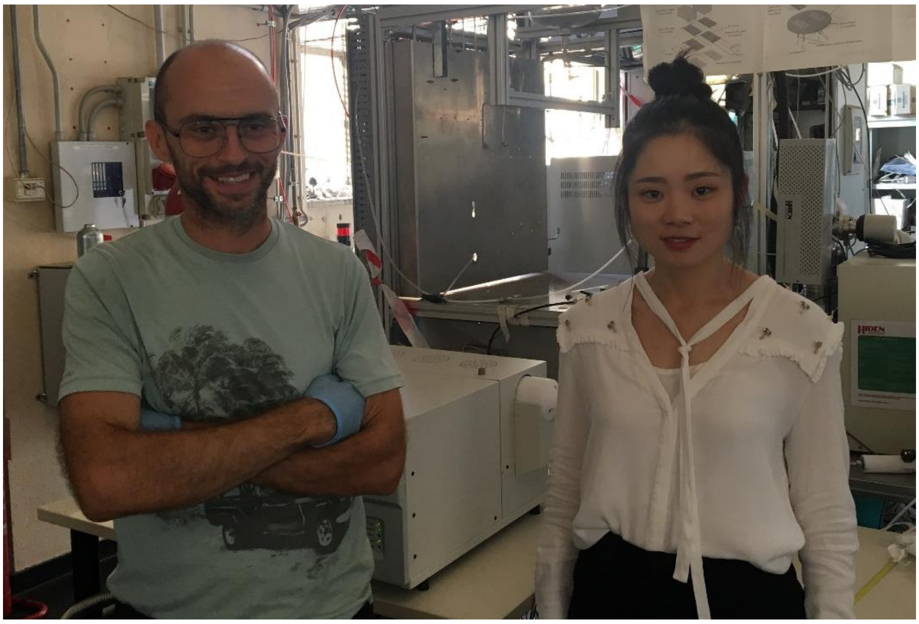


Figure 1: Dr. Davide Papurello from host institution Politecnico di Torino, Italy and Dr. Yeshui Zhang from UCL UK

2. Harsha Mysore Prabhakara (see Figure 2) from the University of Twente in the Netherlands, visited the KTH Royal Institute of Technology in Sweden, to investigate the effect of potassium carbonate promoted Hydrotalcite (HT) on biomass pyrolysis. The effect of Hydrotalcite was investigated and then Hydrotalcite was promoted by K_2CO_3.
3. Many other visits are recoded as Case Studies on the BRISK2 website.

The fifteen partners that take part in BRISK2 and who offer to share their facilities are as follows:

- Aston University, which has expertise in slow, intermediate and fast pyrolysis alongside biomass preparation, bio-oil upgrading, catalysis and hydrothermal processing;
- BEST in Austria, which works on the characterisation of new feedstocks for thermochemical and biochemical conversion processes;
- Centre for Research & Technology Hellas (CERTH) in Greece offers access to a fixed bed gasifier and fuel and residues analytical laboratory;
- ENEA, the Italian National Agency for New Technologies, Energy and Sustainable Economic Development offers pressure reactors for pre-treatment and fractionation as well as technologies for hydrogen production and separation, updraft gasification and steam reforming;
- Energy Research Centre of the Netherlands (ECN>TNO) which offers facilities for combustion, gasification, pyrolysis, tar analysis and removal alongside expertise in transitioning to sustainable energy systems;
- Graz University of Technology in Austria offers technologies in gasification, gas cleaning, tar analysis, combustion of solids and slurries and fuel cell diagnostics.
- Karlsruhe Institute of Technology (KIT) in Germany offers access equipment for hydrogenation, hydrothermal processing, fast pyrolysis and pyrolysis oil hydrodeoxygenation;
- KTH, Royal Institute of Technology in Stockholm. KTH has three installations for fast pyrolysis, hydrothermal processing, gasification product characterisation;

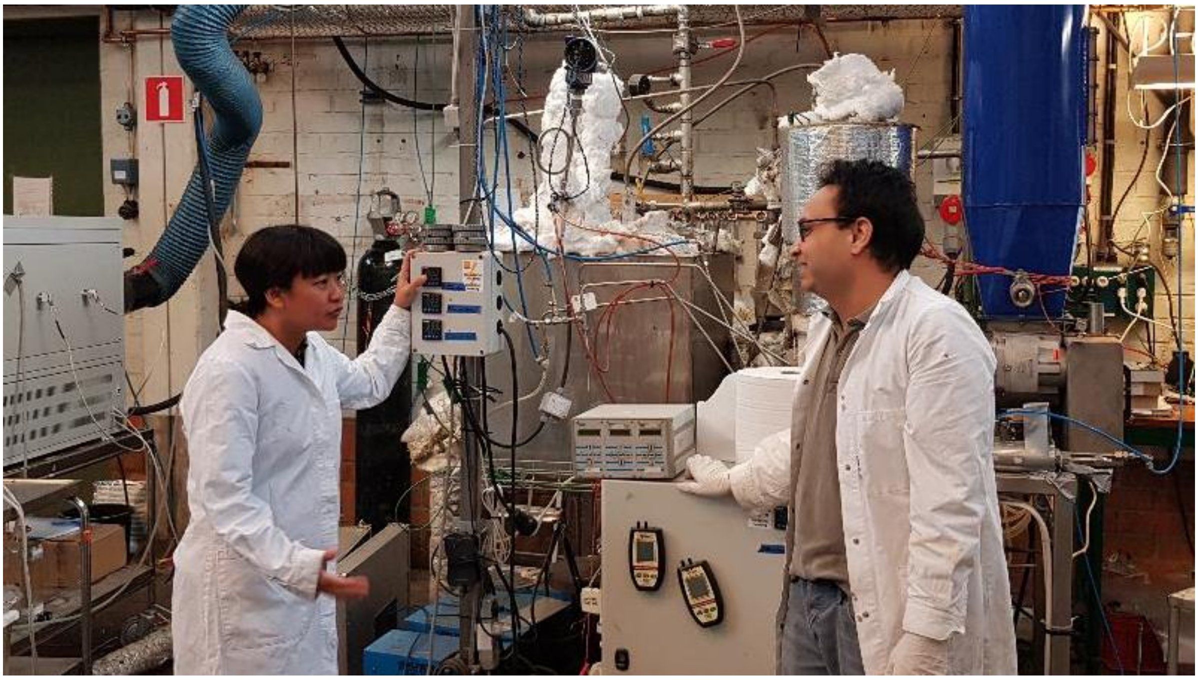


Figure 2: Harsha Mysore Prabhakara from the University of Twente in the Netherlands on his visit to KTH Royal Institute of Technology, Sweden

- National Laboratory of Energy and Geology (LNEG) in Lisbon, Portugal offers biomass and product characterisation, fermentation, product separation, pyrolysis, microalgae production and wastewater treatment;
- National Renewable Energy Center of Spain (CENER) offers facilities in biomass characterisation and preparation, torrefaction, gasification, fermentation and pre-treatment;
- Politecnico di Torino, Italy, offers access to equipment for biomass fractionation, biomass preparation, fermentation, fuel cells, combustion gasification and tar analysis;
- SINTEF in Trondheim, Norway. SINTEF offers access to biomass and product characterisation and analysis, pyrolysis and pyrolysis oil upgrading, and fermentation technologies;
- TUDelft in The Netherlands offers bioresearch scientists access to biomass characterisation, pyrolysis and gasification technologies;
- VTT Technical Research Centre of Finland offers eight installations for gasification, tar reforming, ash analysis, biomass characterisation, catalysis, combustion and pyrolysis;
- Wageningen University in the Netherlands offers access to equipment for catalysis, biomass fractionation, pre-treatment, separation processes, screw and pressure reactors and a belt filter press;

Full details on how to apply can be found on the BRISK2 website. The main requirement is that the researcher holds a science degree or the equivalent qualification in engineering.

Acknowledgments
BRISK2 is funded by the European Union's Horizon 2020 research and innovation programme under grant agreement number 731101.

Karola Woods

BRISK2
BIOFUELS RESEARCH INFRASTRUCTURE

k.woods2@aston.ac.uk

Tel: +44 (0)121 204 3945

School of Engineering & Applied Science
Aston University
Birmingham B4 7ET
England, UK

Aston University
BIRMINGHAM UK

EBRI
European Bioenergy Research Institute

Automated, Continuous Pyrolysis Reactor for Process Research and Optimization

Nicholas Schwartz
Mainstream Engineering Corporation

Mainstream Engineering Corporation has been actively pursuing pyrolysis, hydrothermal liquefaction, and gasification research for more than 10 years. Mainstream currently operates a 1 ton/day (tpd) pilot-scale pyrolysis reactor, which generates commercially available bio-oil (Agrefine™) for research and testing. Pine bio-oil from the reactor is high quality and meets all the requirements listed in ASTM D7544 (*Standard Specification for Pyrolysis Liquid Biofuel*). The 1-tpd pyrolysis reactor was developed to be highly modular and scalable for remote locations and processing opportunistic fuels, such as lignocellulosic waste biomass, mixed waste, yard waste, and agricultural residues.

Mainstream optimized the pyrolysis reactor process conditions using a continuous, bench-scale fluidized bed reactor, which was designed to process up to 1 kg/h of pine biomass. We used pine sawdust with an average particle size of 250 µm and a bulk density of 0.34 g/mL as the reactor feed and the feed rate was maintained between 0.35–0.40 lb/h. To optimize the reactor, we varied temperature between 480 °C and 500 °C and residence time (τ) between 0.5 and 0.9 seconds (Figure 1). Our testing revealed that a 0.8 s residence time at 500 °C maximized the reactor's bio-oil yield at approximately 57 % (dry mass basis). The patented reactor design minimizes secondary cracking reactions, which maximizes the yield of liquid bio-oil product.[1] Mainstream is currently manufacturing fully automated, continuous 1 kg/h pyrolysis reactors for researchers and educational institutions (Figure 2). The pyrolysis unit bridges the gap between fundamental research and real-world, large-scale systems. Mainstream's bench-scale pyrolysis unit provides an immediate method of testing new process conditions, catalysts for bio-oil upgrading, bio-oil collection methods, and testing a wide variety of feedstocks.

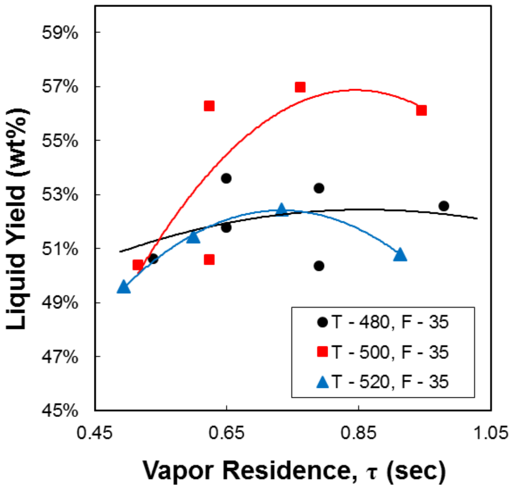


Figure 1: Optimization of the bench-scale pyrolysis unit.

The system has a touchscreen human-machine interface (HMI) to control and monitor process conditions. A two-stage auger feeder can supply a variety of feedstocks (e.g., woody biomass, municipal solid waste, plastics, etc.) to the fluidized bed reactor. Volatile and gaseous products are separated from the pyrolysis char using two cyclone separators. Following char removal, the organic vapors are condensed using a multi-condenser system, which allows for fractional collection of the bio-oil. Following the multi-condenser system, an electrostatic precipitator collects any remaining bio-oil, while the fluidizing gas (N_2) and non-condensable gases (CO_2, CO, CH_4, etc.) are vented. Technical specifications for the bench-scale pyrolysis unit and properties of the bio-oil and char produced at 500 °C can be found on our website.

Our bench-scale pyrolysis unit has been optimized for a range of reactor temperatures and residence times. Mainstream has also used the bench-scale pyrolysis unit to co-

Figure 2: Mainstream's automated, continuous bench-scale pyrolysis unit.

pyrolyze biomass and plastics (e.g., polystyrene). Co-pyrolyzing oxygen-free plastics with lignocellulosic biomass increases the quality of the bio-oil by reducing the oxygen and moisture content, which increases the overall heating value.[2] Operating at optimal conditions for pine sawdust (500 °C and τ = 0.8 s), we observed that polyethylene and polyethylene terephthalate produced either a waxy solid or a char-like solid. In contrast, pyrolyzing polystyrene produced a liquid product. Based on these observations, we co-pyrolyzed polystyrene with pine sawdust. We found that just 10% polystyrene in the feedstock reduced char yields by more than 50%. Additionally, we observed that co-pyrolyzing polystyrene with pine produced significant amounts of styrene monomer that increased when more polystyrene was incorporated in the feedstock (Figure 3A).

However, increasing polystyrene in the feedstock also led to an increase in aromatic byproducts. Specifically, at 30% polystyrene in the feedstock, ethylbenzene became a significant product that was previously observed in trace amounts (Figure 3B). In addition to the development of our automated bench-scale pyrolysis unit, Mainstream is continuing to pursue

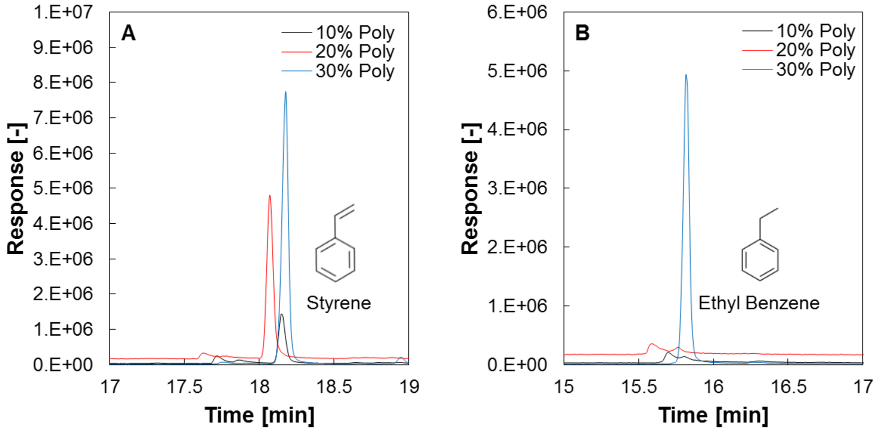


Figure 3: GC Chromatogram showing styrene and ethyl benzene yields obtained by pyrolyzing pine sawdust with varying amounts of polystyrene.

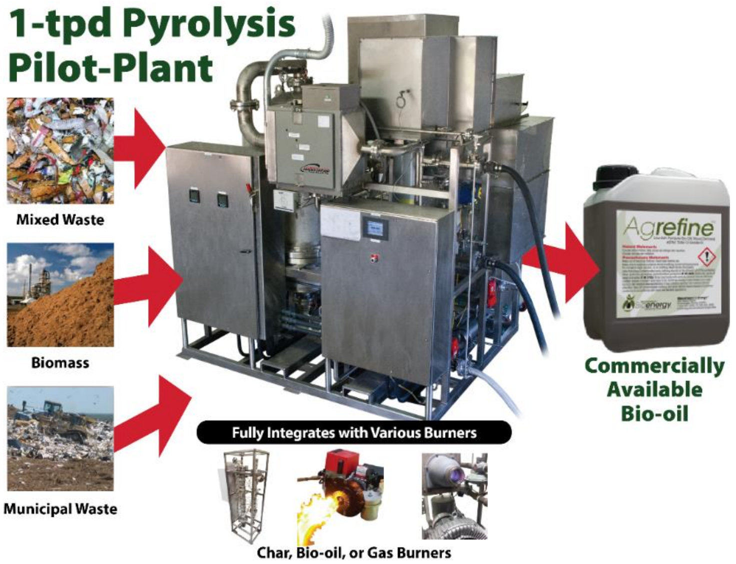


Figure 4: Mainstream's 1-tpd pyrolysis pilot-plant with bio-oil, pyrolysis char, and non-condensable gas burners used for converting byproducts to process heat.

transportable and modular solutions for pyrolysis of biomass and mixed wastes, hydrothermal liquefaction of food waste, torrefaction of municipal solid waste, and gasification for waste-to-energy applications. Mainstream has performed technoeconomic analyses for our 1-tpd pyrolysis system (Figure 4) and a 10-tpd, semi-trailer deployed pyrolysis system for converting waste materials into process heat and bio-oil.[3]

Dedicated burners have been demonstrated to convert pyrolysis products (bio-oil, pyrolysis char, and combustible gases) into process heat, which would allow the 1-tpd pyrolysis system to operate without external fuels. As Mainstream pursues production-scale pyrolysis, we are, and will continue to partner with university and government researchers to implement innovative technologies to make modular, transportable waste-to-energy systems feasible.

References

Yelvington, P.E., Zastrow, D.J., Schwartz, N.R., "Biomass Pyrolysis Reactor with Integrated Quench and Method for Converting Biomass to Liquid Bio-Oil," U.S. Patent US 10,017,700 B1, July 2018.

Schwartz, N., Blaise, M., Paulsen, A., Yelvington, P. "*Co-Pyrolysis of Plastics and Biomass Waste*" 2017 AIChE Annual Meeting, Minneapolis, MN. ISBN: 978-0-8169-1102-8. 2017.Yelvington, P. E.,

Schwartz, N. R., Zastrow, D. J., Amundsen, T.J., "*Transportable Fast-Pyrolysis Process for Distributed Conversion of Waste Biomass to Renewable Liquid Fuels*" paper presented at the 2013 AIChE Annual Meeting, San Francisco, CA, Paper No. 324743, 2013.

Nicholas Schwartz

Mainstream Bioenergy
Harvesting Power.

Mainstream Engineering Corporation
200 Yellow Place
Rockledge, FL 32955
USA
T: +1 (321) 631-3550

nschwartz@mainstream-engr.com
https://www.mainstreambioenergy.com/

Hydrothermal liquefaction within a microalgae biorefinery

Bingfeng Guo, Ursel Hornung, Nicolaus Dahmen

Karlsruhe Institute of Technology

In the last decade, microalgae have been considered as a promising feedstock for biofuel production, due to their fast growth rate and ability to accumulate various valuable biocomponents such as lipids, protein and carbohydrates. Besides, high-quality agricultural land is not required for cultivation of microalgae.

Biorefining of microalgae means to obtain biofuels, energy and high-value products along the complete value chain. Therefore, as shown in Fig 1, a complete microalgae biorefinery has been proposed at KIT with, facilitating co-production of valuable chemicals by extraction and bioenergy from the residues. For this purpose, up-stream processes regarding the microalgae cultivation, photobioreactor design, valuable components extraction have been performed in Karlsruhe Institute of Technology (KIT). For down-stream processing of microalgae biomass, hydrothermal liquefaction (HTL) is considered as one of the most suitable thermochemical techniques.

The biocrude as main product from HTL with a similar energy content to fossil petroleum can be used as renewable feedstock for upgrading to fuel components or co-processed in fossil-based refineries. The gas and the aqueous product are recyclable for further microalgae cultivation and the solid product exhibits the potential to be used as biofertilizer.

However, microalgae biofuel production via HTL is still lacking of commercial competiveness compared to fossil fuels, due to different obstacles in all process steps including algae strain selection, cultivation, harvesting, pretreatment, conversion by HTL, biocrude recovery and upgrading as well as reuse of the aqueous phase. The aim of this study is to investigate the optimization possibilities particularly in the down-stream processing via hydrothermal liquefaction as the core conversion technique within the microalgae biorefinery concept. Specifically, two key processing steps have been investigated in depth.

- Microalgae pretreatment for efficient, valuables extraction before HTL processing and it´s impact on residual biomass HTL behavior.
- Catalytic upgrading of biocrude from continuous hydrothermal liquefaction (cHTL).

The efficient extraction of valuable products from microalgae and utilization of the residual biomass for biofuel production are expected to bring economic benefits to the microalgae biorefineries. Pulsed electric field (PEF) treatment has been proposed as a promising pretreatment for microalgae wet extraction. A combination of PEF assisted valuables extraction from microalgae and HTL of the residual biomass is investigated for the first

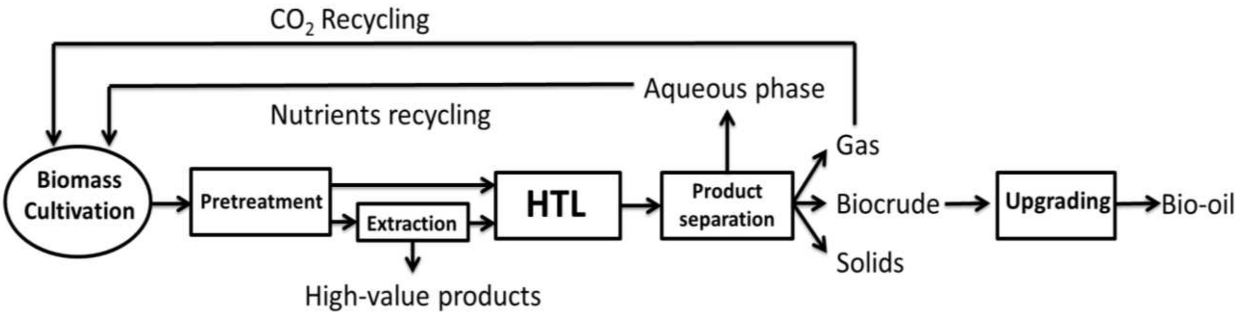


Figure 1: Simplified flowchart of microalgae biorefinery

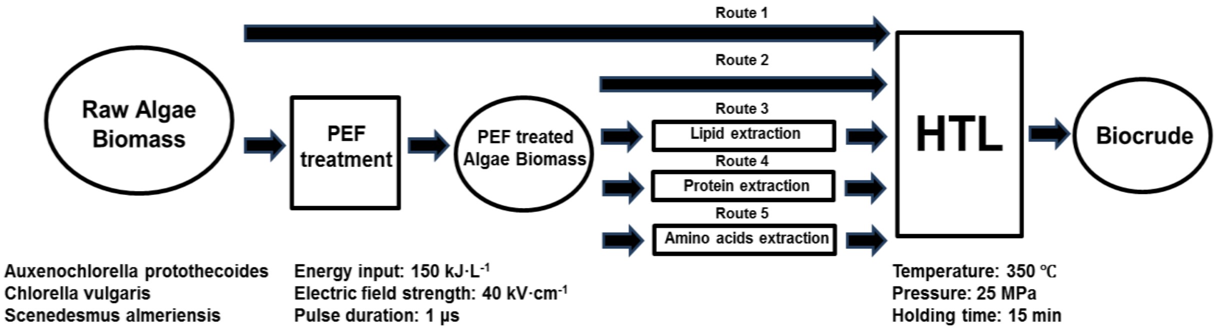


Figure 2: Simplified flow sheet of the PEF-HTL experimental procedure (Guo, Yang et al. 2019)

time. As shown in Fig 2, the microalgae strains *Auxenochlorella protothecoides*, *Chlorella vulgaris*, and *Scenedesmus almeriensis* were cultivated, harvested, treated by PEF, and then subjected to lipid extraction, protein extraction or extraction of amino acids after enzymatic protein hydrolysis, respectively. The residual biomass obtained from PEF treated and PEF-assisted valuables extraction were subjected to HTL in micro-autoclaves at a temperature of 350 °C and a pressure of 25 MPa for 15 min holding time.

For comparison, untreated microalgae were also converted. Product yields and analytical results obtained by ultimate analysis, 1H-nuclear magnetic resonance spectroscopy, Fourier-transform infrared spectroscopy, and gel permeation chromatography show that PEF alone has no significant direct influence on microalgae HTL. In this case, the harsh HTL conditions play a dominating role on the product yields and biocrude quality. However, PEF enhances lipid extraction yield from 4 wt.% to 33 wt.%. Accordingly, biocrude yield decreases from 58 wt.% to 43.2 wt.%. Besides, PEF also boosts protein extraction yield from almost zero to 41.6 wt.% of the total protein content, resulting in an increased biocrude yield of about 2 wt.%. Finally, PEF accelerates the formation of amino acids by enzymatic hydrolysis of the proteins, improving the extraction efficiency up to 150 % in the first 60 min of the extraction.
The extracted residue promises to produce 6 wt.% higher biocrude yield and better quality biocrude with lower nitrogen content.

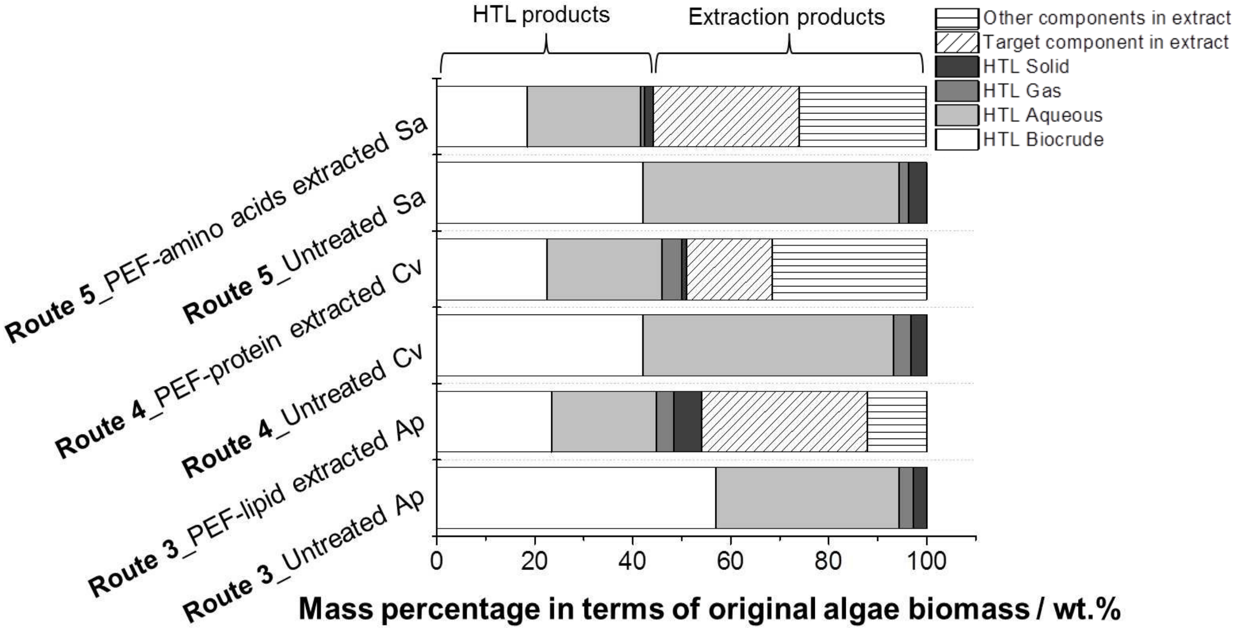


Figure 3: Overall mass balance of PEF-assisted valuables extraction and HTL products (based on the original algae biomass) compared to untreated microalgae for all investigated strains of A. protothecoides (Ap), C. vulgaris (Cv), and S. almeriensis (Sa) (Guo, Yang et al. 2019).

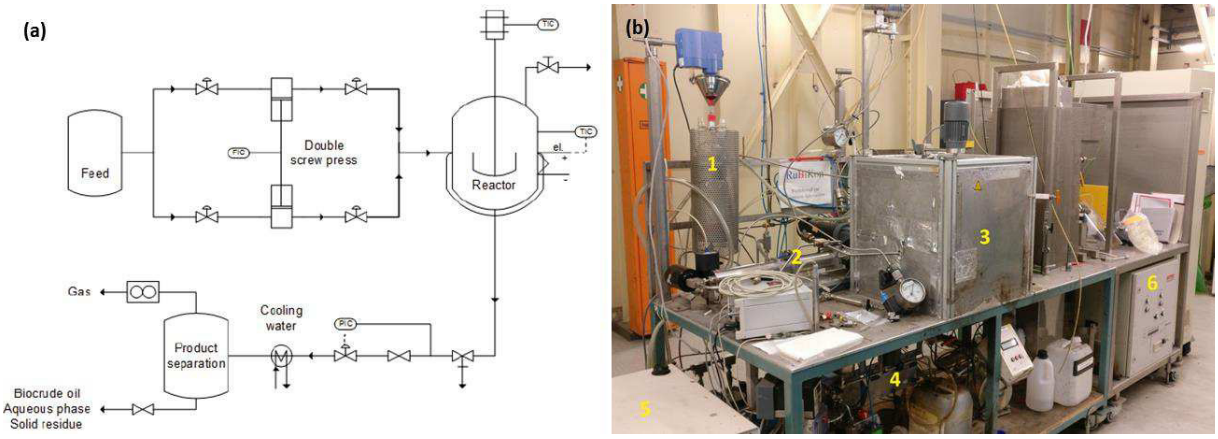
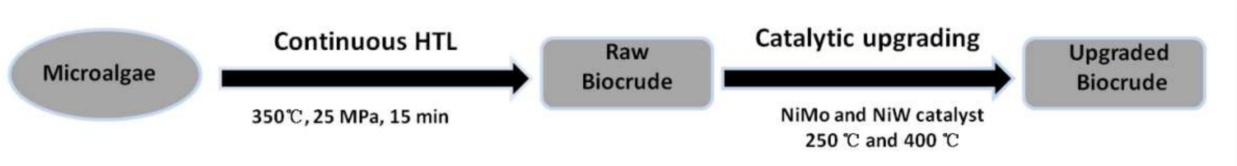


Figure 4: (a) Setup of the continuous stirring tank reactor (Barreiro, Gómez et al. 2015) (b) cHTL reactor –1 feeding system –2 double screw press –3 insulated reactor covering –4 downstream –5 cooling system –6 flow rate regulator.

For all these cases overall mass balances of PEF-assisted valuables extraction and HTL are presented in Fig.3. Biocrude obtained from HTL is usually not suited for direct fuel applications because of their high viscosity and undesired hetero-atoms like nitrogen.To make microalgae biocrude from cHTL applicable for fuel applications in combustion engines, an upgrading step is required.

Therefore, catalytic upgrading of microalgae raw biocrude produced from continuous HTL was performed. Two strains of microalgae were used for being processed in a continuous stirred tank reactor (as presented in Fig 4) at 350 °C and 24 MPa for 15 min residence time. An average of 36.2 wt.% and 31.5 wt.% biocrude yields were achieved for *Chlorella vulgaris* and *Nannochloropsis gaditana*, respectively. The obtained biocrude was then upgraded by hydrotreating using commercial $NiMo/Al_2O_3$ and NiW/Al_2O_3 catalysts at two temperatures (250 °C and 400 °C) in a batch autoclave reactor for 4 hours. Product distribution, elemental analysis, gas chromatography, gel permeation chromatography, thermogravimetric analysis and nuclear magnetic resonance spectroscopy on upgrading products indicate that upgrading by both catalysts lead to improved physicochemical fuel properties. As shown in Fig 5, during upgrading at 250 °C



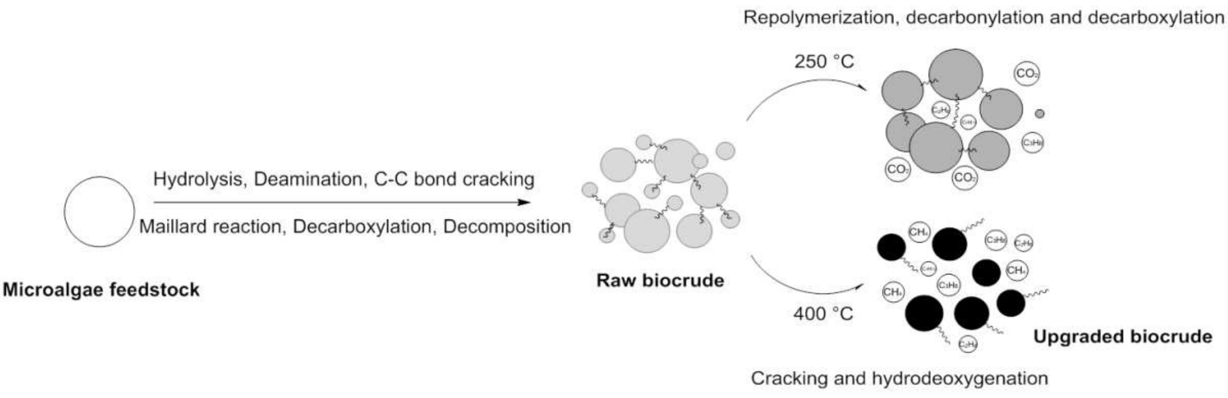


Figure 4: Simplified flowsheet of microalgae HTL and biocrude upgrading (Guo, Walter et al. 2019).

decarbonylation, decarboxylation and repolymerization are the dominant reactions while hydrodeoxygenation and cracking reactions are more promoted at 400 °C. The gasoline, kerosene and diesel oil fractions in the algae biocrude were increased from 18 wt.% to more than 30 wt.% after catalytic upgrading. Already these non-optimized results show the potential of utilizing microalgae extraction residues for biofuel production. The preliminary techno-economic evaluation showed that the production of amino acid liquid fertilizer together with biocrude leads to the most favorable economics compared to lipid, protein or only biofuel production.

Reference

Barreiro, D. L., B. R. Gómez, U. Hornung, A. Kruse and W. Prins (2015). "Hydrothermal Liquefaction of Microalgae in a Continuous Stirred-Tank Reactor." Energy & Fuels **29**(10): 6422-6432

Guo, B., V. Walter, U. Hornung and N. Dahmen (2019). "Hydrothermal liquefaction of Chlorella vulgaris and Nannochloropsis gaditana in a continuous stirred tank reactor and hydrotreating of biocrude by nickel catalysts." Fuel Processing Technology **191**: 168-180

Guo, B., B. Yang, A. Silve, S. Akaberi, D. Scherer, I. Papachristou, W. Frey, U. Hornung and N. Dahmen (2019). "Hydrothermal liquefaction of residual microalgae biomass after pulsed electric field-assisted valuables extraction." Algal Research **43**

Bingfeng Guo

Ursel Hornung

Nicolaus Dahmen

Karlsruhe Institute of Technology

bingfeng.guo@partner.kit.edu

Karlsruhe Institute of Technology (KIT)
Hermann-von-Helmholtz-Platz 1 D-76344
Eggenstein- Leopoldshafen, Germany

HTL Expert Workshop, Nov. 19, 2019, Brussels

Lasse Rosendahl
University of Aalborg, Denmark

Figure 1: Roberto Marchini, Eni Rewind, presenting

On November 19th 2019, an expert workshop entitled "Potential of Hydrothermal Liquefaction (HTL) routes for biofuel production" was held in Brussels. The workshop, co-organized by 5 Horizon 2020 projects and a Norwegian FME research center, was an enormous success in terms of participant numbers, having to capregistration at 100 attendees. The purpose of the workshop was to bring together research, commercialization and policy communities on this topic, and to set a benchmark for the current state-of-the-art, the major and most pertinent challenges to implementation, and the future potential of the technology. Moreover, an overview of demonstration projects in North America was given. Following each session, panel and audience debates were facilitated by Sonja van Renssen who managed to stay on time even though there were a lot of questions and points to be made.

Technology Status

- Process clearly works and scales well
  - Hundreds of tests on dozens of feedstocks
  - Extensively published in journals and DOE publications
- Quality of raw and upgraded HTL biocrude fully documented
- Catalytic Hydrothermal Gasification process works and provides the aqueous "cleanup" step
  - Catalyst life needs further improvement
- The remaining step to full commercialization is to show industrial reliability in 24/7 operation at operating sites

Figure 2: Dr. Doug Elliot presenting

The research front was presented by the Horizon and Norwegian projects, the commercialization front by leading industrial players and policy by the EC representatives. Furthermore, liquefaction scientist emeritus Dr. Doug Elliott gave a historical perspective. Some of the major challenges for commercialization and implementations identified and discussed during the workshop included the aqueous phase and its safe/efficient handling, efficient process implementations and corrosion-resistive materials as well as the common theme of a need for an effective carbon pricing scheme.

The workshop was very positively received, and may be the first of similar focused workshops within the field in the future.

Project and company partners presenting and organizing at the workshop

HyFlexFuel

www.hyflexfuel.eu

HeattoFuel

www.heattofuel.eu

NEXTGEN roadfuels

www.nextgenroadfuels.eu

4refinery

www.sintef.no/projectweb/4refinery

WASTE2ROAD

www.sintef.no/waste2road

BIO4 FUELS

www.nmbu.no/en/services/centers/bio4fuels

European Commission

DG RTD

https://ec.europa.eu/knowledge4policy/organisation/dg-rtd-dg-research-innovation_en

SouthernOil

http://www.sor.com.au/

https://www.eni.com/enipedia/en_IT/financial-corporate-reporting/subsidiary-associated-companies/eni-rewind.page

Reliance
Industries Limited

https://www.ril.com/

steeper ENERGY
The Renewable Oil Company™

https://steeperenergy.com/

ReNew ELP

https://www.armstrongcapital.co.uk/investment/renew-elp/

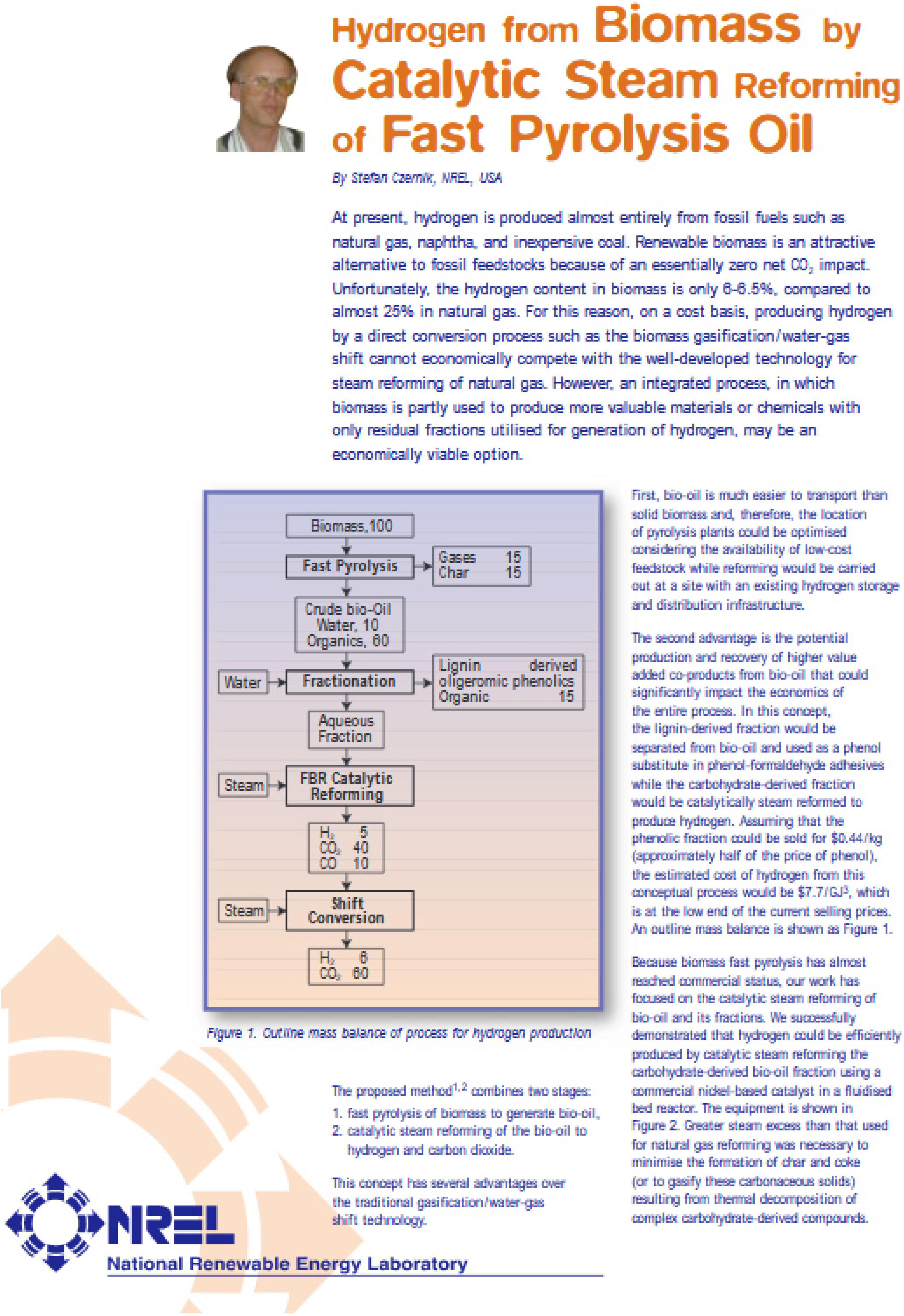
Lasse Rosendahl

AALBORG UNIVERSITY

Aalborg University
Department of Energy Technology
Pontoppidanstræde 111,
DK-9220 Aalborg
T: (+45) 9940 9263
lar@et.aau.dk

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...:



Hydrogen from Biomass by Catalytic Steam Reforming of Fast Pyrolysis Oil

By Stefan Czernik, NREL, USA

At present, hydrogen is produced almost entirely from fossil fuels such as natural gas, naphtha, and inexpensive coal. Renewable biomass is an attractive alternative to fossil feedstocks because of an essentially zero net CO_2 impact. Unfortunately, the hydrogen content in biomass is only 6-6.5%, compared to almost 25% in natural gas. For this reason, on a cost basis, producing hydrogen by a direct conversion process such as the biomass gasification/water-gas shift cannot economically compete with the well-developed technology for steam reforming of natural gas. However, an integrated process, in which biomass is partly used to produce more valuable materials or chemicals with only residual fractions utilised for generation of hydrogen, may be an economically viable option.

Figure 1. Outline mass balance of process for hydrogen production

The proposed method[1,2] combines two stages:

1. fast pyrolysis of biomass to generate bio-oil,
2. catalytic steam reforming of the bio-oil to hydrogen and carbon dioxide.

This concept has several advantages over the traditional gasification/water-gas shift technology.

First, bio-oil is much easier to transport than solid biomass and, therefore, the location of pyrolysis plants could be optimised considering the availability of low-cost feedstock while reforming would be carried out at a site with an existing hydrogen storage and distribution infrastructure.

The second advantage is the potential production and recovery of higher value added co-products from bio-oil that could significantly impact the economics of the entire process. In this concept, the lignin-derived fraction would be separated from bio-oil and used as a phenol substitute in phenol-formaldehyde adhesives while the carbohydrate-derived fraction would be catalytically steam reformed to produce hydrogen. Assuming that the phenolic fraction could be sold for $0.44/kg (approximately half of the price of phenol), the estimated cost of hydrogen from this conceptual process would be $7.7/GJ[3], which is at the low end of the current selling prices. An outline mass balance is shown as Figure 1.

Because biomass fast pyrolysis has almost reached commercial status, our work has focused on the catalytic steam reforming of bio-oil and its fractions. We successfully demonstrated that hydrogen could be efficiently produced by catalytic steam reforming the carbohydrate-derived bio-oil fraction using a commercial nickel-based catalyst in a fluidised bed reactor. The equipment is shown in Figure 2. Greater steam excess than that used for natural gas reforming was necessary to minimise the formation of char and coke (or to gasify these carbonaceous solids) resulting from thermal decomposition of complex carbohydrate-derived compounds.

You can access the full article by using the following link:
http://task34.ieabioenergy.com/wp-content/uploads/2016/10/PyNews-08.pdf

Upcoming Events

26th Feb. 2020 - 27th Feb. 2020, Helsinki, Finland

https://www.wplgroup.com/aci/event/lignocellulosic-fuel-conference-europe/


15th World Bioenergy Congress and Expo

April 20-21, 2020 Berlin, Germany

Theme: Bioenergy : A Path towards sustainable future

20th April 2020 – 21st April 2020, Berlin, Germany

https://bioenergy.insightconferences.com/


EUBCE 2020 *Transition to a Bioeconomy*

28th European Biomass Conference & Exhibition

Marseille - France | 27 - 30 April

Marseille Chanot Convention and Exhibition Centre

27th April 2020 – 30th April 2020, Marseille, France

http://www.eubce.com/

10th May 2020 - 15th May 2020, Ghent, Belgium

http://www.pyro2020.org

Members of IEA Bioenergy Task 34: 2019-2021

Canada
Benjamin Bronson
CanmetENERGY,
1 Haanel Dr
Ottawa ON, K1A 1M1
Tel: +1-613-797-3097
Benjamin.Bronson@Canada.ca

New Zealand
Paul Benett
Scion
49 Sala Street, Private Bag 3020
Rotorua 3046
Tel: +64 7 343 5601
paul.bennett@scionresearch.com

Denmark
Lasse Rosendahl
Aalborg University Denmark - Department of Energy Technology
Pontoppidanstræde 111,
DK-9220 Aalborg
T: (+45) 9940 9263
lar@et.aau.dk

Norway
Kay Toven
RISE PFI
Høgskoleringen 6b
NO-7491 Trondheim
Tel: +47 95 21 17 04
kai.toven@rise-pfi.no

Finland
Christian Lindfors
VTT Technical Research Centre
Ruukinmestarintie 2,
02330, Espoo
T: +358 40 515 0429
christian.lindfors@vtt.fi

Sweden
Linda Sandström
RISE Energy Technology Center
Industrigatan 1
941 38 Piteå
Tel: +46 10 516 911 23 23 85
linda.sandstrom@ri.se

Germany
Axel Funke (Task 34 Leader)
Karlsruhe Institute of Technology (KIT) Hermann-von-Helmholtz-Platz 1
D-76344 Eggenstein-Leopoldshafen
Tel: +49 721 608 22391
axel.funke@kit.edu

USA
Justin Billings
Pacific Northwest National Laboratory
902 Battelle Boulevard
PO Box 999, Richland,
Washington 99352
Tel: +1 509 375 5054
justin.billing@pnnl.gov

Netherland
Bert van de Beld
BTG Biomass Technology Group bv
Josink Esweg 34, 7545 PN
Tel: +31 53 486 1186
vandebeld@btgworld.com

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:

Coordinator	**PyNe/Website administration**	**Your national representative**
Axel Funke	**Alexandra Böhm**	
Tel: +49 721 608 22391	Tel: +49 721 608 28425	
axel.funke@kit.edu	alexandra.boehm@kit.edu	http://task34.ieabioenergy.com/country-members/

Task 34: Direct Thermochemical Liquefaction