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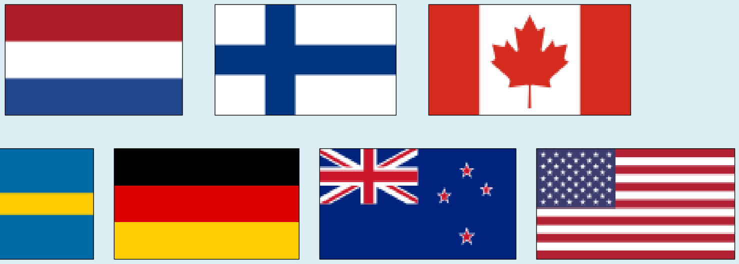
Task 34: Direct Thermochemical Liquefaction



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Celebrating Douglas C. Elliott, 2018 Linneborn Prize Winner

Douglas C. Elliott was honored this year with the prestigious Linneborn Prize for his outstanding and continuous contributions to the development of energy from biomass. He is recognized as a pioneer and leader in multiple technology areas for the conversion of biomass into energy, fuels, and chemicals.

Doug received this award at the 26th European Biomass Conference and Exhibition (EUBCE 2018) held this year in Copenhagen, Denmark in May. For more than 40 years he has advanced research and technologies towards development of fuels and chemicals from biomass through a variety of routes, not least of which is direct thermochemical liquefaction where many of us have benefited from his discoveries, collaborations, mentoring, and friendship.

Doug has been a long time member of our research community, working towards productive international collaborations that have advanced the state of technology for bioenergy.

Doug served as leader of the IEA Bioenergy Task 34 from 2009 to 2015 as well as US team lead. In addition, he contributed foundational research to and participated in many of the organizations that preceded Task 34, such as PyNe, IEABioenergy Task 21, and ThermalNet.

Douglas C. Elliott receiving the Linneborn Prize at EUBCE 2018.

He led and participated in international collaborations that helped stabilize research progress during decades when interest in thermochemical conversion went through both declines and growth due to the changing bioenergy priorities across the world. Doug's partnerships helped sustain international collaborations in order that the momentum in pyrolysis and liquefaction research would not be lost if government interest waned. This work also helped jump-start international teams who needed to restart research and build new capabilities as interest in biomass energy research grew again as being important to our energy future.

His pioneering advancements in catalytic upgrading of pyrolysis oil to form fuel range hydrocarbons continues to bear fruit today. His foundational research has benefited the research groups, applications, and commercial progress towards making liquid transportation fuels from bio-oils, furthering our shared international bioenergy goals.

Inside this Issue:

Doug Elliott: Linneborn 2018

There are also advancements in hydrothermal liquefaction that have their roots in Doug's leadership and the efforts of his teams. Additionally, he was a committed advocate of the utility of hydrothermal liquefaction and shares credit for the technical resurgence of pressurized biomass liquefaction during the last decade, which has resulted in new research and commercial endeavors and around the globe.

The Linneborn Prize was established in 1994 to honor outstanding contributions to the development of energy from biomass. The Prize was named in honor of Johannes Linneborn, who was a pioneer of wood gasification. Doug joins an elite group of winners of this Prize, that includes other colleagues and research pioneers that he worked together with to shoulder the burdens of advancing bioenergy.

For Doug, a PNNL Fellow and Battelle Distinguished Inventor, he adds this prestigious prize to his list of accomplishments that includes a number of U.S. patents, a Presidential Green Chemistry Challenge award for economic conversion of cellulosic biomass to chemicals, as well as three R&D 100 awards and two Federal Laboratory Consortium awards for technology transfer.

Expect more good things from Doug. While he is enjoying retirement, his hand and his voice are still actively guiding current work in research, development, and commercialization of renewable energy from biomass.

Congratulations Doug!

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The Effects of Pretreatment on the Products of Fast Pyrolysis of Pine Wood

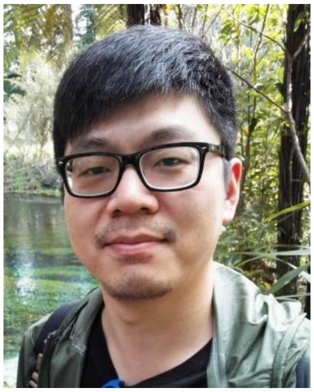

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Figure 1: Pretreated pine wood feedstocks: Top Left: Raw wood (Rwood), Top Right: Acid-leached wood (ALwood), Bottom Left: Torrefied wood (Twood), Bottom Right: Acid-leached and torrefied wood (ALTwood).

Researchers at Scion and University of Canterbury in New Zealand are collaborating on a project investigating fast pyrolysis of pretreated pine wood. Xing Xin is undertaking this study as part of his PhD in Chemical Engineering with the goal of determining whether feedstock pretreatment can improve the yield and quality of pyrolysis oils produced by fast pyrolysis.

The pretreatments investigated included acid leaching with 1 wt% acetic acid solution and/or mild torrefaction at 260 °C (Figure 1). Characterisation of the pretreated wood samples indicated that the acid leaching reduced the inorganic content of the wood by 88%, while mild torrefaction resulted in an increased lignin content, due mainly to decomposition of hemicelluloses.

Scion's 1 kg/h fluidised bed fast pyrolysis plant (1) has been operational for 3.5 years running a range of catalytic and non-catalytic fast pyrolysis experiments (Figure 2). The raw or pretreated wood chips

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Figure 2: Scion's fast pyrolysis plant

The Effects of Pretreatment on the Products of Fast Pyrolysis of Pine Wood

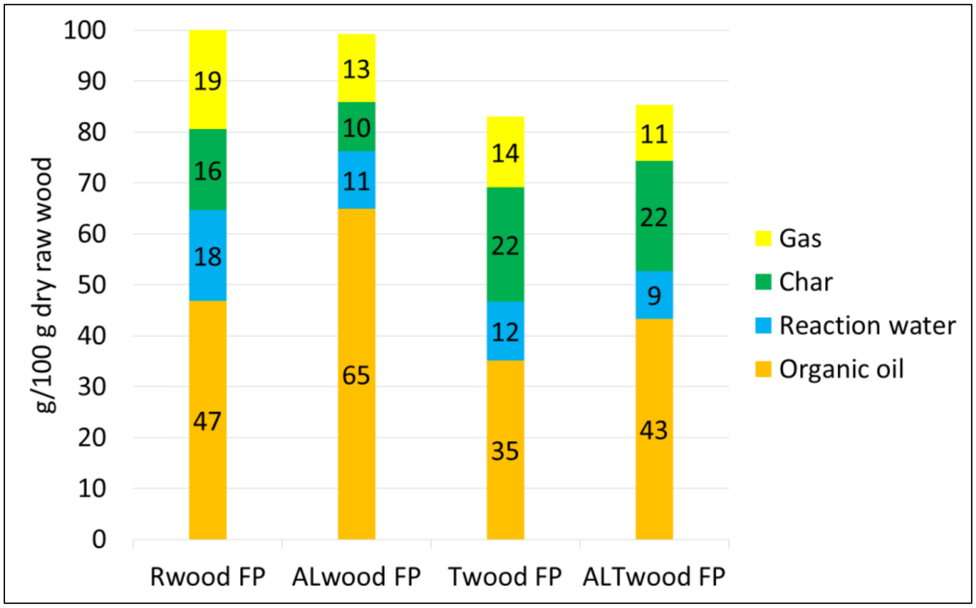

Figure 3: Product distribution for fast pyrolysis of pretreated pine wood feedstocks at 450°C.

were pyrolysed in this plant at a range of temperatures from 360 to 500°C.

The yields of the different pyrolysis products for fast pyrolysis at 450°C (corrected for mass losses on pretreatment) are given in Figure 3. The highest and lowest bio-oil yields was obtained from acid-leached wood and torrefied wood, respectively. The raw wood and acid-leached/torrefied wood gave similar bio-oil yields (Figure 3). All pretreatments resulted in reduced water production during the fast pyrolysis. The torrefied wood feedstocks gave high yields of char and all three pretreatment resulted in pyrolysis gases with lower CO_2 contents.

Elemental analysis showed the bio-oils from raw wood and acid-leached wood had very similar C, H and O contents, whereas the bio-oils from the two torrefied feedstocks had higher C and lower O content (Table 1). Solvent fractionation results revealed that acid leaching significantly increased the “sugars” content in the bio-oil as previously reported (2), while torrefaction led to a small increase in lignin-derived components in the bio-oil. The wood pretreatments also appeared to improve the stability of the pyrolysis oil to accelerated aging at 80°C.

The next stage of this study will investigate the effect these pretreatments have on catalytic fast pyrolysis. Detailed results will be published in the second half of 2018.

Table 1: Elemental content (wt.% dry basis) of pyrolysis oils from pretreated woods

Element	Roil	ALoil	Toil	ALToil
N	0.9	0.7	0.7	0.5
C	51.5	51.7	58.0	53.8
H	6.0	5.7	6.1	5.2
O	41.6	41.9	35.2	40.5

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Standardization of bio-oils produced by direct thermochemical liquefaction

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Active work on standardization of biomass and bioenergy

The ASTM standard D7544 for fast pyrolysis bio oil (FPBO) has been approved. The corresponding CEN standard EN 16900:2017 is not yet fully developed and is currently valid only for replacing light and heavy fuel oil. No standards are yet available for HTL liquids.

There are several ongoing standardisation technical committees (TC) under European Committee for Standardisation (CEN) and International Organisation for Standardisation (ISO). The figure below gives an overview of standardization committees for solid and liquid biofuels, sustainability and bio-based products. Working Group 41 (WG41) under CEN Technical Committee 19 (CEN/TC 19) “Gaseous and liquid fuels, lubricants and related products of petroleum, synthetic and biological origin” is developing standards for fast pyrolysis bio-oil (FPBO).

Standards for fast pyrolysis bio-oil are mandated

The European Commission gave mandate M525 in 2014 to produce standards:

a) A European Standard for quality specification of pyrolysis oil replacing heavy fuel oil in boilers.

b) A European Standard for quality specification of pyrolysis oil replacing light fuel oil in boilers.

c) A Technical Specification for quality specification of pyrolysis oil replacing fuel oils in stationary internal combustion engines

d) A Technical Specification for quality specification of pyrolysis oil suitable for gasification feedstock for production of syngas and synthetic biofuels

e) A Technical Specification for quality specification of pyrolysis oil suitable for mineral oil refinery co-processing

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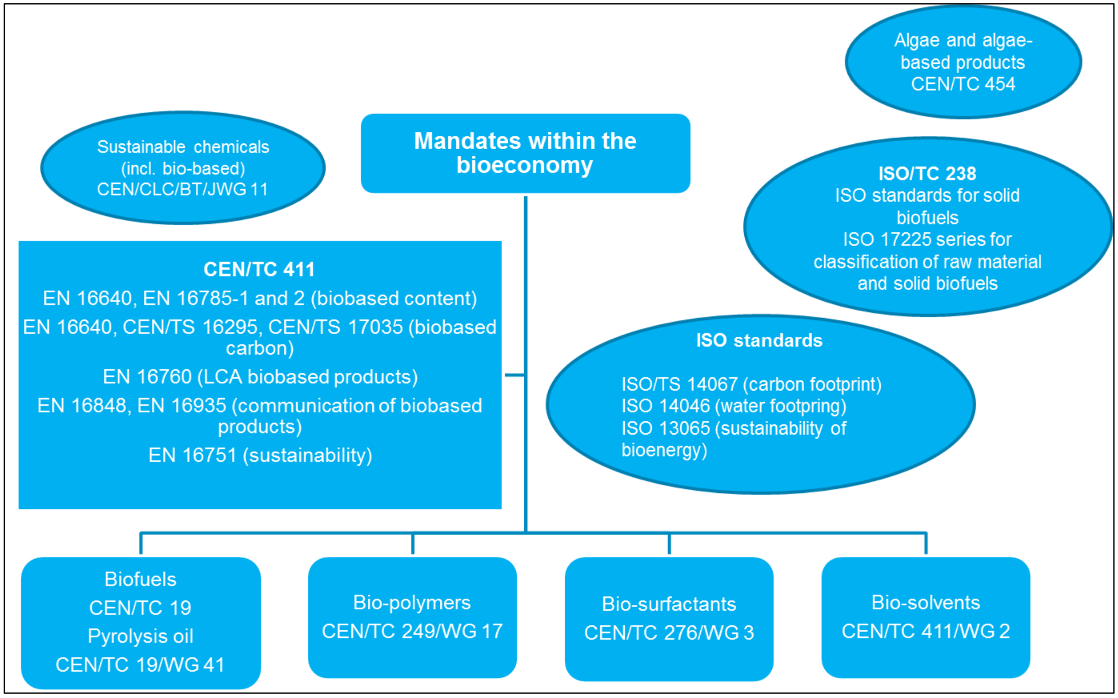

Figure 1. Standards for bio-based products including bio-oils.

Standardization of bio-oils produced by DTL...continued

In 2014, Working Group 41 started developing standard EN 16900:2017 Fast pyrolysis bio-oils for industrial boilers - Requirements and test methods for industrial boilers. This standard covers mandate areas a) and b). The standard was published in 2017 and can be purchased from national standardization institutes. The European Standard (EN 16900:2017) specifies requirements and test methods for FPBOs for boilers used at industrial scale (>1 MW thermal capacity), but not for domestic use. In addition to the quality requirements and test methods for FPBOs, further instructions on storage, sampling, and material compatibility are given. Test methods include modification of the methods recommended for FPBO. The precision data from inter-laboratory test survey (ILS) is also given in the standard. (PyNe Issue 39 pp. 3-5, Energy and Fuels 29(4) pp. 2471-2484).

Working group 41 has also prepared a technical report (CEN/TR 17103:2017) for FPBO use in stationary internal combustion engines, which covers mandate point c). This technical report was published in June 2017 and can be purchased from national standardization institutes. The original mandate was to draft a technical specification (CEN/TS), but due to the lack of data the scope was reduced to a technical report. During the work Working Group 41 encountered the following:

- FPBO is not yet commercialized for stationary internal combustion engines (ICE) and there is neither enough data on the properties of FPBO for ICE use. In addition, parameters for determining combustion properties are not fully understood. Furthermore, long-duration tests in ICE have not yet been carried out.
- Working Group 41 performed an enquiry within the leading engine manufacturers to collect data and proposals for threshold values. Most of the manufacturers did not have experience with FPBO. Several comments made by the manufacturers pointed to the need for further research and development work on several issues (e.g. type of fuel injection system, chemical resistance, effect of solids/char content of bio-oil on erosion/corrosion at fuel nozzles, and ignition properties).
- There are several important properties (e.g. combustion properties, flash point and chlorine) that should be incorporated as grade criteria, but no established test methods for fast pyrolysis bio-oil are available. Research and development is needed to develop these methods to be used for specification of FPBO for ICE.

In order to proceed towards an actual fuel quality specification for ICE, successful long-duration (minimum 500 h) tests in industrial scale engines with measured emissions and material resistance data are needed. In addition, validated test methods for level of S, Cl, and alkali metals are needed.

Several EU-funded projects on future developments in standardization

Several ongoing EU projects address standardization of liquid biofuels. The Residue2Heat project, with the objective of developing renewable residential heating with fast pyrolysis bio-oil and led by OWI (Germany), aims to develop standardized methods for FPBO for small-scale boilers (≤ 200 kW), including both fuel and boiler.

The 4REFINERY project, addressing the integration of bio-liquids in existing refinery processes and led by SINTEF Materials and Chemistry, will provide data for technical specifications concerning co-refining of bio-liquids throughout the entire value chain. This data can also be used for future standardization development. Up-to-date project data will feed into the ongoing work under TC19-WG41. The 4REFINERY project will provide data on both primary and upgraded fast pyrolysis liquids and hydrothermal liquefaction (HTL) liquids. In addition, a REACH dossier on HTL liquids will be initiated.

Different possibilities for future actions are presented separately for FPBO and boilers. Working Group 41 could propose TC 19 to initially make a preliminary work item, including, but not limited to:

- Information about markets of this kind of bio-oil
- Estimation of replacement potential of light fuel oil in small-scale boilers
- Show the need of standardization by industry developing FPBO and related equipment (currently not started, awaiting research results)
- R&D data of FPBO (properties and proposals of possible grades including also blends)
- Additional new experts for Working Group 41, appointment through national standardization bodies (NSBs)
- Development of standardized methods for FPBO separately or embedded in related mineral oil standards
- Inter-laboratory survey (ILS).

ILS should have a fuel sample matrix and strive to achieve duplicate measures (two results are obtained independently of each other).

Acknowledgements:

R2H https://www.residue2heat.eu/

4REFINERY https://www.sintef.no/projectweb/4refinery/

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New Zealand Biofuels Roadmap – An opportunity for fast pyrolysis and upgrading to produce biofuels

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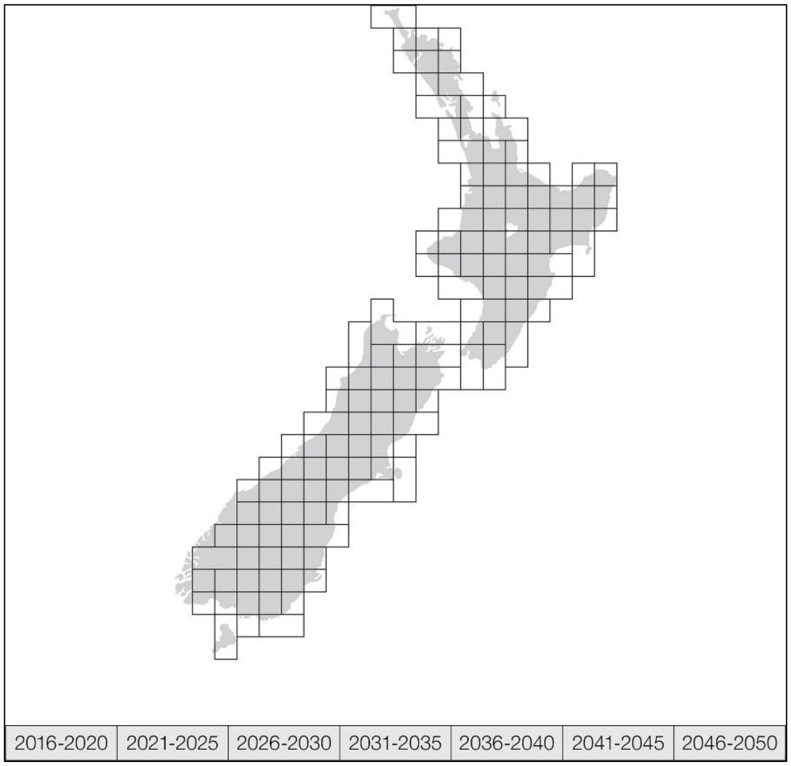

Figure 1. Cells and time horizons used in the BVCM to represent New Zealand spatially

New Zealand consumed 8.6 billion litres of liquid fuels in 2015, almost all from imported fossil fuels. Combustion of liquid fossil fuels was responsible for approximately 23% of New Zealand's domestic greenhouse gas emissions in 2015. Reducing fossil fuel use would have a big impact on lowering the country's carbon emissions and meeting the country's international commitments, such as the Paris Agreement. Biofuels could be a significant part of the solution for reducing New Zealand's greenhouse gas emissions, increasing the country's energy security, enhancing regional development, and maintaining access to international markets for goods and services. However, less than 0.1% of liquid fuels currently used in New Zealand are biofuels. Nation-wide, large-scale deployment of biofuels is a complex task involving multiple stakeholders from existing and new value chains.

New Zealand Biofuels Roadmap

The New Zealand Biofuels Roadmap study was carried out to inform and stimulate debate on the large-scale production and use of liquid biofuels in New Zealand. Specifically, this study sought to understand what a large-scale biofuels industry could look like, for example

- What currently available crops could be grown and where should they be grown?
- What technologies should be used to convert these crops to liquid fuels?
- Which liquid fuels should be targeted as a priority?
- What are the key considerations and implications in developing such an industry?

Quantitative scenario modelling, coupled with qualitative analysis, was used to 'look at the future' and create scenarios of what large scale production and use of biofuels in New Zealand might look like out to 2050 and to identify the lowest cost value chain(s) under these different scenarios.

The Bioenergy Value Chain Model

The Bioenergy Value Chain Model (BVCM) was selected to investigate feasible options over space and time. The New Zealand version of the BVCM divided the country into 50 x 50 kilometre cells, with a planning horizon of seven 5-year periods from 2016 to 2050. Once a specific 'future' or scenario was defined, the model chose from among the many potential biofuel pathways, identifying the lowest cost solution across the whole value chain and timeframe modelled. It then provided the technical, economic and environmental impacts associated

(Continued on page 8)

New Zealand Biofuels Roadmap... continued

with the end-to-end elements of a particular course of action. The model included a broad range of potential crops, feedstocks, transport modes, conversion technologies and final biofuels that might be relevant to a biofuelled New Zealand.

Fast pyrolysis and upgrading could produce large quantities of drop-in biofuels

A wide range of scenarios varying the biofuels demand from 5% to 100% were modelled with and without a main restriction: the ability to use of arable land. The option of not using arable land was studied to understand what would happen under a situation where New Zealand decides that not only is using food crops for biofuel production ethically unacceptable, but using land capable of growing food is also unacceptable.

An example scenario is where the minimum level of biofuel production was set to climb linearly from 0% in 2020 to 30% of 2015 fuel demand in 2050, and without access to arable land. While not necessarily a realistic scenario, the model was run to see what it chose to do and the issues revealed when biofuels are implemented at a relatively high level. From the multiple possibilities, the model selected the lowest cost option in which drop-in petrol (gasoline) and diesel are produced by fast pyrolysis followed by hydrodeoxygenation upgrading, using mainly forest products such as residues, fibre logs (also referred to as pulp logs), new and existing conventional forests (30 year rotation), and new energy forests (15 year rotation), see Figure 2.

A total of 30 pyrolysis plants and 13 upgrading plants are used to produce 2.3 billion litres of biofuels per year in the last period. The pyrolysis plants are located in the less populated regions of New Zealand (Figure 3), close to where the feedstock is produced. The

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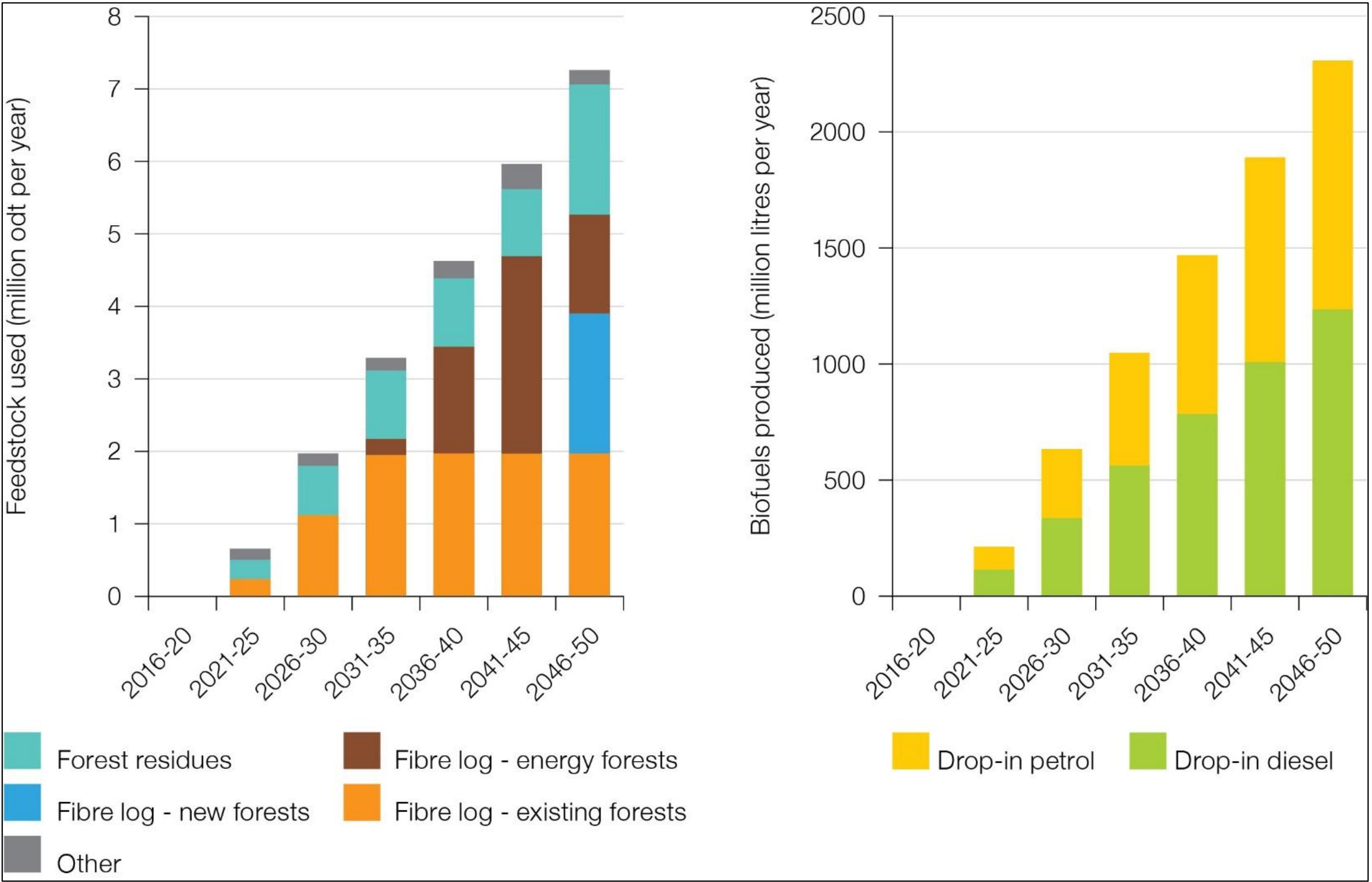

Figure 2. Feedstocks used and biofuels produced as a function of time for 30% substitution scenario when arable land cannot be used (odt: oven dried tonne)

New Zealand Biofuels Roadmap... continued

pyrolysis oil is then transported to the upgrading plants. This approach provides savings in biomass transportation costs, as well as development opportunities for regional economies.

Key findings

- Large-scale biofuel production and use within New Zealand can happen.
- Biofuels can be a large, longer-term answer to reducing New Zealand's carbon emissions, particularly for difficult-to-decarbonise sectors such as aviation, shipping and long-haul road freight.
- Large-scale biofuels opportunities must consider the whole value chain.
- Biofuel production could provide strong regional economic development opportunities.
- Drop-in biofuels from non-food feedstocks, particularly forestry grown on non-arable land, is the most attractive longer-term opportunity.
- Fast pyrolysis followed by upgrading appears to be particularly attractive for producing drop-in petrol, diesel, and marine fuels; but multiple options targeting all fuel types are being developed.
- Government policy support will be needed to kick-start large-scale biofuel production because market forces alone will not be sufficient.

More information

A technical and a summary report have been published with all the details of this study and are available at Scion's website:

http://www.scionresearch.com/nzbiofuelsroadmap

Figure 3. Locations of biofuel production during 2046-2050 for the non-arable land scenario (bubble size is proportional to the volumes produced)

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Sustainability and lifecycle assessment of pyrolysis oil production and applications

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BTG is actively developing different applications of pyrolysis oil, such as small residential heat boilers, diesel engine based CHP, co-refining, and the production of bio-based products from pyrolysis oil fractions. Along with the technical development work, the consultancy unit of BTG carries out detailed sustainability assessments and lifecycle assessments (LCA) to obtain insight in the sustainability risks and environmental performance of fast pyrolysis oil production and its applications.

Sustainability assessment

Sustainability means that the needs of the present generation are met without compromising the ability of future generations to meet their own needs. The concept of sustainability is made tangible by definition of sustainability principles, criteria and measurable indicators. If bioliquids like pyrolysis liquid and biofuels (e.g. pyrolysis oil derived diesel) are counted towards European renewable energy targets and/or receive renewable energy subsidies, they need to comply with a minimum set of European sustainability criteria as defined in the Renewable Energy Directive (RED). Verification takes place by voluntary sustainability schemes that have been recognised by the European Commission. BTG (2013) has screened the available schemes and concluded that the Roundtable on Sustainable Biomaterials (RSB), the International Sustainability and Carbon Certification (ISCC) and the Better Biomass (NTA8080) are suitable schemes for pyrolysis oil certification. Empyro received the Better Biomass certification for the production of pyrolysis oil, whereas FrieslandCampina received this certificate for the use of pyrolysis oil in their boiler.

In several projects BTG has assessed the RED greenhouse gas emissions

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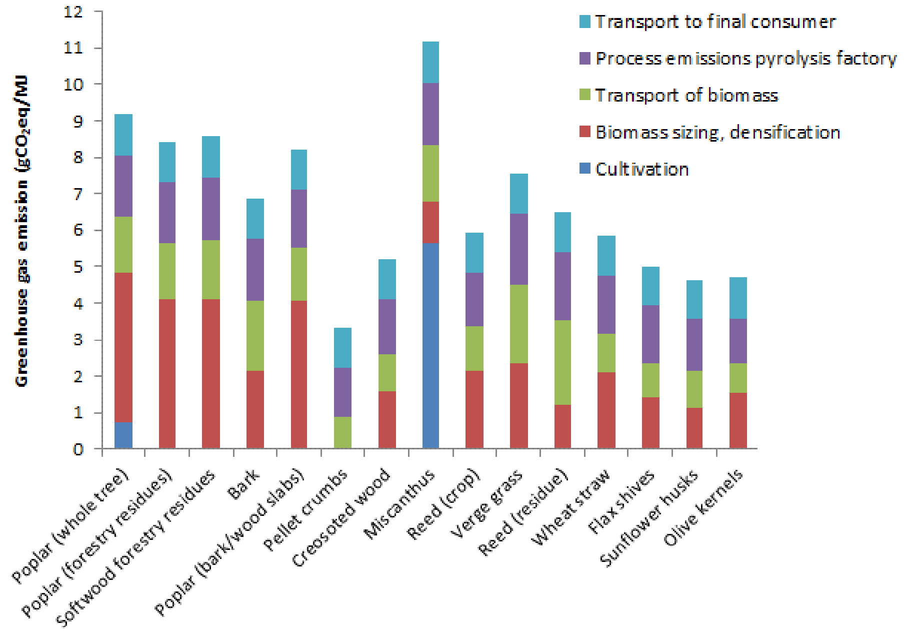

Figure 1: Greenhouse gas emissions from the production of pyrolysis oil using different feedstocks.

Sustainability and lifecycle assessment...continued

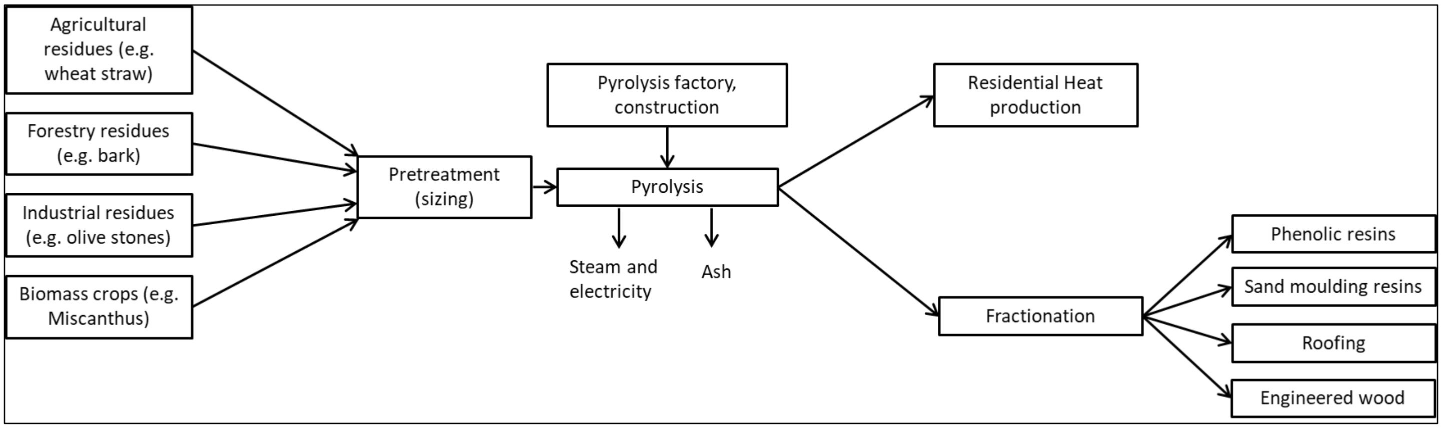

Figure 2: System boundaries of the different LCA's currently being performed by BTG

from production and transport of pyrolysis oils from different biomass feedstocks. An overview of the results is given in Fig. 1.

Cultivation becomes an important factor once artificial fertilisers are applied, like in the case of Miscanthus. Sizing includes chipping and further sizing with a hammer mill or hay buster to obtain a small particle size suitable for pyrolysis oil production. For all feedstocks, the transport distance of biomass to the pyrolysis plant, and of pyrolysis oil to the final consumer were set to 100 km. Transport emissions are relatively high for feedstocks with a low density and LHV such as reed and verge grass. Differences in moisture and ash content between feedstocks impact the pyrolysis oil yield and the amount of surplus energy that can be used for steam generation. Following the RED, energy allocation is applied to divide the upstream emissions between the pyrolysis oil and the generated steam, available for third parties.

In case the pyrolysis oil is used for heat generation, the resulting emission reduction can be estimated by the use of the fossil fuel comparator of heat production of 80 gCO2-eq/MJ, following the methodology of the Renewable Energy Directory. The emission reductions of pyrolysis oil use in heat applications are in the range of 89 to 96%, well above the current minimum required reduction of 60%, as well as the expected future threshold of 70%.

Lifecycle assessment

Lifecycle assessment (LCA) covers the creation of an inventory of flows from and to nature for a product system, and an assessment of their impacts. As an example, in the 'Residue2heat' project BTG has carried out a screening LCA for pyrolysis oil production from forestry residues, bark, wheat straw, and miscanthus followed by the use of the pyrolysis liquid in residential boilers (20-200 kW). In 'Groen Goud' maize silage is evaluated as a potential feedstocks. In 'Bio4Products' the LCA will be extended to upgrading the pyrolysis oil via a fractionation step and the use of the resulting fractions in different bio-based products. Figure 2 shows the system boundaries of the different LCAs that are currently being performed.

Assessment

ReCiPe 2016 was used as impact assessment method, which has a much broader scope than GHG emission reduction. It contains 17 midpoint impact categories that can be merged into three endpoint categories: i) damage to human health, ii) ecosystems and iii) resource availability. ReCiPe 2016 is a commonly used LCA impact assessment method. The method is described in detail by Huijbrechts et al (2016).

Fig. 3 shows the endpoint impacts of 17.8 GJ of heat – the average yearly per capita domestic energy consumption for heating and hot water within the EU – using oil, natural gas, pellets and pyrolysis oil (FPBO) produced from a number of feedstocks. The feedstock "pellet wood," a typical mixture of biomass sources used for the production of pellets, was added to enable a comparison between wood pellets and pyrolysis oil. Bioenergy has a lower impact than fossil fuel heating options with respect to the endpoints 'damage to human health' and 'damage to resources.' Concerning 'damage to ecosystems' bioenergy has a similar impact, either slightly higher or slightly lower, depending on the allocation of the biomass. However, the origin is different: where fossil heating causes damage to the ecosystems by global warming, the bioenergy options have an impact due to the occupation of land by forests and crop land. Overall, the heating options using fast pyrolysis bio-oil score better than the fossil fuel heating options.

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Sustainability and lifecycle assessment...continued

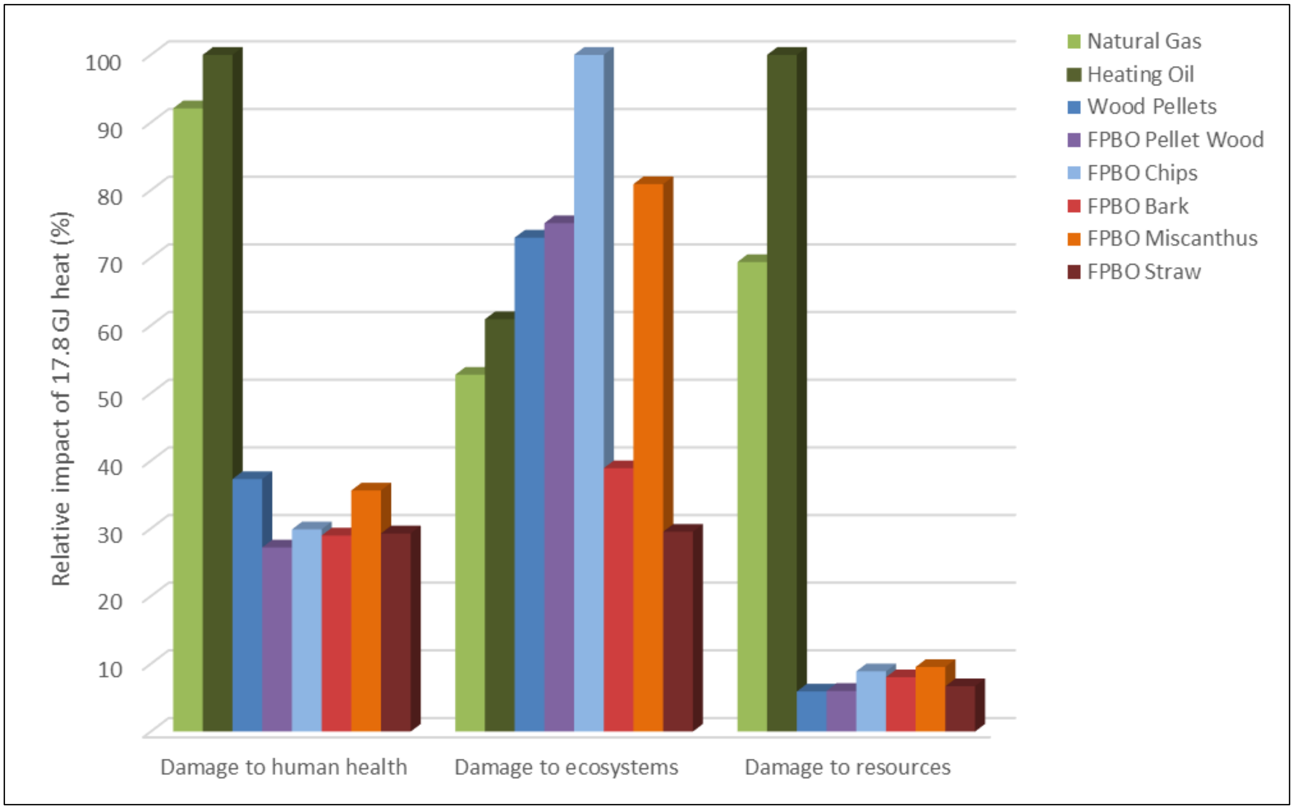

Figure 3: The Endpoint scores of the ReCiPe 2016 impact assessment for the production of 17.8 GJ heat from natural gas, heating oil, wood pellets, and pyrolysis oil from five different biomass sources.

Currently, the use of other biomass feedstocks, as well as the use of pyrolysis oil fractions, is being evaluated in projects like Groen Goud and Bio4Products. These will be full LCAs evaluating the entire value chain (cradle to grave) for a number of potential applications of pyrolysis oil fractions, such as phenolic resins, sand moulding resins, roofing material, and engineered wood. The initial results of these LCAs are promising and demonstrate the sustainability of pyrolysis oil from various biomass feedstocks in a wide range of applications.

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Boosting biomass liquefaction productivity and co-processing next generation biofuels in downstream refinery processes

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The 4REFINERY EU project aims at developing and demonstrating the production of next generation biofuels from fast pyrolysis and hydrothermal liquefaction integrated with mineral hydrocarbon refining processes. The project will make efforts to advance the primary liquefaction routes with the goal of providing an overall carbon yield of minimum 45%. Studying the entire value chain from biomass feedstock to blended fuel will provide deeper and much needed knowledge about the effect of different biomass pre-processing pathways on the final product characteristics. Project results will include a comprehensive toolbox for business case evaluations of the most promising value chains based on process deployment into existing refineries.

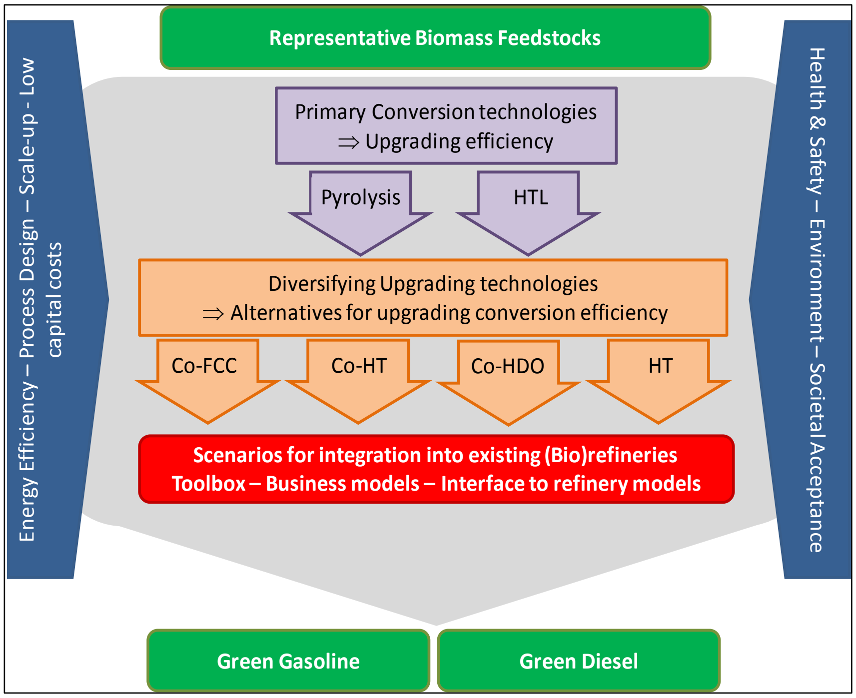

Figure 1: The 4REFINERY vision

The 4REFINERY project was kicked off in May 2017 with an ambitious goal of accelerating the co-processing of advanced biofuels in downstream mineral oil refinery processes from TRL 3-4 to TRL 4-5. The main efforts of the project will focus on increasing the organic yield from biomass liquefaction processes through various intermediate process steps, scale up testing procedures define scenarios for the best further implementation in existing refineries, and develop solutions to answer key societal and environmental challenges.

The project will focus on three major biomass feedstock types for the liquefaction pre-processing: forest residue, straw and eucalyptus. The entire value chain from harvesting biomass, via pre-processing at liquefaction plants to co-processing the biofuel in downstream processes of existing refineries will be addressed.

Specific targets of 4REFINERY

- Increase overall carbon yield from < 30 wt-% to 50 wt-%
- Feedstock cost < 80 €/t
- Fuel production cost < 900 €/t_{oil}
- Increase GHG emission savings > 80%
- Rural area job creation
- Paying farmers for wastes and residues
- Create low-risk, economic market roll-out

A variety of value chains are available for assessment, depending on for instance:

- Feedstock type, availability and location
- Pre-processing technology and plant size
- Bio-liquid upgrading technology
- Centralized and de-centralized processing units
- Standalone biomass liquefaction units or integration into existing refineries

Biomass pre-processing, or liquefaction, includes conventional fast pyrolysis and hydrothermal liquefaction. Fast pyrolysis bio oil is known to be highly unstable and unsuitable for blending with mineral hydrocarbons due to the high water content (~25-35 wt%, depending on the feedstock type and moisture) and the large amount of oxygenated compounds. A number of upgrading technologies can be applied to improve the fast pyrolysis bio-liquid quality in order to enable co-processing with mineral hydrocarbon derivatives. Upgrading technologies process the bio oil at elevated

(Continued on page 14)

4REFINERY project... continued

temperatures and pressures, often in the presence of a catalyst, in order to alter the chemical composition of the liquid. 4REFINERY will test bio-liquid upgrading through stabilization, deoxygenation and a combination of these. Downstream refinery co-processing includes:

- Co-feeding bio-liquid in the fluid catalytic cracker (FCC) together with vacuum gas oil (VGO) for gasoline production
- Feeding fast pyrolysis bio-liquid and a mixture of fast pyrolysis bio-liquid and straight run gas oil (SRGO) to the hydrotreater for gasoline/diesel production
- Feeding hydrothermal liquefaction bio-liquid and a mixture of hydrothermal liquefaction bio-liquid and straight run gas oil (SRGO) to the hydrotreater for diesel production
- Co-feeding fast pyrolysis bio-liquid with rapeseed oil to the hydro-deoxygenation process for diesel production

By utilizing inexpensive biomass and applying low capital cost technology at small scale the aim is to reduce cost for further treatment due to scaling up and simultaneously also reduce operational costs. The use of existing infrastructure facilitates rapid implementation of new developments at commercial scale and increases the competitiveness of the biofuel compared to fossil fuels.

The assessment of the different value chains within the project will include thorough techno-economic assessments, life-cycle analyses, pilot testing and scaling up of testing procedures, including risk assessment for mitigation of risks associated with scaling up processes. Addressing the whole value chain will provide important information about the relations between product properties, the quality of the renewable feedstock types, the final co-processed fuel and the associated process parameters along the value chain. The final results will be presented as a set of defined best scenarios for implementation into existing refineries. The business cases are expected to provide potential for better conversion efficiency, less greenhouse gas emissions, improved cost-competitiveness and increased understanding of underlying mechanisms. Results will also include an adaptive toolbox for assessing the implementation of biomass liquefaction technologies into existing refineries for future use.

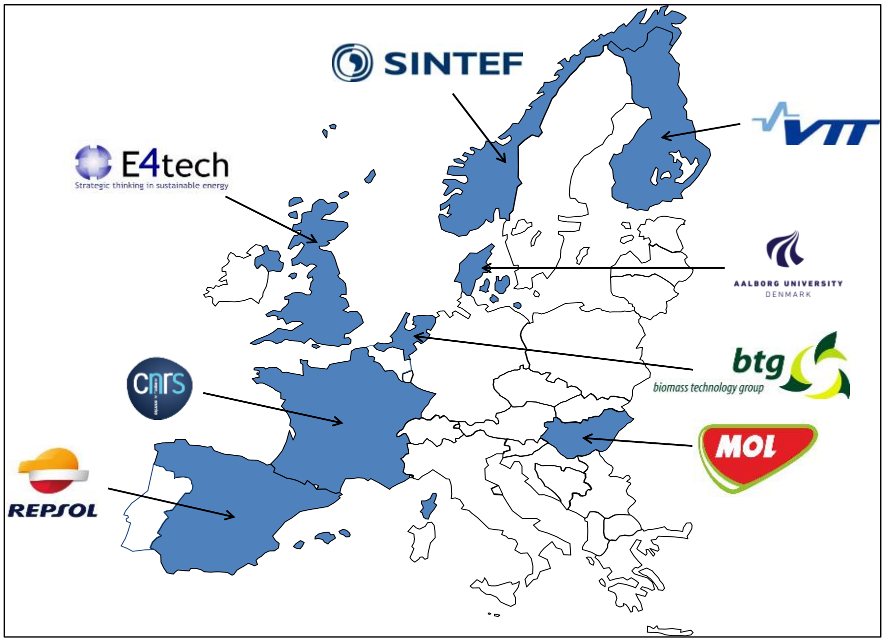

Figure 2. Partnering organizations

The project is coordinated by Sintef (Norway) and involves partners representing the entire value chain from pre-processing of bio-liquids to co-processing in refineries; VTT Technical Research Centre of Finland (Finland), Aalborg University (Denmark), E4tech (UK), BTG Biomass technology Group (The Netherlands), MOL (Hungary), CNRS (France) and Repsol (Spain).

The total project budget is 6 M€ and the project will run until May 2021.

4REFINERY has a dedicated web portal, which is updated throughout the project at:

https://www.sintef.no/projectweb/4refinery/

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A standard for carbonyl content determination in pyrolysis oil: ASTM Standard D3148-17

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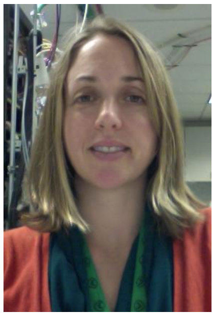

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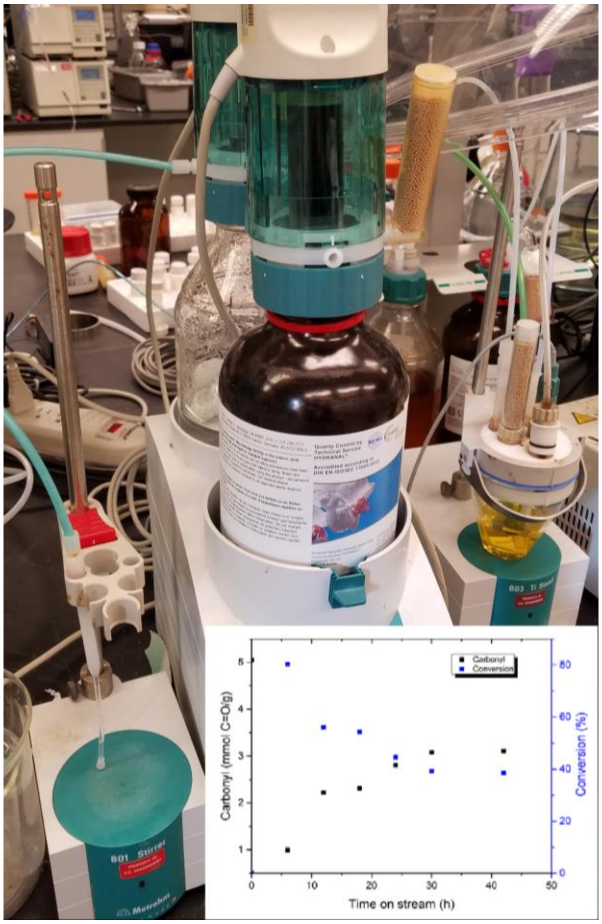

Figure 1: Carbonyl Titration System

Standardization has been defined as a framework [1] or a process [2] where stakeholders come into agreement on how a certain good or service is to be created or performed within set guidelines. This involves the development of methods or techniques to ensure consistent quality, compatibility, safety of operation, or repeatability and to facilitate the commoditization of a product [1, 2]. Consensus among producers, manufacturers, users, governments and other institutions is necessary to approve and implement meaningful standards. Some of the most well-known international organizations involve the International Organization for Standardization (ISO), ASTM International (formerly The American Society of Testing and Materials), and the European Committee for Standardization (CEN). These organizations have volunteer members from different interest groups who develop, update and approve standards for the commodities that we use.

The production of biofuels is not an exception. For years, biomass has been considered as a viable source of renewable liquid transportation fuel. In recent years, several ASTM standards specifying the incorporation of biomass-derived liquids into jet fuel such as Fischer-Tropsch (FT), highly esterified fatty acids (HEFA) or ethanol-to-jet fuels were approved [3] and incorporated in ASTM D7566, Specification for Aviation Turbine Fuel Containing Synthesized Hydrocarbons. Other jet fuel production pathways are also being tested and considered [3, 4].

Fast pyrolysis is one of the mature thermochemical conversion pathways to producing liquids from biomass [5], which include catalytic fast pyrolysis and hydrothermal liquefaction. Oasmaa et al. listed pyrolysis units around the world that have a capacity of processing 10 kg biomass/h or more [5]. Large-scale fast pyrolysis plants are situated in Canada (Ensyn) and in the Netherlands (BTG). The condensable vapors produced in the fast treatment of size-reduced biomass in the presence of inert atmosphere at temperatures between 450-550°C produce a complicated mixture of quasi-equilibrated carbohydrate and lignin degradation products upon quenching and cooling. Pyrolysis oil was initially intended as a biopower source, to be burned in burners and generators. Due to the water and oxygenates present in the liquid mixture, fast pyrolysis oil has unwanted characteristics, such as its low heating value and acidity, that need to be addressed through physical or chemical treatment [6-9]. It is thus important to understand what constitutes pyrolysis oil. Several publications have reported its chemical properties and characterization methods [10, 11]. In 1994, a report on the results of the round-robin on ultimate analysis of bio-oil was reported [12]. Several round-robin studies on bio-oil physical characteristics such as pH and viscosity were conducted and contributed to the development of some of the

(Continued on page 16)

A standard for carbonyl content…continued

Table 1 Existing Standards for Pyrolysis Oils

Standard Number	*Standard Name*	*Brief Description*
ASTM D7579-09	*Standard Test Method for Pyrolysis Solids Content in Pyrolysis Liquids by Filtration of Solids in Methanol*	*Filtration procedure to determine the solids content of pyrolysis oil using solvent mixture consisting of 50:50 methanol and dichloromethane*
ASTM D7544-12	*Standard Specification for Pyrolysis Liquid Biofuel*	*Specification of bio-oil grades for use in various types of fuel-burning equipment at varied operating conditions*
EN 16900:2017	*Fast Pyrolysis bio-oils for industrial boilersRequirement and test methods.*	*Specification of two grades of pyrolysis oil for industrial boiler use*
CEN/TR 17103:2017	*Fast pyrolysis bio-oil for stationary international combustion engines - Quality determination*	*Description of key fast pyrolysis bio-oil properties and their importance to the fuel quality for stationary internal combustion engines, including diesel engines and gas turbines*
ASTM E3146-17	*Standard Test Method for Determination of Carbonyls in Pyrolysis Bio-Oils by Potentiometric Titration*	*Titration procedure for the determination of carbonyl content in bio-oils*

standards in Table 1 [12-15]. Early efforts of defining pyrolysis oil grades were reported by Diebold, et al. [16].

As a source of liquid transportation fuel, pyrolysis oil needs to be converted into hydrocarbons [7]. This process entails high temperature and high pressure catalytic hydroprocessing in the presence of hydrogen. Direct application of the technology based on traditional petroleum hydroprocessing is impossible for long-term operation. This is because pyrolysis oil contains functional groups that are thermochemically unstable, causing the formation of carbon residues that eventually plug the reactor and makes low temperature stabilization necessary. Multiple step processing has been proposed at PNNL. A stabilization step at temperatures between 140-160°C using Ru-based catalysts (carbon or titania) was found to enable long-term processing of pyrolysis oil sourced from pine and forest residues produced by the Technical Research Centre of Finland (VTT) [8, 17, 18]. Previously, without the low temperature step, the reactor would plug within 50 hours of operation. Hydrogenation of sugars, removal of carbonyls and some aromatics were found to accompany the effect of active hydrogenation catalysts. Following the trend by NMR and carbonyl measurement, signals from sugars and aldehydes appear as the catalyst deactivates [17, 18]. Carbonyl measurement became a metric of catalyst activity and pyrolysis oil processability. Potentiometric titrations for carbonyl quantification based on the Nicolaides [19, 20] and Faix [21] methods were tested in a round-robin participated in by several research institutions [22]. This activity is part of a US DOE BETO-funded project that aims to develop characterization methods for bio-oil and subsequently submitting them for standardization. Analytical techniques are chosen both for easy measurement in a commercial testing laboratory setting as well as more involved techniques that allow for better characterization to inform catalyst and process development. The project is a joint effort of three national laboratories: National Renewable Energy Laboratory (NREL), Pacific Northwest National Laboratory (PNNL) and Oak Ridge National Laboratory (ORNL). In the round-robin study, the Nicolaides method reported higher variability compared to the Faix method (see Table 2). Both methods rely on the reaction of hydroxylamine hydrochloride with the carbonyl bond, forming an oxime, with a concomitant release of hydrochloric acid and water. The Nicolaides method reacts the solution containing the acid with pyridine at room temperature to form a conjugated acid that is then titrated with a known amount of base (0.1N NaOH) as a first endpoint, followed by another endpoint that measures excess hydroxylamine hydrochloride. An excess of the hydroxylamine hydrochloride is needed to force the reaction to completion and long stirring times (at least 12 hours) are needed. On the other hand, the modified Faix method elevates the reaction temperature to 80°C and requires only 2 hours of stirring time. Instead of pyridine, triethanolamine is added to quench the liberated hydrochloric acid, and the excess triethanolamine is titrated. The increased temperature treatment of the Faix method allows for a more complete carbonyl conversion at a shorter time and removes the need for a secondary titration [21, 23]. Considering the shorter time needed for the analysis and the smaller

Table 2 Results of the carbonyl content determination between Nicolaides and Faix methods. Adapted from ref.

	Sample A		Sample B	
	Nicolaides	Faix	Nicolaides	Faix
Average carbonyl content, mmol C=O/g bio-oil	3.10	3.84	3.14	3.89
% Average RSD	8.5	4.7	9.1	6.1

(Continued on page 17)

A standard for carbonyl content...continued

variability, the standard proposed to ASTM was based on the modified Faix method. In 2017, an official ASTM method was approved by ASTM's E48 committee. The proposed method became the ASTM E3146-17 standard, Standard Test Method for Determination of Carbonyls in Pyrolysis Bio-Oils by Potentiometric Titration. An official ASTM inter-laboratory study (ILS) is required to be accomplished within 5 years of passing a standard method. As such, an ILS with multiple samples (fast pyrolysis, catalytic fast pyrolysis and catalytically upgraded oils) is planned to be rolled out by 2020 to measure the inter-laboratory repeatability of the method and its applicability to other biomass-derived liquids aside from fast pyrolysis oil.

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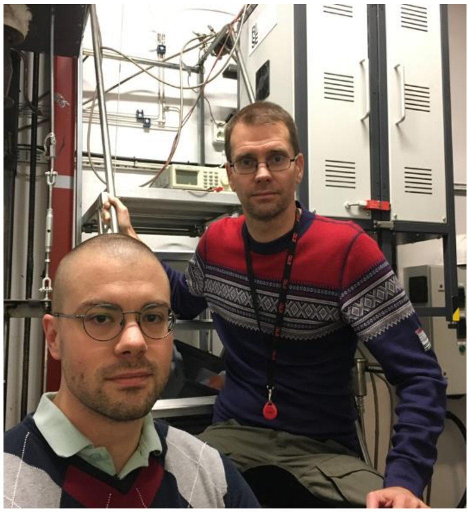
Pyrolysis Oil - a Feedstock for Carbon Black Production



Henrik Wiinikka (in the back) and **Pal Toth** (in the front) next to the drop tube furnace producing the GCB
RISE Energy Technology Center

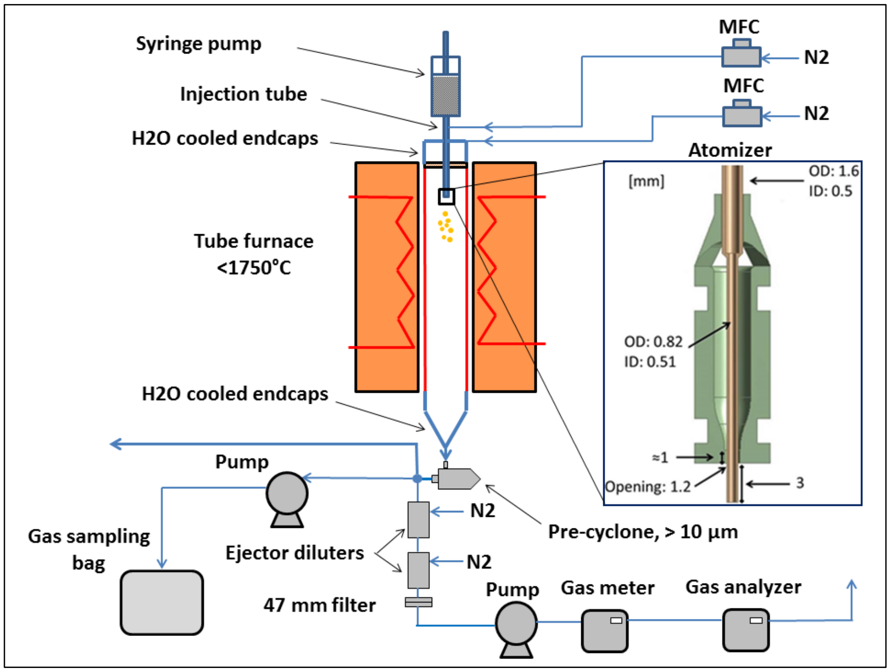


Figure 1: A schematic sketch of the experimental setup.

Carbon Black (CB) is a man-made, paracrystalline nanocarbon particle. CB is one of the top 50 industrial chemicals (C.A.S no 1333-86-4) with a global production of ~11 million tons [1] made today from fossil-based feedstocks. The majority of CB is used as filler in and reinforcement's agents in tires and other rubber product. The remaining finds use as an essential ingredient in hundreds of different applications, such as pigment in printer inks, coatings, and plastics as well as in various electronic applications [2]. In a recent paper [3], we show that biomass pyrolysis oil can be used as feedstock for production of renewable "Green Carbon Black" (GCB) in a continuous high-temperature spray process that is flexible and scalable.

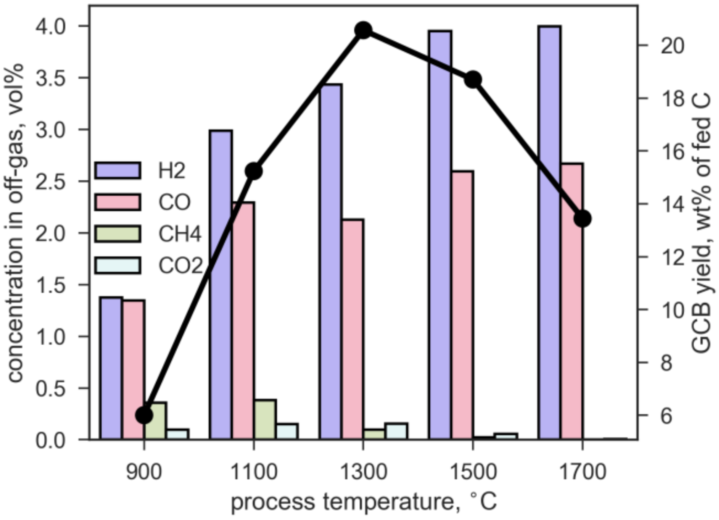


Fig 2: GCB yield and off-gas composition in terms of major constituents (H_2O was not measured)

GCB production and characterization

The GCB was produced in a high temperature (900-1700°C) custom-made reactor where pyrolysis oil made from pine (80 wt%) and spruce (20 wt%) in a cyclone pyrolyzer [4] was injected as small droplets into the hot atmosphere inside the reactor (see **Fig. 1**). The GCB nanoparticles were collected on a filter and thereafter characterized with respect to particle size, micro- and nanostructure using a High Resolution Transmission Electron Microscope (HRTEM). The structural analysis from the GCB was compared with four types of commercial-grade CB, fine-disperse (N375), medium-disperse (N550), coarse thermal black (N990), and CB from pyrolysis of used tires (recycled).

Yield and nanostructure of the GCB

The GCB yield on a fed carbon basis together with the measured gas composition is presented in **Fig. 2**. The maximum yield was obtained at a process temperature of 1300°C. From a structural point of view the reactor temperature must exceed 1100°C otherwise the produced nanoparticles cannot be considered as CB. Visual inspection of typical HRTEM image of the produced GCB (see **Fig. 3**) confirmed the presence of micro- and nanostructure typical to CB. As expected, the process temperature does not only affect the yield of the GCB but also the structural properties of the produced nanoparticles. Results from the quantification of the structural parameters of GCB and the reference CB samples using advanced HRTEM image analysis techniques

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Pyrolysis Oil - a Feedstock for Carbon Black Production

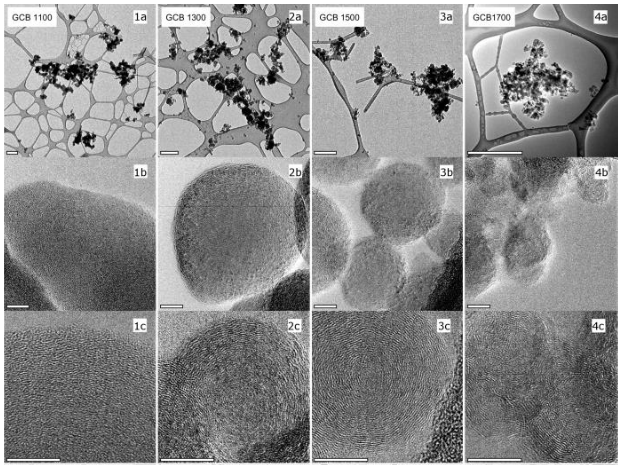

Figure 3: Example of HRTEM micrographs obtained from different GCB samples. Scale bars in the top row indicate 500 nm. Scale bars elsewhere indicate 10 nm.

[5,6] are presented in **Fig 4** were similar to those of CB; however, interlaying spacing, a parameter that is indicative to the compaction of the carbon structure, only showed satisfactory similarity at process temperatures exceeding 1300°C. The process temperature affected the size of the agglomerates, probably due to surface oxidation by CO_2 and H_2O molecules at the highest process temperatures. Many of the structural parameters of GCB

Outlook for the future

If upscaling of the demonstrated process can be shown to be possible and GCB is proven compatible with CB as a chemical product, pyrolysis oil-based CB could not only reduce the carbon footprint of the CB industry, but also introduce a renewable-based CB as an added-value product in bio-refineries as well.

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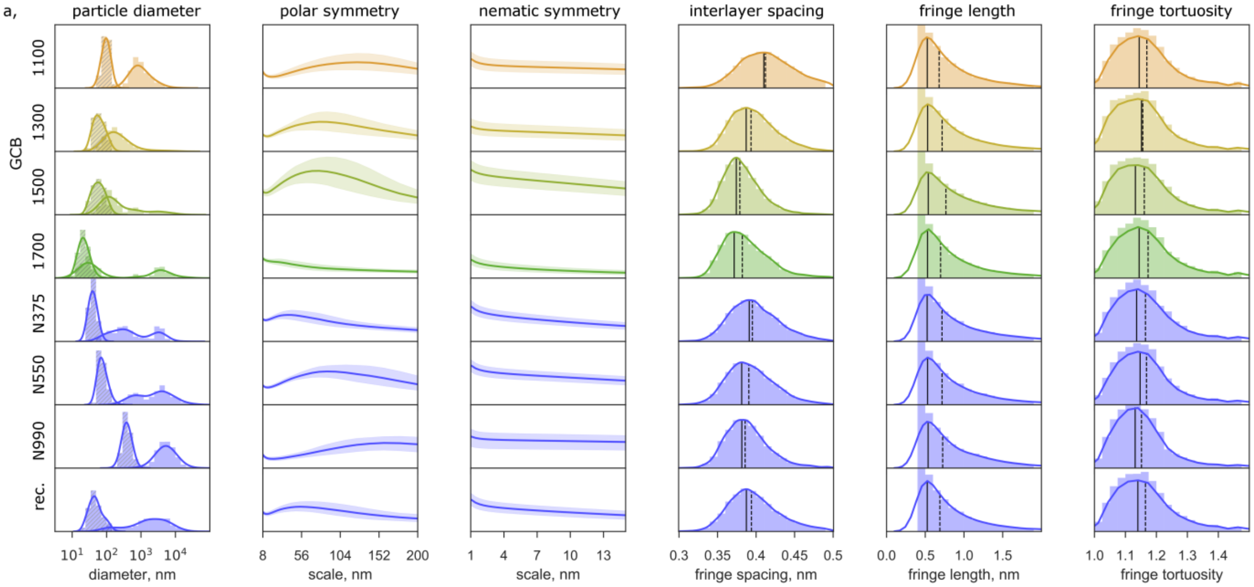

Figure 4. Structural properties of the GCB and reference CB samples, extracted from HRTEM images. (a) A comparison of the distribution of structural properties across the various samples. Hashed bars indicate agglomerate size distribution in the case of particle diameter distributions. Error bands on symmetry profiles correspond to 95%

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Task 34: Direct Thermochemical Liquefaction