Direct Thermochemical Liquefaction

Characteristics, processes and technologies

IEA Bioenergy: Task 34

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INTRODUCTION

It is the fundamental concept of a bioeconomy to replace fossil based production pathways by using biomass that can be regrown, be it dedicated crops or residues e.g. from food production. The variety of commodities used in everyday life demands for a transformation of these biomass resources in one or the other way. With very few exceptions, all conversion processes for biomass produce solid, liquid, and gaseous products in varying yields and composition. Liquefaction could be generally defined as conversion process with the aim to produce liquid products (as primary product and/or with the highest yield).

Liquid commodities are visible to the customer primarily in the form of transportation and heating fuels, but they are also of utmost importance to many industrial processes. Liquids are easy to handle and store; many basic chemicals for the production of everyday goods are liquids, too. Due to these reasons, conversion of biomass to liquid products is often associated with a higher value addition than the analogue processes of carbonization (for solid products) and gasification (for gaseous products).

The commodities used in a bioeconomy need to be derived from a vast variety of feedstocks. It is obvious that there will be no single biomass source that is capable of mobilizing the large mass potential to supply a cross-regional economy; especially with large scale, industrial production. Instead, there are diverse sources of biomass feedstocks even at regional level. Different woods and perennial energy crops can be grown in a sustainable manner and could represent a fairly homogeneous feedstock for a local conversion unit. Alternatively, it is desirable to use by-products and residues from agriculture and forestry to avoid land use competition. The arising challenge is to enable refining of such a multitude of sometimes complicated feedstocks (heterogeneity, ash content, water content, low bulk density etc) to a limited and well-defined range of commodities such as the fuels and chemicals used today.
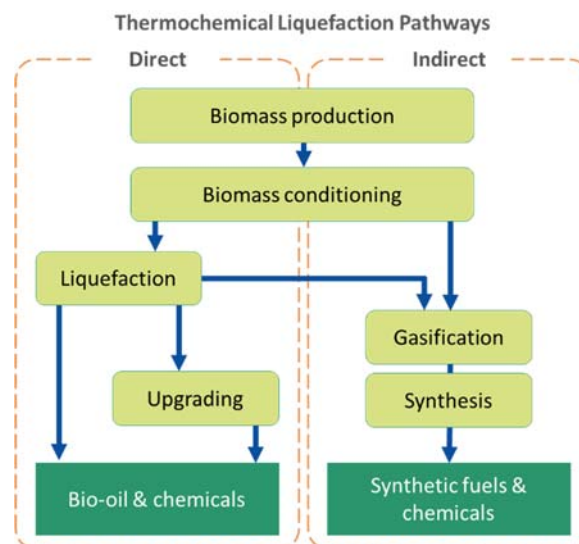

Figure 1: Difference between direct liquefaction (scope of IEA Bioenergy Task 34) and indirect liquefaction via gasification (scope of IEA Bioenergy Task 33)[1].

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[1] For more information on different IEA Bioenergy Tasks please visit **www.ieabioenergy.com**

Biomass Depolymerization Principles

The three major components of all plants are typically classified as cellulose, hemicellulose, and lignin. They all represent biopolymers and can be considered macromolecules. Cellulose is the only major building block of plants with one specific chemical formula across biomass species. In contrast to cellulose, hemicellulose and lignin exhibit a highly diverse structure. They rather stand for a group of chemically related biopolymers which are made of similar monomer building blocks.

Cellulose is a linear polysaccharide made of monomeric D-glucose units and typically forms thread-like crystalline fibers. Hemicellulose is also a polysaccharide; it contains a variety of five and six ring sugars and is branched in contrast to cellulose. Hemicellulose is often referred to as the linkage between cellulose and lignin in the plant. Lignin provides the elasticity and mechanical strength to the plants. It is also a biopolymer but – different to cellulose and hemicellulose – it is composed of phenyl propanoids with a varying amount of methoxyl groups.

The conversion of solid biomass to liquid products requires destruction of the macromolecules that make up the feedstock. Most commonly, short chain molecules are targeted among the variety of products that are obtained. Biomass can be converted to liquids either by direct liquefaction, i.e. producing bio-oil in a one step process, or by indirect liquefaction (see Figure 1). In the latter case macromolecules are broken down by gasification to (primarily) gaseous products consisting of essentially CO and H2. These two compounds can then be used for a variety of catalytic synthesis reactions as e.g. Fischer-Tropsch or methanol synthesis. This multistep process (chain) represents an increased effort but is also capable of producing well defined and tailor made products. In the following, only direct liquefaction will be discussed, which can also be viewed as pre-treatment step to enable indirect liquefaction.

There are several pathways to achieve depolymerisation of the biomass macromolecules, which is a prerequisite to achieve liquefaction (see Figure 2). In nature, biomass is being decomposed by microorganisms effectively and some of these mechanisms can be exploited in biotechnological processes. This biochemical depolymerisation takes place at comparably low temperatures and is enabled by enzymes that primarily target the polysaccharides contained in biomass to produce carbohydrates. These carbohydrates can then be further metabolized to yield specific chemical substances such as e.g. ethanol. Biochemical depolymerisation of lignin is currently exploited only to a limited extent in technical processes.
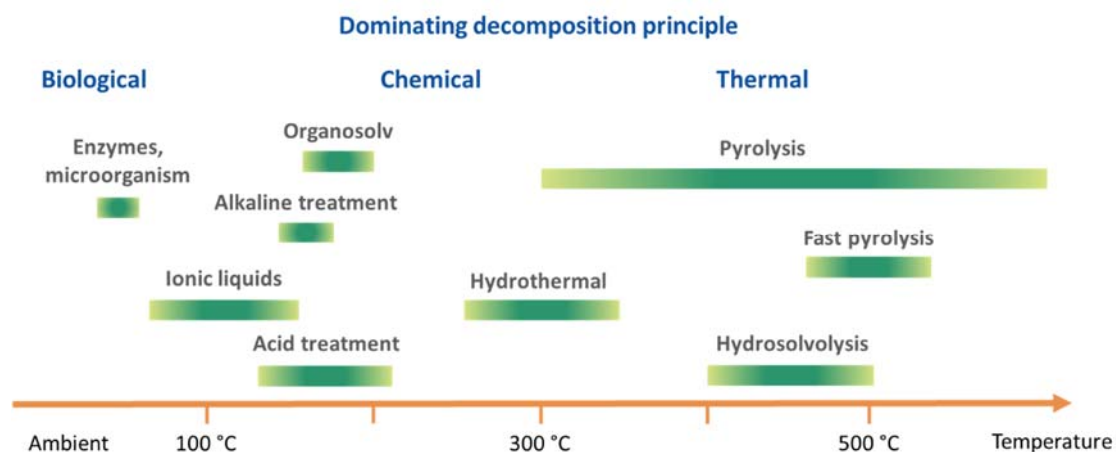

Figure 2: Schematic of different degradation strategies for biomass macromolecules.

Table 1: Comparison of different DTL process characteristics

	Fast Pyrolysis	HTL	Solvolysis
Temperature	Around 500 °C	250-370 °C	300-450 °C
Pressure	Atmospheric	Up to 20 MPa	Up to 20 MPa
Residence time	Seconds	Minutes	Minutes
Reaction medium	Produced gases (primarily CO2, CO, CH4, and H2)	Water (sometimes catalysts added, e.g. K2CO3 or Na2CO3)	E.g. oils, ethylene glycol, water-phenol, bio-oil
Bio-oil yield (wood)	60-70%	40-50%	30-50%

Biomass macromolecules can also be solvated in a variety of chemical processes; these operate in a medium temperature range. Only little alteration of the macromolecules chemical nature takes place during processes such as alkaline treatment (e.g. the KRAFT pulping process) and application of organic solvents (e.g. organosolv). Typically, the primary target is to recover fibrous cellulose for paper production in industrial scale while lignin is solubilized and only partially decomposed. With increase in processing temperature, depolymerisation by thermal degradation becomes more and more important until the process is classified as thermochemical conversion. The reaction medium applied during processing may improve depolymerisation, e.g. liquid water will induce efficient hydrolysis of biomass components even in a medium temperature range. There is no precise temperature criterion for classification as thermochemical biomass conversion; typically hydrothermal conversion is included and these processes can already be conducted at temperatures around 250 °C (see Figure 2).

Thermochemical conversion enables complete degradation of all biomass macromolecules in technical processes, i.e. cellulose, hemicellulose, and lignin. Hemicellulose is the biopolymer with the lowest stability towards thermal degradation; lignin in contrast degrades at higher temperatures over a broad temperature range. Thermochemical conversion produces a large variety of fragments from the initial biopolymers and the resulting bio-oil is thus a multi-component mixture of chemically different molecules. This process intrinsically avoids the use of chemicals and is viewed robust enough to decompose a large variety of different feedstocks since thermal degradation is less feedstock specific than chemical and biochemical conversion. It is the basic principle of direct thermochemical liquefaction (DTL) and will be covered in more detail in the following.

PROCESSES FOR DIRECT THERMOCHEMICAL LIQUEFACTION

Thermochemical depolymerisation of biomass macromolecules produces intermediates that are reactive. Consecutive reactions of these intermediates further change their chemical nature and/or lead to competing re-polymerization reactions to form long chain molecules again. It is therefore not only important to consider depolymerisation (often referred to as primary reactions) but also to realize differences in the pathways of consecutive reactions (often referred to as secondary reactions). The process conditions of thermochemical treatment define the nature and extent of both primary and secondary reactions. One suitable way of classification is by describing the medium in which the majority of the

reactions take place. This medium can potentially act as a reactant (see Table 1).

Dry conditions can be achieved at low pressures so that the inherently present water – which is not only contained in the feedstock biomass but also produced during conversion – is vaporized. Gas phase reactions dominate the secondary degradation, and will lead to pyrolysis, including the DTL process 'fast pyrolysis'. In contrast to dry processing, solvolysis takes place in liquid media. The term 'solvolysis' is chosen to underline the importance of the medium to solubilise the products from thermochemical conversion instead of chemically depolymerizing the biomass macromolecules. Water can be such a solvent simply by choosing pressure so that water remains liquid at reaction temperature. Secondary reactions will then take place in the hot aqueous phase and the process is referred to as hydrothermal, including the DTL process hydrothermal liquefaction (HTL). Finally, a solvent other than water can be chosen; in most cases organic solvents are used, which can also act as hydrogen donors by chemical reactions. In such cases DTL has always been the primary aim and it is simply referred to as solvolysis.

Fast Pyrolysis

Pyrolysis is a process that also takes place during combustion and gasification of biomass (and many other carbonaceous solids as e.g. coal). Biomass releases combustible gases (so called volatiles) at elevated temperatures, which potentially ignite once in contact with oxygen. The resulting flames is the fire that we observe e.g. in a fireplace. They consume the oxygen surrounding the solids and thus lead to further thermal degradation of the biomass under inert, i.e. oxygen depleted, conditions to produce char. Once volatile production ceased, oxygen will reach the hot char and leads to further oxidation until ash remains, producing the warm glow that can be enjoyed and exploited e.g. for cooking. Pyrolysis is the part of a fire where volatiles are released and char is being produced in a hot, oxygen depleted ambience. Hence, pyrolysis in a technical application is defined as heat treatment of a feedstock without the addition of oxygen to the reaction vessel.

Pyrolysis of biomass produces only solid and gaseous products if secondary reactions in the gas phase come to an end, i.e. thermodynamic equilibrium is achieved. It is thus important to
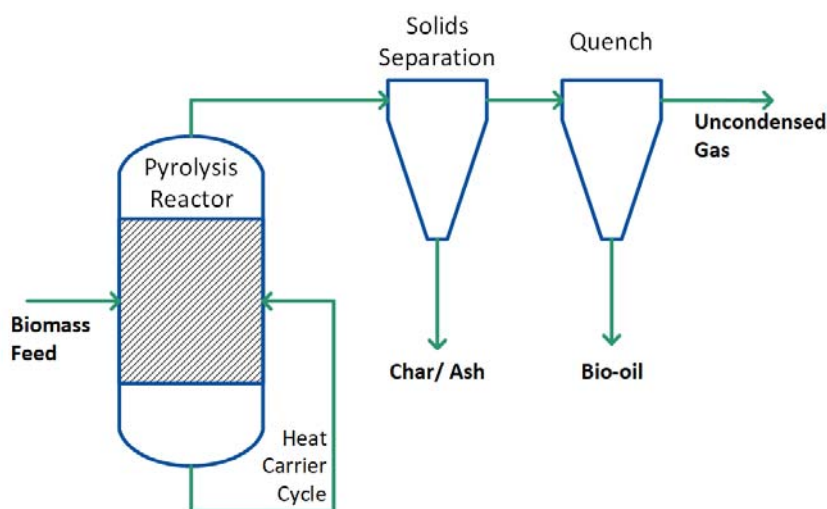

Figure 3: Scheme of fast pyrolysis process.

cool down the produced gas phase instantly (i.e. 'quench') to achieve a short hot gas residence time in the order of a few seconds. This will reduce secondary reactions and maximize liquid yield. Consequently, the produced fast pyrolysis bio-oil (FPBO) cannot be regarded chemically stable and will undergo further reactions at ambient temperature, often referred to as 'aging'. Also, more liquid intermediates are produced by primary depolymerisation of the macromolecules with higher reaction temperature inside the biomass particle. This can be achieved by increasing the heat flux into the particle, which will also lead to fast heating of the biomass particles. Pyrolysis with the aim of direct liquefaction is called 'fast pyrolysis' and always characterized by fast heating of feedstock and fast cooling of products.

One way to realize high heat flux into the biomass particles is by grinding the feedstock to a small particle size and mix them with a preheated heat carrier such as e.g. sand. This can be achieved in a fluidized bed or by mechanical mixing e.g. by a rotating cone or screws (see Figure 3). Other means of realising a high heating rate include ablative reactors, where the feedstock is pressed onto a heated surface (by mechanical or centrifugal force); and heating by radiation, the latter being restricted to laboratory applications as of today.

Fast Pyrolysis Example: Empyro[2]

In January 2014 Empyro BV started construction of its fast pyrolysis plant for production of bio-oil in Hengelo, the Netherlands. Start-up of the installation commenced in early 2015 and production has gradually increased since. In October 2017 the Empyro plant reached 100% of its nameplate capacity after a period of gradual improvements. Empyro passed the 20 million litre mark and gained more than 20,000 hours of operating experience. The plant produces FPBO from wood residues, electricity to cover its own use, and steam. The steam is supplied to the neighbouring salt factory. The majority of the FPBO is supplied to the dairy company FrieslandCampina for onsite boiler operation.

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In December 2018 it was announced that Empyro will become part of Twence, which focuses on the recovery of raw materials and the production of renewable energy. Both parties will work together on optimizing this plant further and will build an installation for the pretreatment of roadside grass as a future feedstock. The developed fast pyrolysis technology will remain in the hands of BTG-BTL together with TechnipFMC.

[2] This highlighted project does not represent any preference over technology. It has been chosen on basis of commercial maturity and amount of public available data.

Apart from reaction conditions, product recovery largely influences FPBO quality such as e.g. the water content. Condensation temperatur naturally plays a decisive role, but also aerosole recovery and process internal FPBO aging need to be considered. The initial condensation step is conducted with a quench in most cases to achieve the high cooling rate required to keep hot gas residence time to a minimum. In industrial applications the condensed FPBO is recirculated, cooled and then used as quenching medium. In research test rigs other quenching media are applied, too.

Hydrothermal Liquefaction

All biomass comes along with an inherent moisture content and the use of many residues for dry processing is limited by the economic and energetic cost of water removal, i.e. drying, before processing. Hydrothermal processing avoids the need of drying as pre-treatment step by maintaining a pressure above water vapour pressure. Consequently, water remains liquid and acts both as solvent and primary reaction medium. This raises the need to achieve pumping of a stable slurry against that pressure in a continuous process, but also offers some unique advantages for biomass conversion. Liquid water is actively promoting hydrolysis of cellulose and hemicellulose and thus could also be considered a reactant. Hydrolytic degradation is very efficient and much lower temperatures can be applied than in dry thermochemical conversion (see Figure 2). Moreover, the formation of solids can be largely prevented during HTL of biomass under optimized reaction conditions.

After primary degradation of the biopolymers essentially all products are solubilised in hot water. This is enabled by drastic changes in the properties of water, which is a polar solvent at ambient conditions and changes to a non-polar solvent at temperatures >200 °C. At the same time ionic reaction conditions are leveraged in the aqueous phase over free radicals that would prevail during dry thermochemical processing. The chemistry thus becomes remarkably different. One important consequence is that even though the fragments of the original biopolymers still undergo secondary reactions, the formation of gas and solids is inhibited to a certain extent. It is therefore no longer required to maintain similar strict limits to reaction time as for fast pyrolysis.

In principle, a similar spectrum of components is formed by HTL as compared to fast pyrolysis but there are differences in their share. The two most remarkable differences are the almost
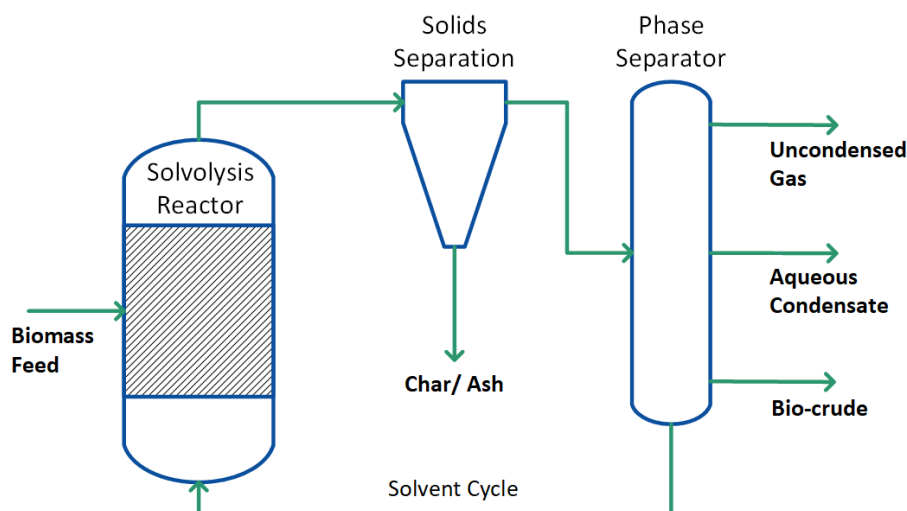

Figure 4: Scheme of solvolysis/ HTL process.

Hydrothermal Liquefaction Example: Steeper[3]

Steeper Energy is partnering with Silva Green Fuel to construct an industrial scale HTL demonstration plant at a former pulp mill located in Tofte, Norway leading to a future commercial scale project. Steeper will license its proprietary Hydrofaction™ technology to Silva, who will build the facility with a capacity of 4,000 litres a day. The demonstration plant will use woody residues as feedstock that are converted to bio-crude and, in turn, will be upgraded to renewable diesel, jet or marine fuel. Steeper's Hydrofaction™ technology was selected by Silva after an exhaustive due diligence review of 40 different technologies.

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complete absence of sugars due to more efficient dehydration reactions in water and the higher amount of phenols produced by HTL. The latter are typical degradation products from lignin but seem to be more stable in water at the low temperature applied, thus preventing their secondary reaction to from gaseous products. Also, derivatives from sugar degradation are capable of forming phenol.

The solvent properties of water change again upon cooling down, leading to phase separation. Polar compounds like acids, alcohols, and aldehydes remain in the aqueous phase whereas non-polar compounds, primarily phenols, concentrate in the organic-rich phase, which needs to be separated to yield the bio-crude (see Figure 4). Some of the qualitative differences between bio-crude and FPBO are also related to this phase separation during product recovery.

Solvolysis with organic solvents

Solvolysis for liquefaction of carbonaceous materials applying organic solvents has a long tradition, the liquefaction of coal and lignite with the Bergius-Pier process possibly being the

[3] This highlighted project does not represent any preference over technology. It has been chosen on basis of commercial maturity and amount of public available data.

most prominent example. The same principles can be applied for biomass even though a much higher amount of oxygen is present in the feedstock. In many cases solvolysis takes place in a hydrogen enriched atmosphere (i.e. high pressure) or by addition of hydrogen transfer agents to further promote hydrogenation. This again raises the need for pumping of stable slurries against reactor pressure in a continuous process.

The nature of the solvent used during solvolysis will decide the type of secondary reactions that take place and hence the quality of the produced bio-crude. It is mandatory for economic processes to reduce the amount of solvent that needs to be added. It follows that stability and recovery of the solvent are a key challenge.

PRODUCT CONDITIONING

Although being different in chemical nature, there are challenges related to the use of bio-oil which are very similar to those of fossil crude oil: it has a complex, partially unknown chemical composition and needs to be refined to become a useful product. In the field of bioeconomy, the pretreatment of biomass to e.g. liquid intermediates are often referred to as primary refining while the production of well-defined chemical commodities or products is the secondary refining. Secondary refining of bio-oils from DTL can be divided into post-treatment that does not alter the chemical nature of the bio-oil and upgrading that includes chemical reactions. Refining needs to be well aligned with the intended bio-oil application due to the cost associated with it.

Bio-oil Applications

Bio-oils produced by direct thermochemical liquefaction represent a mixture of numerous organic compounds. This characteristic is due to the variety and complexity of the depolymerized macromolecules inside the feedstocks combined with the comparably unspecific nature of the applied thermochemical depolymerization. Fossil oil also represents
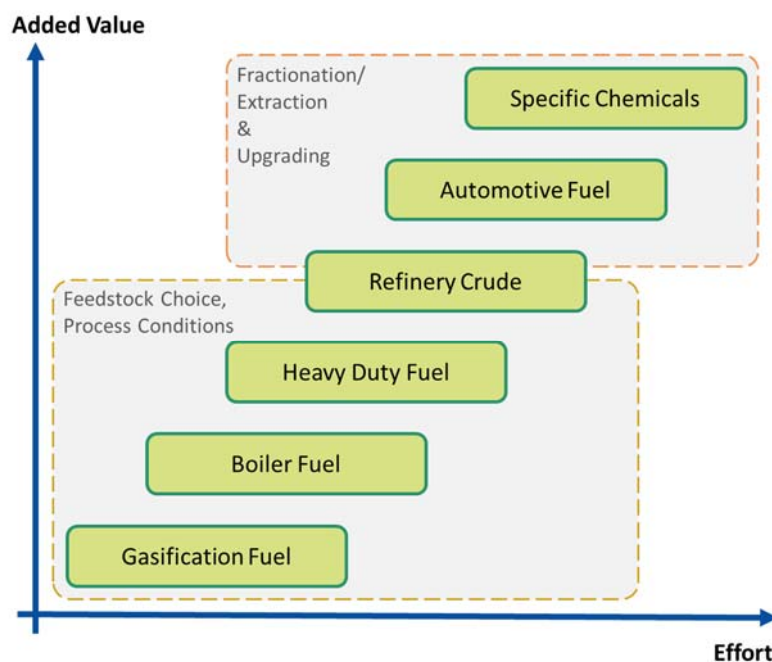

Figure 5: Different applications for bio-oils, qualitatively arranged according to their value and associated effort for production/ refining.

a complex mixture of numerous organic compounds; however, the chemical nature of the compounds is very different between fossil and bio-based oils. There are several possibilities how bio-oils can substitute the consumption of fossil oil; their use can be broadly characterized as liquid fuel and chemicals. Similar to fossil oil, bio-oil needs to be processed (i.e. upgraded) in order to allow specific applications even though liquefaction is typically connected with high added value. Each processing step is always associated with cost and inefficiencies. It follows that bio-oil should be upgraded as little as possible but as much as required for the intended application (see Figure 5).

Post-treatment

Bio-oils from DTL do contain a certain amount of solid particles, which are an inherent by-product of the conversion process and represent a mixture of ash and carbonaceous material (char, coke). Solid particles are unwanted for almost all applications and most DTL conversion processes are designed to minimize particle content. Additional filtration may be required depending on the demand of the intended application. Another common strategy to adjust bio-oil physical characteristics is blending with other liquids. It is suitable for lowering the typically high viscosity of FPBO and bio-crude. Also, combustion characteristics can be favourably influenced, be it on the DTL production site or during feeding/ injection into the combustion chamber.

More complex processing includes fractionation of the bio-oil into commodities with specific use. While technically possible, it is unlikely that fractions will be produced that contain single chemical compounds due to the low concentration of single species in bio-oil and the associated high cost of extracting them in a product fraction. But it seems feasible to divide bio-oil into fractions with different focus such as energy, chemical, and material application.

Upgrading

Catalytic hydrotreatment of bio-oil is the most widely discussed possibility to upgrade bio-oil. It is also widely referred to as hydrodeoxygenation (HDO) because it aims at removing oxygen from oxygen containing compounds in the bio-oil, increasing the share of aromatics, alkenes, and alkanes. Cracking reactions lead to formation of short chain molecules and the resulting upgraded bio-oil exhibits generally more favourable properties like higher energy density, lower viscosity, less acidity etc. The underlying reactions are not yet very specific and the upgraded bio-oil still contains a wide variety of chemical compounds as a consequence. HDO can also be integrated in the pyrolysis process, be it in-situ to directly affect pyrolysis (catalytic fast pyrolysis) or ex-situ, primarily as vapour reforming step before condensation. The possibility of in-situ upgrading is especially of interest for DTL solvolysis in organic solvents.

HDO can be conducted in multi-step processes with increasing effort both in hydrogen use and processing intensity (temperature, residence time). Mild HDO targets improvement of general bio-oil characteristics and stabilization of primarily FPBO, while deep HDO will lead to more 'pure' mixtures of aromatics, alkenes, and alkanes.

General Properties of DTL Oils

Apart from the general complexity of their chemical nature, there are some characteristics that are specific to bio-oils produced by DTL and worthwhile mentioning (see Table 2). Bio-oils come along with a certain solid content, which is different from fossil fuels. This fact also leads to a potentially higher ash content which is directly related to the feedstock. Nitrogen and sulphur content are also dependent on the feedstock choice and typically lower than in fossil fuels. Bio-oils do contain a significant amount of water due to inherent feedstock

Table 2: Summary of properties for fossil fuels and typical bio-oils from DTL (adapted from Lehto et al. Fuel oil quality and combustion of fast pyrolysis bio-oils, VTT Technology 87, ISBN 978-951-38-7930-3)

Analysis	Heavy fuel oil 180 / 420	Light fuel oil	Typical FPBO from wood	Typical bio-crude from wood
Water, %	≈0	≈0	15-30	3-10
Solids, %	-	-	<0.5	n.d.
Ash, %	max 0.08	max 0.01	0.01-0.1	n.d.
Nitrogen, %	0.4	0.02	0.0-0.5	0.0-1.0
Sulfur	max 1	max 0.001	0.0-0.1	0.0-0.5
Viscosity (40 °C), cSt	180/ max 420 @ 50 °C	2.0-4.5	15-100	$5 \cdot 10^3 - 1 \cdot 10^6$
Density (15 °C), kg/dm^3	0.99	max 0.845	1.1-1.3	0.9-1.1
LHV, MJ/kg	min 40.6	42.6	13-18	30-38

moisture and reaction water produced during conversion. Together with the higher amount of oxygenated organic compounds, this leads to the fact that bio-oils have a lower heating value than fossil fuels. Their density tends to be somewhat higher than fossil fuels.

FPBO is a product of incomplete pyrolysis reaction and as such chemically not stable due to reactive oxygen containing compounds. Ongoing reactions include polymerization/ condensation and etherification/ esterification, which lead to changes in physical properties. Most notably, viscosity and water content increase over time. It also follows that FPBO is non-distillable because these 'aging' reaction increase with temperature, leading to the formation of solid residues during distillation. Bio-crude (both from HTL and solvolysis with organic solvents) is characterized by a much lower oxygen content than FPBO. The associated lower amount of oxygen containing compounds and recovery after phase equilibrium with the aqueous phase also leads to a much lower water content than FPBO. Both characteristics are also represented in an energy density that is much closer to fossil fuels than FPBO. On the downside, bio-crude shows a very high viscosity, even compared to heavy fuel oil.

PERSPECTIVES

Liquid commodities play a vital role in today's industry due to their effectiveness for the production of everyday consumer products. Direct thermochemical liquefaction processes are a promising pathway to efficiently transform biomass to liquid fuels and intermediates for further downstream processing capable of being integrated in existing infrastructure such as e.g. refineries. They represent a key enabling technology to access biogenic resources for a future bioeconomy. Consequently, there are increasing industrial efforts in this field to realize and extend commercial solutions.

Pyrolysis, including fast pyrolysis, of wood (residues) is a state-of-the-art industrial process. FPBO today is primarily sold to replace fossil heating oil in boilers and to produce additives in food production for flavouring (so-called 'liquid smoke'). Especially the former application is currently experiencing a substantial growth; however, it represents a comparably low value application (see Figure 5). There are solutions for higher value applications but they do not experience a significant market pull yet, due to the low cost of their fossil counterparts in the current policy framework. The development of high value material use and innovative upgrading processes is ongoing R&D work. Also, as for any biomass conversion process, feedstock cost is decisive for the manufacturing cost and consequently the product price. Broadening the feedstock range to residues other than wood while maintaining marketable product characteristics is a challenge that still needs to be addressed in order to develop commercial solutions.

HTL experienced tremendous process development over the past decades and there are promising endeavours for demonstration in industrial scale. Similar to FPBO, high value use of the produced bio-crude still requires further R&D work. Current technical challenges are primarily linked to pumping of stable slurries against the required pressure, efficient separation of the bio-crude from the aqueous phase, and further use of the latter.

Solvolysis of solid biomass with organic solvents is still subject to R&D work. It is critical to develop a process with a stable solvent phase in order to allow for stable continuous operation. Similar to HTL, recovery of the produced bio-crude is also important for its quality. Distillation, possibly even inside the reactor, is an alternative for product recovery for the case of solvolysis in organic solvents. Utilization and treatment of the aqueous phase with its organic load also needs to be considered.

IEA Bioenergy Task 34 has been set up in order to facilitate the commercial implementation of direct liquefaction technologies. It represents a hub for stakeholders from industry and research in the field of direct thermochemical liquefaction to facilitate knowledge exchange. Dissemination of ongoing developments and activities are another core of the work to provide meaningful and validated information to the public and stakeholders from policy. Main elements are the bi-annual PyNe newsletter, design of a public information platform (http://task34.ieabioenergy.com/), and the publication of reports relevant to the field. IEA Bioenergy Task 34 is also actively supporting work to address decisive challenges during commercialization that represent a cross sectional issue. Similar to fossil crude oil, bio-oils from direct thermochemical liquefaction do not represent single chemical substances or even well-known mixtures thereof. Development of methods for their characterization is required as well as creating standards to allow for a well-defined marketable product. IEA Bioenergy Task 34 supports this work by organizing Round Robins to test developed methods and conducting workshops with relevant stakeholders to promote knowledge exchange. This work has been part of the development to achieve standards for FPBO as fuel for boilers (ASTM D7544 and EN 16900:2017) in the past and other bio-oil uses will be supported in future.

FURTHER READING

Additional, regularly updated information can be found on **http://task34.ieabioenergy.com/** including references for more specific topics and a download section for other reports from IEA Bioenergy Task 34.

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