Hydrothermal liquefaction of organic resources in biotechnology: how does it work and what can be achieved?

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Abstract

Increasing the overall carbon and energy efficiency by integration of thermal processes with biological ones has gained considerable attention lately, especially within biorefining. A technology that is capable of processing wet feedstock with good energy efficiency is advantageous. Such a technology, exploiting the special properties of hot compressed water is called hydrothermal liquefaction. The reaction traditionally considered to take place at moderate temperatures (200-350 °C) and high pressures (10-25 MPa) although recent findings show the benefits of increased pressure at higher temperature regions. Hydrothermal liquefaction is quite robust, in theory all wet feedstock, including residues and waste streams can be processed. The main product is a so-called bio-crude or bio-oil, which is then further upgraded to fuels or chemicals. Hydrothermal liquefaction is currently at pilot/demo stage with several lab reactors and a few pilots already available as well as there are a few demonstration plants under construction. The applied conditions are quite severe for the processing equipment and materials, and several challenges remain before the technology is commercial. In this review, a description is given about the influence of the feedstock, relevant for integration with biological processing, as well as the processing conditions on the hydrothermal process and products composition. In addition, the relevant upgrading methods are presented.

Keywords

Introduction

The production of biofuels and biochemicals from biomass has historically been based on two distinct conversion pathways: biological and thermochemical. Biological routes have been widely applied for processing of a large variety of feedstock to produce biofuels (Anastasakis and Ross, 2011; Matsui and Koike, 2010). The biological routes, however, present two major drawbacks: (i) the relatively low production rates and (ii) the production of a stream of fermentation residue with high moisture content (> 90 wt. %), high organic content and very high lignin content that cannot be further processed biochemically (Theegala and Midgett, 2012). This residue stream provides an energy and carbon source. Conventional thermochemical technologies such as pyrolysis and gasification are not suitable for conversion of high-moisture content biomass due to the high energy consumption associated with the evaporation of the moisture fraction, resulting in poor energy efficiencies.

The considerable attention hydrothermal liquefaction (HTL) receives is due to its relatively low processing temperature, high energy efficiency and its low-oxygen content product (bio-oil or bio-crude) compared to pyrolysis bio-oils. The technology uses subcritical and supercritical water for hydrothermal conversion of biomass. As temperature increases around the critical point (374 °C and 22.064 MPa), several properties of water changes almost suddenly. The density decreases and compressibility increases sharply. The relative permittivity (dielectric constant) of water decreases rapidly (Wasserman et al., 1995; Kruse and Dinius, 2007) due to higher mobility of the electrons shared by the oxygen and hydrogen atoms. Therefore, the polarity of the water molecule reduces significantly which increases the solubility of non-polar organic components. The dissociation constant of the water increases with increasing temperature, up to the critical point where it drops suddenly. The increased dissociation constant of water leads to higher concentrations of H^+ and OH^- ions at equilibrium below the critical point. This causes acceleration of acid- or base catalyzed reactions (Akiya and Savage, 2002; Hunter and Savage, 2004) such as in biomass hydrolysis. The solubility of salts in water under subcritical

conditions decreases significantly compared to room temperature, and this effect varies between different types of salts (Hodes et al., 2004).

Hydrothermal liquefaction (HTL) exhibits several benefits that makes this technology a promising alternative to conventional thermal processes for conversion of high-moisture biomass into bio-oil, and for further upgrading into biofuels, and chemicals (Anastasakis and Ross, 2011). HTL is mostly considered as a conversion that takes place near, but below the critical point of water i.e. at moderate temperatures (200-350 °C) and high pressures (10-25 MPa) where the process utilizes the special properties of near-supercritical water and avoids the sudden shifts in crucial water properties around the critical point. However, by keeping the reaction pressure above 300 bar, it is possible to increase the temperature above the critical point while maintaining the desired water properties (Jensen et al., 2017). The energy used to heat up the feedstock in the HTL process can be recovered effectively with the existing technology. The special reaction conditions applied enhance the breakdown of complex macromolecules into smaller molecules and into three different fractions: a solid phase (char or hydrochar), a liquid phase consisting of a bio-oil phase and an aqueous phase, as well as a gas phase, containing mainly CO_2. The bio-oil can then be separated to light and heavy fractions and/or further processed into a wide variety of biofuels and biochemicals, in combination with recovery of nutrients/minerals for potential use as fertilizers.

Despite the numerous benefits offered by HTL, there are several challenges remaining. The highly complex chemistry involved in this process makes the quantification and qualification of the end-product components a difficult task. Additionally, due to the high reactivity and instability of the intermediate products, appropriate operating conditions are needed for stable formation and optimization of the desired end-products. To minimize the unwanted solid products, HTL is often carried out using a catalyst (typically alkali-based catalysts), resulting in increased liquid yields. However, the presence of a catalyst in hydrothermal conversion, liquefaction and gasification, is not straightforward due to the harsh conditions in hydrothermal media and further understanding is needed. Catalysts also increase the overall process costs. Instead, the presence of inorganic metal components in the processed feedstock could also have a remarkable in-situ catalytic effect while avoiding the challenges associated with the use of an external catalyst. This research field is rather unexplored and needs more focus.

HTL and biotechnology

Hydrothermal conversion of the nonconverted streams in biotechnology

HTL is a promising technology to integrate with biological conversion technologies. In most cases, the integration is considered through utilization of the unconverted lignin-rich streams from biological conversion. Hence a considerable part of this paper will review the HTL conversion of relevant feedstock, including waste streams, lignin and lignin-rich residues. Another relevant feedstock is aquatic biomass.

Hydrothermal pretreatment

Anastasakis and Ross (2011) investigated hydrothermal liquefaction of the macroalgae, *Laminaria saccharina* in 75 mL batch constant volume reactors. They found that the obtained biocrude fraction was low, while the salt from the algae was distributed between the aqueous and solid phases. They also found carbohydrates in the aqueous phase which makes it interesting for further fermentation. Hydroxymethilfurfural (HMF) is a degradation product of cellulose under HTL conditions (Kruse and

Gawlik, 2003). Further HMF reactions are dependent on the reaction conditions applied. Under radical conditions other furfurals are produced. Furfurals and HMF are inhibitors in consequent biological processes (Pienkos and Zhang, 2009) and therefore if HTL is used as a pretreatment the production of those products should be limited.

Biological treatment of the aqueous phase

Water treatment and reuse are central issues in hydrothermal processes. Large amounts of water with dissolved organics need to be treated at a commercial HTL plant. The suggested treatments are recirculation for improved bio-oil yields (Hu et al., 2017), supercritical gasification (Elliott et al., 2015), anaerobic digestion (Wirth and Mumme, 2013) and integration with paper mills (Orebom et al. 2018). The integration possibilities with anaerobic digestion facilities for increased energy recovery are promising. The ratio between the HTL oil product and methane from anaerobic digestion is dependent on the HTL temperature (Posmanik et al., 2017). Combining HTL with anaerobic digestion for cow manure showed increased energy recovery when the digestate from anaerobic conversion was further processed in an HTL reactor (Eboibi et al., 2015). Integration of HTL with existing paper mills will probably one of the possibilities first realized, and there are already existing agreements between Licella and Canfor (Licella).

HTL process performance – what can be achieved?

The HTL process is currently on pilot/demo scale level, with several pilots available and a few demos under construction worldwide. The status and the main bottlenecks of the process towards commercialization are extensively reviewed recently by others (Gollakota et al., 2018; Elliott et al, 2015). The major commercial players are Licella, Steeper Energy and Altaka Energy. The current status of commercialization of the HTL technology is shown in Table 1.

An extensive number of experimental investigations on hydrothermal liquefaction of biomass feedstock under various process conditions are reviewed continuously (Akhtar and Amin, 2011; Barreiro et al., 2013; Elliott et al., 2015; Gollakota et al., 2018). The experimental results show large variations in the products distributions (yields) and qualities of those. In reality, it is very difficult to separate the feedstock impact from the influence of the processing conditions including catalysis. In general, it can be concluded that by processing under the same conditions, feedstock has a huge impact on the HTL products. Bio-oil is a result of the energy concentration during the HTL process and it has significantly higher calorific value than biomass. The calorific value of the oil was measured around 30 MJ/kg for household waste (Minowa et al., 1995), approximately 35 MJ/kg for swine manure (He et al., 2000), 34.9 MJ/kg was obtained for beech wood (Demirbas, 2006), 36.5 MJ/kg for seaweed (Anastasakis and Ross, 2011) and in the range of 22.8-36.9 MJ/kg for microalgae (Biller and Ross, 2011). Blending and mixing of the different resources may become important to obtain an optimal product composition for different end-use strategies. On the other hand, bio-oil still resembles the feedstock it was produced from, has an oxygen content of 10-20%, as well as a relatively high water and acid content causing similar disadvantages as pyrolysis oil, such as corrosion and potential thermal instability.

Feedstock composition

The main constituents of biomass, i.e. lignin, hemicellulose, cellulose, proteins and lipids, behave quite differently during hydrothermal liquefaction due to differences in their molecular structure. Therefore, the heterogeneity in the composition of different biomass feedstock leads to large variations in

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product yields distribution, composition and properties (Huang et al. 2013). In general, the bio-oil product of HTL has a complex composition, consisting several hundred components and similarly to pyrolysis oil it is difficult to qualify and almost impossible to fully quantify.

The exact pathways of biomass to bio-oil conversion under sub- and supercritical conditions are still unclear, there are pathways presented in literature. With increasing temperatures and reaction times, first a depolymerization of the biomass constituents occurs, forming monomers which are dependent on the origin. The first step is fast. The monomers then undergo further reactions, forming more stable intermediates. Dependent on the reaction conditions, and thus the favored reaction pathways, the intermediates will degrade to produce gas, or recombine to produce light and heavy bio-oil as well as char (Hietala et al., 2016; Pedersen and Rosendahl, 2015; Faeth et al., 2013; Toor et al., 2011). Two main reaction conditions can be distinguished based on the water properties. In subcritical water and at high pressures (300-350 bar) in supercritical water, ionic reactions are preferred, while supercritical water at somewhat lower pressures (up to 250 bar) favor radical reactions. The latter is often result in gasification reactions (Jensen et al., 2017) and char formation. Both reaction pathways are active in in the hydrothermal system, the hydrothermal liquefaction products are dependent on whether ionic or radical reactions are favored. Bühler et al. (2002) concluded that the overall degradation of glycerol followed a non-Arrhenius behavior. They also proposed a set of reaction pathways occurring as a result of competing reaction pathways, ionic and radical, under ionic and radical conditions.

Hydrothermal liquefaction of cellulose and hemicellulose fractions lead to the formation of sugars and enhance the production of bio-oil and aqueous organic fractions. The decomposition of hemicelluloses occurs at lower temperatures and with shorter residence times due to its amorphous structure (Gullón et al., 2010). Cellulose has a more crystalline structure and an intermediate degree of polymerization (500–10,000), therefore its decomposition in aqueous conditions occur at higher temperatures than hemicelluloses. Microcrystalline cellulose starts to degrade forming hexoses and oligosaccharides above 230 °C and the decomposition was nearly complete at 295 °C (Sakaki et al., 1996). Kruse and Gawlik (2003) has performed 80 experiments on baby food (equivalent to food waste) to analyze the possible pathways of carbohydrate reaction mechanisms. They concluded that the cellulose degradation to sugars is very quick followed by further reactions forming several products. Hydroxymethilfurfural (HMF) is formed under ionic and acidic conditions. Further reactions of HMF are very dependent on the reaction conditions, giving mainly levulinic acid under ionic conditions or other furfurals under radical conditions.

Lignin is one of the major constituents of lignocellulosic biomass with a complex aromatic structure. Lignin cannot be converted biochemically, hence conversion of lignin-rich streams offer a way to increase the overall carbon efficiency in biorefineries. During thermal treatment, lignin decomposes to mainly phenolic compounds (Toor et al., 2011), because the aromatic rings withstand the hydrothermal conditions opposed to their substituent groups (Barbier et al., 2012). The lignin content of the feedstock affects the conversion, the required conversion temperature increase (Zhong and Wei, 2004), bio-oil yields decrease, and char yields increase (Bhaskar et al., 2008) with increased lignin content in the feedstock.

Fang et al. (2008) suggested a set of reaction pathways describing lignin decomposition and further reactions. In homogeneous phase, lignin dissolves via hydrolysis forming monomers, and the monomers react further to form oil, aqueous and *phenolic* char. In the heterogeneous reaction pathways lignin pyrolyzes forming monomers, gases and polymers, the latter leading to *polyaromatic*

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char formation which was heavier and had different structure than *phenolic* char. Forchheim et al., (2014) developed a kinetic model of lignin decomposition based on experiments carried out in batch reactors between 320-380 °C and 15-480 min. According to this model, lignin first decomposes to methoxyphenols and reactive intermediates. The methoxyphenols are short lived and at higher temperatures and residence times they react to phenols and catechols, while the reactive intermediates form catechols and stable intermediates. The authors found that they catechol yield increased with the residence time and the yield of phenols with temperature and residence time. Char is formed from the reactive intermediates in the first step and catechols, while gases are formed from phenols and the reactive intermediates. The gas yield (especially CH_4 and CO_2) increased with temperature and residence time. The structure of the obtained char had a strong dependence on the processing temperature (Hu et al. 2014), at 280 °C lignin was not decomposed completely while at 330 °C the char was highly porous with large pores and high surface area. At 350-365 °C the char obtained was thermally stable with low surface area and highly ordered crystalline structure. Mattson et al. (2016) has fractionated and analyzed the bio-oil product of kraft lignin HTL. They have added phenol to suppress the repolymerization reactions during HTL. By analyzing the light and heavy oil as well as suspended solids structure they concluded that all of them were produced by the same type of deoxygenation reactions at 350 °C and 250 bar. By this, they confirmed that all of the lignin was first dissolved and then recombined forming both the light and heavy fractions, included suspended solids. The light fraction was thermally stable after accelerated aging while the heavy fraction was slightly affected by the aging process (Lyckeskog et al., 2017).

It must be mentioned that the origin of lignin, namely which pretreatment was used to obtain the purified lignin used in the different studies can significantly affect the results. Zhang et al. (2008) compared five types of lignin, kraft lignin from two different suppliers, one organosolv and lignin residues of hardwood and switchgrass hydrolysis. The residues contained significant amount of hemicellulose and cellulose after the hydrolysis process as well as the ash content of the switchgrass sample was very high (23.2%). Organosolv lignin contained high amount of hemicellulose and the sample had high volatile content. The authors found that the lignin pretreatment affected strongly the product yields after hydrothermal liquefaction and suggested that due to large varieties, the optimum conditions for HTL should be chosen individually for these types of feedstock.

Algae have a number of interesting properties which makes them interesting to cultivate and further process to chemicals, fuels or energy. The main advantage of algae cultivation is that they have high photosynthetical efficiencies and they do not need arable land to grow. The drawbacks are the low biomass productivity, inefficient harvesting practices and high water content of the algae feedstock. Elliot et al. (2013) demonstrated the continuous HTL conversion of microalgae in a bench-scale reactor at 350 °C and 200 bar. They claim that algae streams up to 35 wt. % could be reliably processed with high yield (80 % dry, ash-free basis) biocrude production. Biller and Ross (2011) obtained 5-25% bio-oil yield on ash free basis. They have also observed that the majority of the carbon ended up in the aqueous phase as well as the majority of nitrogen was found in the gas phase. 20% of the nitrogen was found in the oil product. Shuping et al. (2010) has performed liquefaction of *Dunaliella tertiolecta* microalgae and obtained a maximum bio-oil yield of 25.8%. Anastasakis and Ross (2011) investigated hydrothermal liquefaction of the macroalgae *Laminaria saccharina* and obtained low bio-oil yields.

Lipid conversion is mainly relevant in HTL conversion of microalgae and fatty waste streams. When fatty acids decompose, they give long-chain hydrocarbons. Watanabe et al. (2006) studied the

decomposition of stearic acid and proposed a reaction mechanism through ketones to low molecular hydrocarbons with acids as additional products.

Proteins are found mainly in animal and microbial biomass and they are the main nitrogen source in the feedstock. Proteins decompose similarly to the other biomass constituents, starting with a fast decomposition to amino acids followed by further decarboxylation to produce amines and carbonic acid. Amines undergo deamination to produce organic acids and ammonia. Depending on the reaction conditions, repolymerization occurs, yielding long chain hydrocarbons and aromatic ring type structures like phenols or nitrogen heterocyclics such as indole or pyrrole (Barreiro et al., 2013).

Reaction pressure

During hydrothermal liquefaction below the critical point pressure is traditionally maintained to avoid solvent vaporization and thus keep the solvent in liquid phase. There are relatively few experimental articles investigating the effect of pressure on biomass conversion in an HTL system. At supercritical conditions, the pressure had only a slight effect on the decomposition kinetics of cellobiose (Kabyemela et al., 1998). A slight decrease in fragmentation was observed, which is attributed to a so-called cage effect where the increased solvent density suppresses the breakage of the C-C bonds. Yin et al. (2010) observed reduction of the bio-oil yield when the initial pressure of the CO process gas increased, but this effect was not observed for the other process gases they investigated. An increase of pressure from 150 to 270 bar had no significant effect on the amino acid yields when proteins were hydrolyzed at 250 °C (Rogalinski et al., 2005). Based on the results of these studies, pressure has negligible effect at low temperatures. Pressure has, however, a huge influence on the water properties around the critical point. Water becomes highly compressible above the critical point, and that leads to a considerable pressure influence on the density and other properties dependent on density, such as the ionic product, that controls whether the reactions are mainly ionic or radical (Kruse and Dinjus, 2007). Bühler et al. (2002) found a considerable pressure dependence when they studied glycerol liquefaction around the critical point of water. The experiments were carried out at 349-475 °C and 250-450 bar. They also found that the reaction rates of ionic reactions are higher at subcritical conditions as well as higher pressures, while radical reactions dominate the high temperature-lower pressure region. Jensen et al. (2017) proved that by increasing the pressure from 200 to 380 bar the desired properties of sub-critical water can be maintained even at supercritical conditions while coke-forming radical reactions can be eliminated. In addition, the sudden shifts of water properties around the critical point can be avoided, since the shifts are smoother at higher pressures, which gives increased control on the HTL process. The chemical reactions and thus the reaction rates and product distributions can in theory be tuned by altering the solvent densities by pressure. In that case, the increased compressibility around the critical point is exploited where the density is extremely sensitive to the pressure (Eckert and Chandler, 1998). This method is however currently not practiced in hydrothermal liquefaction of biomass, probably due to the large number of reactions involved in a complex system that is not fully understood yet.

Reaction Temperature

The reaction temperature has a significant effect on the products yield distribution. During hydrothermal liquefaction first depolymerization occurs followed by repolymerization at later stages of liquefaction as discussed above. The repolymerization leads to formation of char and suspended solids which are normally undesired. Hence, intermediate temperatures give the highest amounts of bio-oil (Akhtar and Amin, 2011). At temperatures below 280 °C under hydrothermal conditions, the

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decomposition of cellulose and especially lignin is incomplete (Yu et al., 2008). In the lower temperature range, the total oil yield increases with temperature (Karagöz et al., 2006), up to a feedstock dependent optimum, and decreases above this range (Zhong and Wei, 2004). The yield of liquid products and bio-oil heating values increase, but yields of solid residue decrease, with increasing process temperature (Demirbas, 2006). Increasing the temperature above 374 °C, however, leads to increase in the gas formation. According to experimental investigations (Zhou et al., 2010; Yin et al., 2010; Zhang et al., 2009; Sugano et al., 2008) the oil yield for woody and herbaceous biomass showed a maximum at temperature range 300–315 °C. Xiu et al. (2010) found that the oil yield showed increase with increasing temperatures from 260 to 340 °C during manure liquefaction. Yin et al. (2010) observed the highest bio-oil yield at 310 °C for cattle manure in a batch reactor. Shuping et al. (2010) conducted liquefaction experiments with microalgae *Dunaliella tertiolecta* reporting 360 °C as the optimum temperature for maximizing the weight yield of bio-oil production, while Liu et al. (2012) found an optimum temperature for maximizing the bio-oil yield for cypress around 280 °C. The common feature of these studies that the reaction pressure is usually kept at a maximum of 250 bar. The bio-oil yield can be further increased at higher temperatures if the pressure is kept sufficiently high (Jensen et al., 2017). As discussed above, ionic reactions are dominant in supercritical water above 300 bar even above the critical point of water.

Heating rate

Increasing heating rates have been shown to increase the rate of biomass decomposition and to decrease the char formation both in pyrolysis and HTL. This effect is more moderate for hydrothermal liquefaction compared to pyrolysis. The reason is accredited to the water stabilizing the highly reactive fragments (Akhtar and Amin, 2011). Karagöz et al. (2005) observed low conversion rates and low oil and high solid yields for pure lignin at very low (3°C/min) heating rates. Fang et al. (2008) obtained 18.4 C% solid residue in non-catalytic experiments and complete decomposition of lignin in the presence of catalyst (Ru/TiO$_2$) in supercritical water for organosolv lignin using a microreactor and 30 °C/min heating rate. Zhang et al. (2009) observed an increase in liquid oil yield from 63% to 76% and a decrease of solids yield from 22 to 8.6% when heating rates increased from 5 to 140 °C/min. They also reported an empirical correlation to estimate the yield of liquid oil as a function of heating rate. Upon comparison of HTL with low and high heating rates, higher bio-oil yields were obtained for the higher heating rate fast HTL (Faeth et al. 2013) but when normalized to the reaction ordinate (reaction severity) factor, conventional slower and fast HTL exhibited similar trends. Hietala et al., (2016) observed that with higher heating rates, the maximum bio-oil yield was obtained at higher temperatures, 250-300 °C vs. 300-400 °C if reaction times 3-7 min were applied. The results imply that at least the same or higher biocrude yields can be obtained with much lower residence times when high heating rates are applied which is favorable for the overall economics of the process.

Residence time

In an HTL system, the reaction time needs to be sufficiently high for producing bio-oil in the desired amounts and qualities but not too high to avoid reactions that forms gases and heavy compounds. The effect of residence time on hydrothermal liquefaction of biomass has been investigated extensively, although most of the studies apply batch reactors with long residence times and slow heating rates. Increase in residence time at low temperatures (150 °C) favored the liquid oil yield during conversion of sawdust (Karagöz et al., 2004) while the opposite was true for somewhat higher temperatures (250–280 °C). At 310 °C, the bio-oil yields decreased significantly with increasing residence times (Yin et al.,

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2010). Barbier et al. (2012) found a decrease in the water insoluble yield and decreasing H/C and O/C ratios (increased aromatic degree), while the oxygenated hydrocarbons (light organic acids and ketones) increased in the water-soluble fractions with increasing residence time from 5 to 40 min during hydrothermal liquefaction of lignin. On the other hand, nitrogen-containing compounds seem to transfer from the aqueous phase to oil phase with time (Hietala et al., 2016, Faeth et al., 2013).

There are several recent studies investigating non-isothermal HTL at very high heating rates and short residence times for tracking intermediates and kinetics (Faeth et al., 2013; Hietala et al., 2016). Hietala et al. (2016) pointed out that after 5 minutes the biocrude yields remained nearly the same at lower temperature regions and decrease slightly at 400 °C. They obtained the maximum bio-oil yield beyond the point of solids depletion, which they attributed to secondary reactions. They also found that the effect of the residence time is dependent on heating rate and final reactor temperature. Glucose and xylose underwent Retro-Aldol and dehydration reactions followed by condensation and dehydration to form bio-crude between 1-3 minutes in a rapidly heated microreactor (Pedersen and Rosendahl, 2015).

Biomass particle size

The particle size of biomass has been shown to have a small effect on the oil yields in hydrothermal liquefaction in batch systems. Zhang et al. (2009) observed no significant changes in the oil yield for particle sizes of 2.54mm (1 inch), 2mm and 0.5mm at 350 °C. This was explained by the high liquid-to-solid heat transfer coefficient under near-critical conditions compared to the thermal inertia of solid biomass. In the range of 106–850 μm the product yields and qualities were not affected for sweet sorghum bagasse in batch and continuous systems at 280 °C (Jansen et al., 2016). However, in continuous large-scale systems, pumping and feeding are expected to be major bottlenecks, and smaller particle sizes are recommended until the pumpability limits are established (Elliott et al., 2015) in addition, valves and pressure regulators are blocked if the particle sizes are too large, especially in smaller pilots (Jazrawi et al., 2013). Particle size is probably the most important factor in obtaining pumpable biomass slurries for higher than 15% solid loading (Dãrãban et al., 2015). Besides the initial particle size, reactions that lead to changes in the particle size distribution such as size reducing pretreatment (Dãrãban et al., 2015), degradation or agglomeration are also important in continuous systems (Jazrawi et al., 2013).

Solvent

In general, oil yields increase when using water as solvent compared to alcohols and acetone when the experiments are performed near the critical point of the solvent, due to the higher reaction temperatures allowed for subcritical processes in water, as water has its critical point at higher temperature. However, at the same temperature in a supercritical extraction process acetone gives higher oil yield than ethanol, ethanol than methanol and methanol than water (Caglar and Demirbas, 2001). Others also found that the oil yield increases considerably (by 38%) when ethanol is used as a solvent compared to methanol (Kücük and Agirtas, 1999) at the same temperature of 290 °C.

In general, increasing the solvent to biomass ratio leads to higher production of bio-oil and reduce the amount of solid residues (Wang et al., 2013) and gases (Boocock and Sherman, 1985). Increasing the solvent to biomass ratio probably enhances the stability and solubility of decomposition products (Sato et al., 2003) by reducing secondary re-polymerization and gas formation.

Reducing gases and hydrogen donor solvents

Presence of reducing gases and hydrogen donors during hydrothermal liquefaction is applied for stabilization of the reactive fragments and to limit product repolymerization and thus solids formation (Xu and Etcheverry, 2008). It is especially interesting for aromatic compounds with high-hydrogen-deficit such as during hydrothermal treatment of lignin where hydrogen donor solvents suppress repolymerization (Kim et al, 2014). The oil yield increased slightly with increasing residence time at 300 °C in the presence of gaseous and liquid hydrogen donors (Yan et al., 1999). The effect of various gaseous atmospheres on the bio-oil yield produced from hydrothermal liquefaction of cattle manure has been investigated experimentally by Yin et al. (2010), showing that the bio-oil yield reached a maximum at 310 °C regardless of the reducing environment. However, under the reducing atmosphere, the overall bio-oil yield increased. H_2 gas (Etchevery, 2008) or syngas, mixture of CO/H_2 (Wang et al., 2007), improves the performance of hydrothermal liquefaction and has a positive influence on bio-oil yield and quality. To reduce the reactor complexity and costs, hydrogen donor solvents represent an advantage compared to reducing gases. This type of solvent not only donates hydrogen but also acts as a hydrogen carrier. Tetralin is one of the most popular solvents for hydrogenation of fragmented species (Wang et al., 2007; Li et al., 2016) although ethanol (Brand et al., 2013) isopropanol (Kim et al, 2014) glycerol (Pedersen et al., 2015; Wolfson et al., 2009) and steam (Dutta et al., 2000) are found to have a hydrogen donor effect. Supercritical water can also donate hydrogen but considerably less than tetralin (Isa et al., 2015). Catalytic hydro-liquefaction is also a promising way to produce the bio-oils more efficiently and with a higher quality (Xu and Etcheverry, 2008; Li et al., 2018).

Effects of catalysts and capping agents

Catalysts can be divided into two major groups, homogeneous and heterogeneous catalysts. Homogeneous catalysts are used to increase the oil yield, decrease the solid residues and assist the water-gas-shift reaction (Toor et al., 2011). Alkali carbonates and hydroxides are used most widely, which also increase the pH value. Addition of 1.0 wt. % of Na_2CO_3 in the liquefaction of corn stalk increased the bio-oil yield from 33.4 to 47.2% (Song et al., 2004). K_2CO_3 suppressed char formation, and increased liquid yields from 17.8 to 33.7% in woody biomass liquefaction (Karagöz et al., 2006).

Capping agents are used to limit the repolymerization reactions and thus solids and char formation during HTL. Fang et al. (2008) observed suppression of lignin repolymerization when phenol was added to the reaction mixture in lignin decomposition reactions in supercritical water. Phenol was suggested as a capping agent to suppress repolymerization of lignin by others as well (Okuda et al., 2008). Phenol as a capping agent suppressed the repolymerization of lignin fragments in HTL of lignin already at 2% phenol concentration in the feed when recirculation was applied (Belkheiri et al., 2018). Boric acid is another capping agent suggested for this purpose as well, although phenol proved to be more efficient (Toledano et al., 2014).

In situ heterogeneous catalysts are mostly employed to enhance gasification reactions, which in HTL means mainly the oxygen removal pathways (Toor et al., 2011). The type of heterogeneous catalysts of interest are mainly nickel-based (Minowa and Ogi, 1998), but experimental data are available for palladium, ruthenium and platinum as well (Toor et al., 2011). Catalytic hydrothermal gasification is also a proposed way to destruct organics in the aqueous phase for reduction of wastewater treatment needs (Elliott et al., 1994a and 1994b).

Non-reactive upgrading of crude bio-oils

The properties of crude HTL oils are significantly improved as compared to fast pyrolysis oils (Doassans-Carrère et al., 2014; Sudasinghe et al., 2014). HTL oils are nearly free of reactive acids and aldehydes, making the oils very storage stable. Still, upgrading is required to produce fuel additives or chemical intermediates. The upgrading steps can be classified into separation and reactive upgrading. For industrial operation a combination of the following described processes is foreseen. To avoid significant energy losses due to cooling and re-heating of the crude oil, the optimal conditions for non-reactive upgrading should be comparable to HTL and the downstream HDO conditions.

Crude oil fractionation

Fractionation of crude oils is performed based on the molecular size and the related thermodynamic differences of the compounds. Distillation as the workhorse in crude oil refining, fractionates the volatile fractions and, as importantly, separates them from the heavy residues. The required energy is calculated by the energy transfer duty. Lange proposed a simplified approach to estimate the operational distillation costs by calculating the distillation resistance (Lange, 2017). The heavy bottom fraction can be burned for heat production or is cracked to smaller compounds.

The light oil fraction consisting of monoaromatics can be directly hydrotreated (Pedersen et al., 2017; Hoffmann et al., 2016). The heavy oil fraction consists of asphaltene-type of compounds and higher amounts of heteroatoms, making upgrading very challenging. This is, however, required for an economic production as this heavy fraction can account for as much as 50 % of the crude oil yield. For separation of individual compounds membrane separation seems highly interesting. Servaes et al. applied methoxide-polymer hybrid membranes demonstrating the separation of individual guayacols from a lignin solvolysis product mix (Servaes et al., 2018). Membrane operation requires, however, clean and stable oils without solid particles to minimize fouling, and pore blockage. Cleaning can be achieved by operation in reverse flow and pulse feeding of solvents.

Separation of aqueous phase

The aqueous phase is a product of the feedstock moisture content, water formed by dehydration, etherification etc. It contains significant amounts of polysaccharide-based compounds, such as monosaccharides, anhydrosugars and furans. Separation of this phase by decanting must be performed at elevated temperatures, at which the viscosity is still low. The aqueous phase can then either be recycled to increase the overall solids yield (Li et al., 2015; Zhu et al., 2015; Ramos-Tercero et al., 2015; Biller et al., 2016), or used for biogas production by anaerobic digestion (Posmanik et al., 2017; H2020 project HyFlexFuel). Other alternatives are aqueous phase gasification (Watson et al., 2017) and aqueous phase reforming (Mehmood and Watson, 2015) to produce hydrogen for upgrading.

Purification methods

Removal of catalyst poisons for reactive compounds can be achieved by selective adsorption. Ion exchange resins trap any remaining acid groups and inorganic ions but can also be applied to fractionate crude oils into compound classes according to their functional groups (Chen et al., 2017). The catalyst beds can be regenerated by addition of a solvent. Still resins have a rather low mechanical stability and tend to swell. Inorganic ion exchange media are cheap and can be regenerated by burning off any organic deposits. Solvent extraction is commonly used for bio-oil analysis. For industrial operation solvent-free operation is, however, preferred with respect to process complexity and costs.

Catalytic upgrading of crude bio-oils

The target of catalytic upgrading processes is to improve the chemical properties towards fuel specifications. The catalytic processes applied, have all been developed for fossil fuel processing. This means that the significantly higher reactivity of bio-based compounds requires adjustment of the catalyst and process conditions. Removal of heteroatoms can be achieved in several ways, as discussed in the following sections.

Fluid Catalytic Cracking

Carbon-rejection processes, such as FCC are applied to crack larger compounds and extract oxygen in form of CO and CO_2 and other heteroatoms. FCC is the dominant process to convert heavy compounds into light fractions. It is operated at low pressure using low cost solid acid catalysts. Rapid coking and catalyst regeneration intervals are achieved by circulating the catalyst between the cracking and regeneration section. The complex operation and the need for replacement of depleted catalysts make these types of processes only feasible at large scale. FCC crackers are currently not operating at full capacity and addition of crude HTL oils can improve the process economics. Still, refineries are reluctant to add non- or partly upgraded HTL oils. The main reason is that the catalyst activity has been tuned over several decades resulting in a balance between cracking to products and formation of coke. Any disturbances due to more rapid catalyst deactivation, changing product spectrum etc. will have a major impact on the economics. Due to that, prior to co-processing, the HTL crude oil is required to undergo a mild hydrodeoxygenation step to convert high and medium reactive oxygenates into less reactive compounds. Co-FCC of HTL oils with petroleum-based feedstocks is the current focus of study in current research projects, among them the H2020 project 4Refinery. Analysis of crude and hydrotreated HTL oils shown promising characteristics (Jensen et al., 2016). Interestingly, pilot tests have shown that during co-FCC of bio oils the biomass derived compounds preferably react to coke, while the overall yield of liquid products is not changed significantly. Co-FCC of catalytic fast pyrolysis oils up to 5% has shown only minor increase of coke formation, which has been explained by the hydrogen donor activity of hydrocarbons and increased steam levels due to water levels in bio oils (Stefanidinis et al., 2018).

Hydrodeoxygenation (HDO)

Catalytic hydrogen addition to remove heteroatoms and saturate double bonds has the advantage that carbon losses to gaseous compounds are minimized. Commonly alumina supported CoMo or NiMo catalysts are applied in sulfide state (Biller et al., 2015; Yu et al., 2017). Increased hydrogen pressure improves the oil yield and deoxygenation activity, and reduces the viscosity (Yu et al., 2017).

The catalyst is activated applying strict protocols slowly increasing the process severity and feedstock reactivity to form a soft coke layer on the surface of the active phase. By this, the catalyst is less active but retains its stability for long term operation. Other hydrogenation/hydrodeoxygenation catalysts, such as supported noble metals and Raney-catalysts have shown insufficient long-term performance, to justify the costs. Related to this is that the HDO catalyst functions as metal ion trap to protect downstream catalytic processes, such as hydrocracking, isomerization etc. Further, minor cracking of heavy crude fractions has been observed, although the catalyst contains no specific acid functions to promote catalyzing these.

Hydrocracking and adjustment of fuel properties

For upgraded HTL oils hydrocracking is an important process to reduce the aromatic content and crack polyaromatic compounds into monomers, and by that, increase the yield towards light oil fractions. In addition, even completely deoxygenated bio-oils still require significant improvement of the fuel properties. This is achieved by applying process conditions similar to HDO but using a bifunctional catalyst that presents both acid groups for cracking of large molecular weight compounds and metal clusters for hydrotreatment. Commonly CoMo and NiMo catalysts supported on zeolites are applied (Tanneru and Steele, 2015). The extent of hydrocracking has to be carefully balanced. Complete saturation of aromatic rings would require significant amounts of hydrogen. Direct hydrocracking of crude HTL oils has been achieved for glycerides (Zhou et al., 2016). In the case of lignocellulose conversion, however, the crude oil contains significant amounts of inorganics and highly reactive oxygenates. As a result, large amounts of coke are produced, and the catalyst deactivates rapidly (Tanneru and Steele, 2015). Industrially an initial deoxygenation step by FCC or HDO is, therefore, preferred. Adjustment of fuel properties is then achieved by isomerization processes. The product is finally blended with premium fuels to match the fuel specifications.

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Compliance with Ethical Standards

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Tables:

Table 1 Status of HTL commercialization

Name	Technology	Status	Commercialization agreements	References
Altaca	CatLiq®	Running pilot 60 kg/h feed	Demo under construction, further agreements are not known	Unsal et al., 2015
Licella	Cat-HTR™	Running pilot 10,000 t/y	Agreement with Canfor in Canada for biodrude production integrated in Canfor's pulp mill. Agreement with Armstrong Energy (UK) and Neste for processing end of life plastics, commercial facility	Licella
Steeper Energy	Hydrofaction™	Running pilot 30 kg/h	Agreement with Silva Green Fuels for industrial scale demo facility	Steeperenergy, Jensen et al., 2017