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A Review on Key Design and Operational Parameters to Optimize and Develop Hydrothermal Liquefaction of Biomass for Biorefinery Applications

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ABSTRACT:

An increase in environmental awareness has resulted in a significant shift in research towards more renewable and sustainable energy sources and better waste valorization technologies. Within this vast field, biomass conversion technologies and biofuels have attracted much attention due to their adaptability potential to pre-existing infrastructure. Hydrothermal liquefaction is one of the most efficient biomass processing methods and has become a promising technology for future applications. Although many studies have been performed on this process, there is still much to discover about the technology; notably, there are critical gaps in substrate-specific reaction optimization, reactor design, and the effect of catalysts. In order to facilitate future studies reporting on these research gaps, this review summarizes the science and engineering applications of hydrothermal liquefaction of biomass. The effects of reaction temperature, retention time, biomass solid content, biomass type, solvent, and catalyst type on bio-crude yield and quality are discussed. In addition, reaction pathways, reactor types, and process economy are reviewed. In particular, due to their value for future full-scale applications, the emphasis is given to continuous-flow reactor systems. The secondary goal of this review is to serve as a reference point for the new researchers in the field.

Keywords: Hydrothermal liquefaction, Bio-crude, Biomass, Microalgae, Macroalgae, Cyanobacteria, Municipal sludge, Biofuel, Thermochemical, Pretreatment, Biofuel, Wastewater treatment, Energy

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1 Introduction

Advancements in technology, human population growth, and economic developments have resulted in an increase in our energy demand[1]. Due to this increase, renewable energy studies and efficient valorization of energy sources have become prominent research topics within the sustainable development sphere. Over the last decades, biomass has been the focus of renewable fuel generation technologies. The current biomass to biofuel conversion processes, as we know it today, can be categorized into three main groups as direct combustion, thermochemical, and biochemical processes. Notably, one of the thermochemical conversion methods, hydrothermal liquefaction (HTL), has received much attention from researchers and the industry due to its significantly high potential for biofuel production and waste valorization.

Hydrothermal liquefaction is a biomass processing method performed in an aqueous environment, typically at a temperature between 200-374°C and pressure between 15-220 bars. The most significant advantage of the HTL process is that without the application of a drying process, it can utilize biomass sources with high moisture content such as algae, municipal sludge, lignocellulose, or organic fraction of municipal solid waste. Due to its broad range of substrate processing ability, HTL systems can be used for direct fuel production as well as waste valorization applications. In addition, lower reaction temperatures compared to the other thermochemical conversion methods and suitability for the utilization of alkaline catalysts decrease the risk of corrosion in HTL reactors.

Within a range of 1 to 60 minutes, the HTL process can convert biomass into bio-crude, which is a petroleum-like liquid that can be upgraded and used in petroleum refineries. Being highly polar, water can stay in liquid state up to a temperature of 373.94°C and pressure of 220 bar[2], and can act as a potent solvent due to its lowered dielectric constant at high temperatures. Being able to change the process temperature allows for the manipulation of the dielectric constant of water; thus, the severity of the hydrolysis process can be controlled[3]. Water's dielectric constant is 80.1 at 20°C and decreases below 20 at 300°C[4], making it a better solvent than commonly used solvents such as acetone, methanol, or ethanol. The HTL process mimics the natural occurrence of petroleum from biomass, which usually occurs over millions of years. However, simulating this natural process in such a short period results in a lower quality fuel (bio-crude) with 8-20% O_2 compared to petro-crude. This defect can be overcome with the application of fuel upgrading processes to bio-crude, such as hydrodeoxygenation. Along with biocrude, hydrochar, HTL aqueous, and gas phases are also being produced as coproducts in the HTL process.

Increasing interest in the HTL process has led to valuable literature published in this area. This review article aims to contribute to the existing literature to accelerate the development of this promising technology beyond research-based applications. Particular attention was given to the optimization of the HTL process conditions (reaction temperature, retention time, biomass solid content, type of biomass, and type of solvent) required to maximize bio-crude yield. Furthermore, the effects of catalysts, as another crucial parameter in the HTL process, are summarized under alkaline, acid, metal-based, and mineral catalyst sections.

2 Hydrothermal liquefaction

2.1 Hydrothermal liquefaction to date

The first hydrothermal liquefaction research was performed by Professor Ernst Berl in Darmstadt, Germany. His results in the 1920s indicated that bio-crude production from biomass in hot water with alkali catalyst was possible[5]. In 1933, he continued his HTL research at Carnegie Institute of Technology in Pittsburgh, Pennsylvania. In the 1940s, his research attracted significant attention due to his publications and magazine articles[6–10]. However, no significant progress was achieved until the petroleum fuel shortage in the late 1960s[11] when the Arab oil embargo in the mid-1970s[12] revealed the necessity of developing a sustainable fuel production process. In the 1970s and 1980s, the most important studies were performed by Pittsburgh Energy Research Center (PERC)[13], Lawrence Berkeley Laboratory (LBL)[14], Rust International Corporation[11] in the USA, and Shell Research Institute in the Netherlands. Pacific Northwest National Laboratory (PNNL) in Washington, USA, has been the pioneering research institute in the HTL field since 1990.

Although the early studies focused on liquefaction of wood, other types of substrates have also been considered in the investigation of HTL over time. While HTL of lignocellulosic biomass is still actively being studied, scientists mostly focus on waste plant material and energy crops instead of wood biomass. Since 2009, due to the algal biofuel technologies' increasing popularity, numerous HTL studies were performed to investigate algal bio-crude production on various microalgae, macroalgae, and cyanobacteria species. The number of HTL studies conducted between 2001-2019 is presented in Figure 1. While various HTL investigations continue at full speed, in recent years, municipal sludge HTL applications have increased due to the recent promising continuous-flow reactor designs with high heat recovery rates up to 80%[15]. Today, pilot-scale continuous-flow HTL systems around the world, foremost PNNL[16], Aarhus University[17], Aalborg University[18], Genifuel[19], New Mexico State University[20], and The University of Sydney[21], are carrying the process one step closer to full-scale application. The increasing number of HTL studies in the literature indicates that, especially in the wastewater treatment field, HTL process will continue to be a popular research field in the next decade. Furthermore, we may even witness the HTL process replacing anaerobic sludge digestion at wastewater treatment plants in the future.

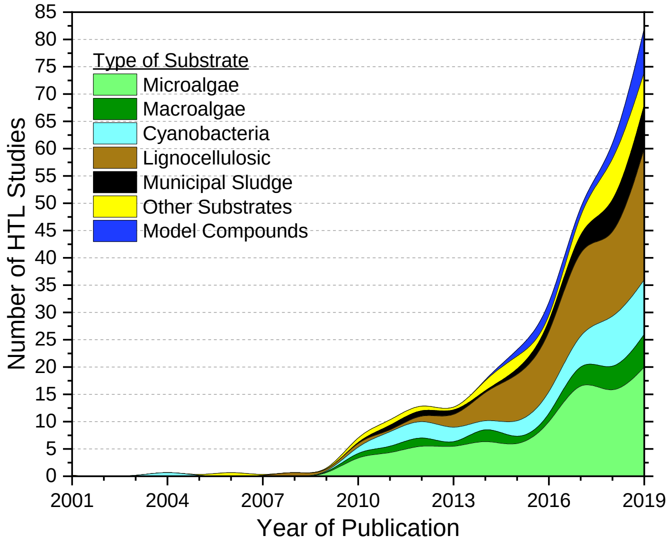


Figure 1. Research trend of HTL and types of substrates used in studies

2.2 Reaction pathways in HTL

Reaction pathways in HTL can be separated into three main groups: depolymerization (hydrolysis), decomposition, and recombination (repolymerization). Although many of the exact HTL reactions remain unclear due to the large number of organic compound types, studies in the literature were able to reveal some of the major pathways. Potential reaction pathways of HTL are summarized in Figure 2. The selectivity of these reactions can vary depending on pH, severity of HTL process (temperature, pressure, ramping and retention time), type and concentration of solvent, and type and concentration of catalyst.

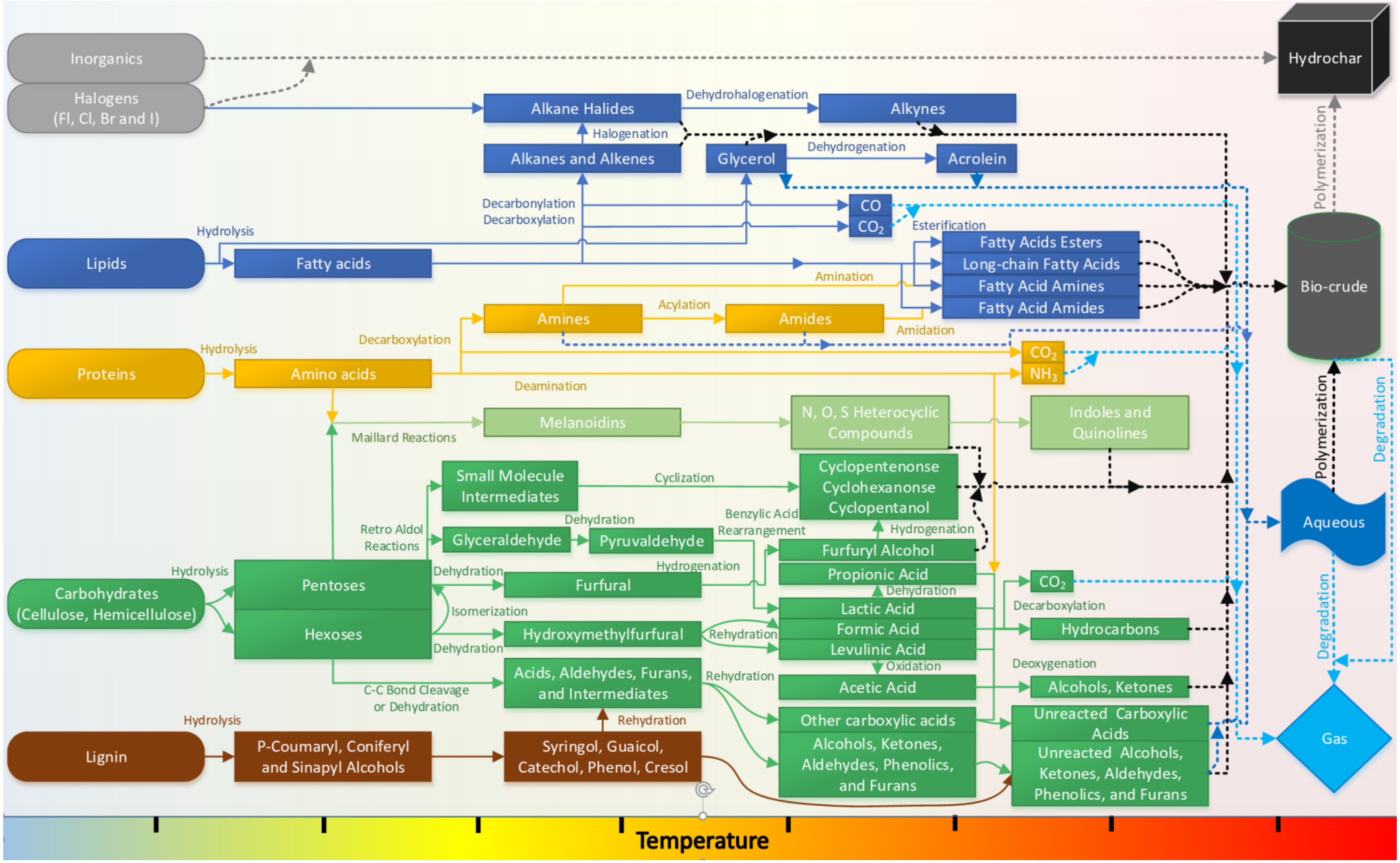


Figure 2. Potential hydrothermal liquefaction reactions and pathways[22–41]

In the HTL process, the Maillard reaction is one of the important recombination pathways for the production of bio-crude[42]. In Maillard reaction, carbonyl groups of reducing sugars react with the free amino groups of amino acids and form nitrogenous polymers and melanoidins[43,44], which contribute to bio-crude generation. This contribution was investigated by Qiu et al.[45] by using different ratios of leucine and glucose as HTL substrate. According to their findings, at 300°C and 4.2% solids concentration for 40 minutes, leucine and glucose resulted in 14% and 7% bio-crude yield, respectively. However, their mixture at 2:5 weight ratio (leucine: glucose) achieved up to 34% bio-crude yield under the same HTL conditions. Fan et al.[46] studied the effect of Maillard reactions on bio-crude yield at reaction temperatures of 250, 300, and 350°C. At 350°C, for lactose, maltose, lysine, lactose + lycin and maltose + lycin substrates, they measured 15.2%, 13%, 19.7%, 58% and 59.9% bio-crude yields, respectively. Tang et al.[47] also reported that at 280°C and 60 minutes retention time, the highest bio-crude yield was observed with a protein to glucose mixture ratio of 3:1 (wt.%). According to the findings in these studies, when carbohydrates or proteins alone are used as the substrate, they result in lower than 10% and 20% bio-crude yield, respectively. This highlights the importance of taking advantage of Maillard reactions to achieve higher bio-crude yields. Therefore, to reach an optimum bio-crude yield, the biomass needs to be balanced in terms of protein and carbohydrate content, or it can be co-liquefied with another balancing substrate.

In order to investigate the effect of HTL on model compounds, Lu et al.[48] studied HTL of soybean oil, soy protein, cellulose, xylose and lignin's binary, ternary, quaternary and quinary mixtures to reveal the effect of substrate composition on HTL products at 350°C for 30 minutes. For individual model compounds, they reported bio-crude yields of 82 wt% for lipids, 21.1 wt% for proteins, 4.6 wt% for cellulose, 6.6 wt% for xylose, and 1.4 wt% for lignin. For the binary mixtures, they reported yield increases for protein-carbohydrate and protein-lignin mixtures; and cellulose-xylose mixture was found to be ineffective for bio-crude production. A mixture of lipid and lignin showed an antagonistic interaction. The highest energy recovery was observed for the quinary mixture, underlining the importance of a balanced substrate in the HTL process to benefit from synergistic effects. Biller and Ross[49] used representative model compounds in HTL processes, such as albumin, asparagine, glutamine, soya protein for proteins, glucose and starch for carbohydrates, and sunflower for lipids. Similar to the other studies in the literature, they reported bio-crude yields of 86% for lipids, 23% for proteins, and 10% for carbohydrates.

According to the average biochemical compositions presented in Figure 3, microalgae and municipal sludge are the most suitable substrate types for taking advantage of Maillard reactions. Microalgae composition can vary depending on the species. Therefore, some species might not be suitable for the HTL process. On the other hand, municipal sludge has fewer varying characteristics, and its composition can be slightly adjusted by changing the primary and secondary sludge blending ratio. There are two main composition differences between the two sludge types. The first is the high protein content of secondary sludge that can be used for balancing the substrate composition to take advantage of Maillard reactions. The second is the high lipid content of primary sludge[50,51], which can be directly converted into bio-crude in the HTL process.

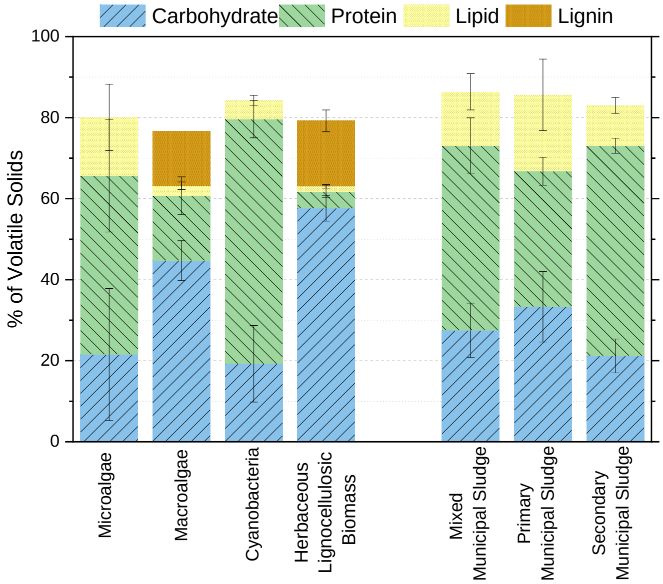


Figure 3. Biochemical composition distributions of microalgae[49,52–56], macroalgae[30,57], cyanobacteria[49,52,53,58,59], lignocellulosic[60,61], municipal sludge[62–64], primary and secondary municipal sludge[62,64]

Figure 3 also shows that macroalgae and lignocellulosic biomasses are carbohydrate-rich due to their cellulose and hemicellulose contents. This causes them to have a lower bio-crude yield compared to the other types of biomasses. Excessive organic acids form during the process and decrease the pH as a result of the HTL pathway of carbohydrates. Acidic conditions cause HTL reactions to favor hydrochar production rather than bio-crude. Therefore, to balance the pH, an alkaline catalyst needs to be used in HTL of macroalgae and lignocellulosic biomasses. Like microalgae, cyanobacteria biochemical composition also differs depending on the species. On average, cyanobacteria have high protein content and less lipid content compared to microalgae. This causes bio-crude production from cyanobacteria to mostly rely on Maillard reactions.

In summary, from the results of HTL studies on model compounds, lipids can be converted into bio-crude in high yields. Carbohydrates and proteins, on the other hand, need to be in a specific ratio to benefit from Maillard reactions. There are varying results in the HTL literature for the optimum ratio for carbohydrates and proteins. Therefore, revealing the optimum ratio is required to fill that gap in the literature either by using model compounds or co-liquefaction of substrates.

2.2.1 Depolymerization

Depolymerization (hydrolysis) reaction is the first step in the HTL process. In these reactions, lipids are broken down into fatty acids and glycerol, proteins are broken down into amino acids, and carbohydrates are broken down into monosaccharides[65]. No significant bio-crude forming occurs at this stage. If the severity of the HTL process is adjusted only for the depolymerization step, effluent can be used in fermentation processes to produce biofuels (i.e., methane, hydrogen, and ethanol). Depending on the substrate's characteristics, the level of HTL temperature required for depolymerization varies between 150-250°C.

Hydrothermal depolymerization is a widely investigated technology under the name of hydrothermal pretreatment. The technology is mostly used to increase the biodegradability of municipal sludge or enhance the hydrolysis of lignocellulosic biomass[66–68]. Most of the candidate substrates, such as woody and herbaceous plants, microalgae, macroalgae, cyanobacteria, and manure, contain lignocellulose in different ratios. Depolymerization of lignocellulosic biomass results in various pentoses and hexoses along with monolignols[32], as presented in Figure 4. Hydrolysis of lignocellulosic biomass. All the monosaccharides obtained from the hydrothermal depolymerization of lignocellulosic biomass are valuable platform chemicals[69] that have great potential in developing sustainable chemical and biofuel industries. In the HTL, these monosaccharides can contribute to bio-crude formation by reacting with amino acids. Lignin depolymerization products, monolignols, on the other hand, remain in the aqueous phase mostly in phenol and catechol forms[70]. Monolignols were found the contribute to bio-crude in HTL if a water – phenol mixture aqueous phase is used[71,72].

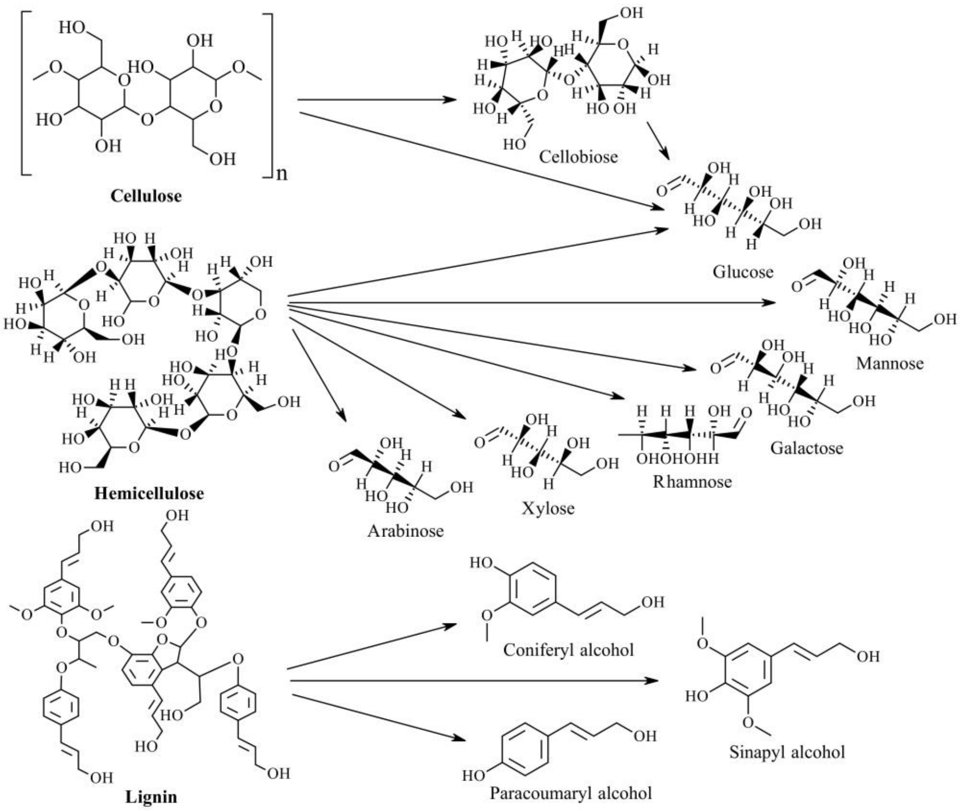


Figure 4. Hydrolysis of lignocellulosic biomass

2.2.2 Decomposition

Hydrolyzed smaller molecules go through several thermal decomposition reactions such as dehydration, decarboxylation, decarbonylation, deamination, dehydrogenation, and some bond cleavages due to high temperatures. The decomposition of different compound groups in HTL occurs at 180-340°C range[73]. In the HTL process, carbohydrates are the first group to start decomposing at 180°C. Over 200°C, proteins and lipids begin to decompose. For the total decomposition of proteins and lipids, 300°C and 640°C temperatures are required, respectively[74]. Since some lipids, such as long-chain fatty acids, are directly included in bio-crude, total decomposition of lipids is not required in the HTL process. Obtaining the highest efficiency in the HTL process is directly related to the balance of decomposition reactions. The intensity of HTL operating conditions should be high enough to allow organic compounds to decompose into bio-crude forming compounds, but at the same time, it should not be too severe to decompose bio-crude into gases. For wastewater treatment applications, decomposition reactions in the HTL process allow for treating most pharmaceuticals[75] and converting microplastics into bio-crude[76].

The first degrading group, carbohydrates, have several decomposition pathways ending with short-chain (volatile) fatty acids, basic alcohols, ketones, furan compounds, furanic acids, and furanic alcohols. Except for large furanic molecules, decomposition of carbohydrates does not contribute to bio-crude formation significantly. However, products of carbohydrate decomposition can form larger molecules in recombination reactions. Important carbohydrate decomposition pathways are summarized in Figure 5. Hydrothermal decomposition of carbohydrates Due to the formation of furanic compounds in the HTL, carbohydrate-rich substrates, such as lignocellulose and macroalgae, can form bio-crude and aqueous phase with higher oxygen percentages than the other substrates.

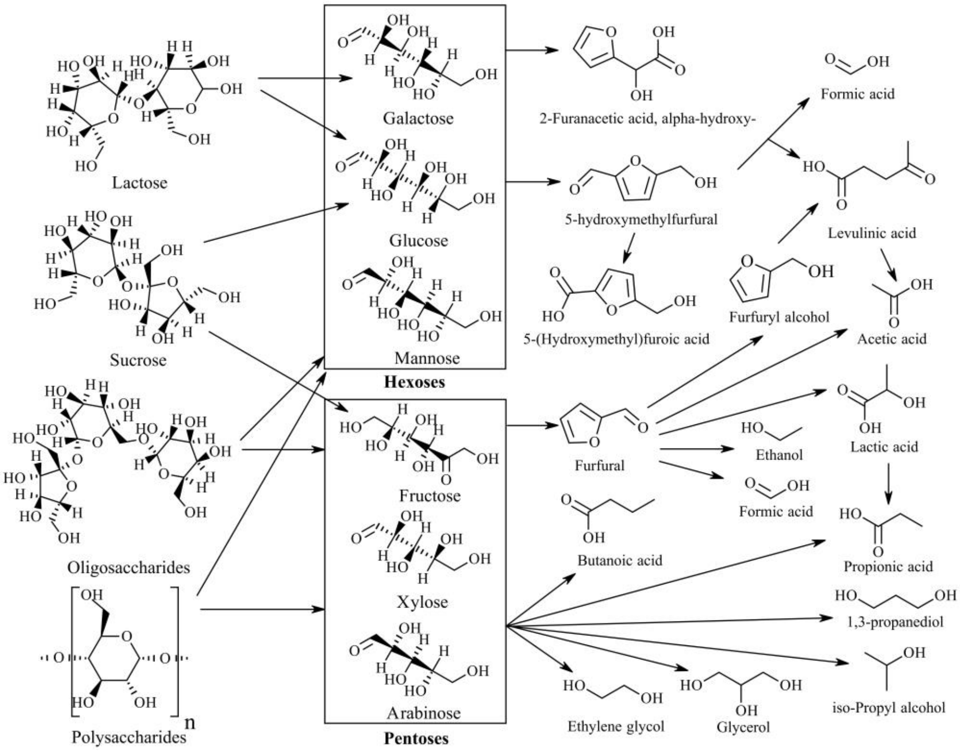


Figure 5. Hydrothermal decomposition of carbohydrates[77–79]

The second decomposing group in HTL is proteins. Protein decomposition pathways mostly consist of deamination and decarboxylation reactions of amino acids. Depending on the type of amino acid, decomposition temperature, reaction pathways, and products differ[80]. Amino acid deamination reaction is the primary source of ammonia in the HTL aqueous. Therefore, HTL aqueous phase of protein-rich substrates can have up to 16 g/L ammonia, causing pH levels over 8[81]. Protein decomposition end products are mostly simple amines, amides, aldehydes, short-chain fatty acids, and N-heterocyclic compounds. Like O-heterocyclic compounds (furan derivatives) in carbohydrate decomposition, large N-heterocyclic molecules are the only significant direct bio-crude contribution of protein decomposition. Decomposition reaction examples of some amino acids (indicated in red) are presented in Figure 6. Hydrothermal decomposition pathways of amino acids.

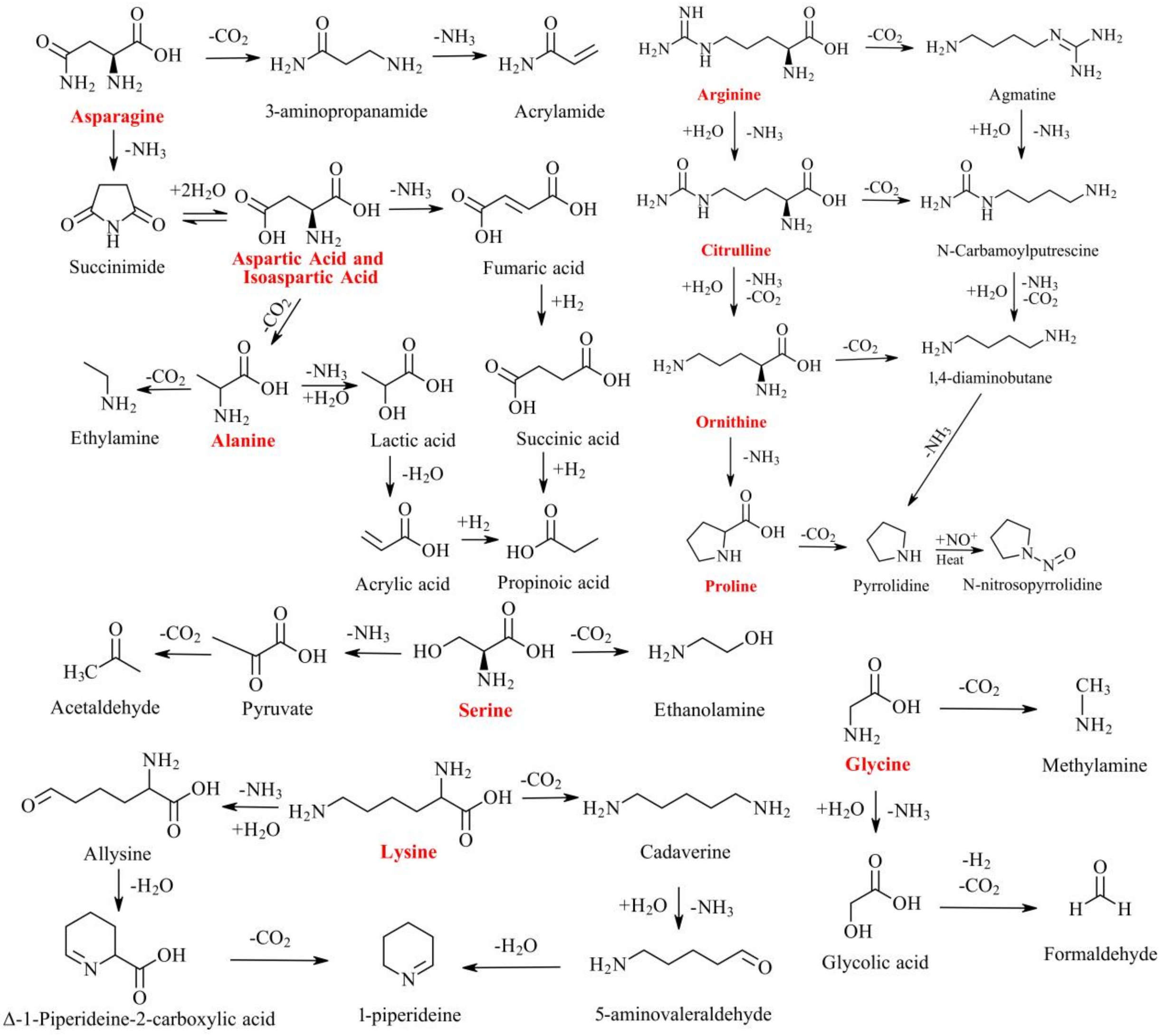


Figure 6. Hydrothermal decomposition pathways of amino acids[82–102]

In terms of pH, substrate's carbohydrate and protein amount should be in a specific ratio in the HTL so that decomposition products, carboxylic acids and ammonia, would balance each other. If the substrate is protein-rich, alkaline conditions can occur in the HTL, which is reported to be beneficial for bio-crude production[103]. On the other hand, in HTL of carbohydrate-rich substrates, such as lignocellulosic biomass, acidic conditions can promote the formation of hydrochar and lower the bio-crude yield[104].

The last decomposing group in HTL process is lipids. Lipids have the highest contribution to bio-crude production among biomass fractions due to their larger molecule sizes. This contribution occurs by the decomposition products of long chain fatty acids, alkanes, and alkenes. Due to the formation of phosphoric acid and long chain fatty acids, lipid decomposition can cause a pH drop. The majority of sterols also decompose thermally[105] into various smaller molecules, such as ketones and aldehydes, that can later go into recombination reactions. Lipid decomposition pathways are presented in Figure 7.

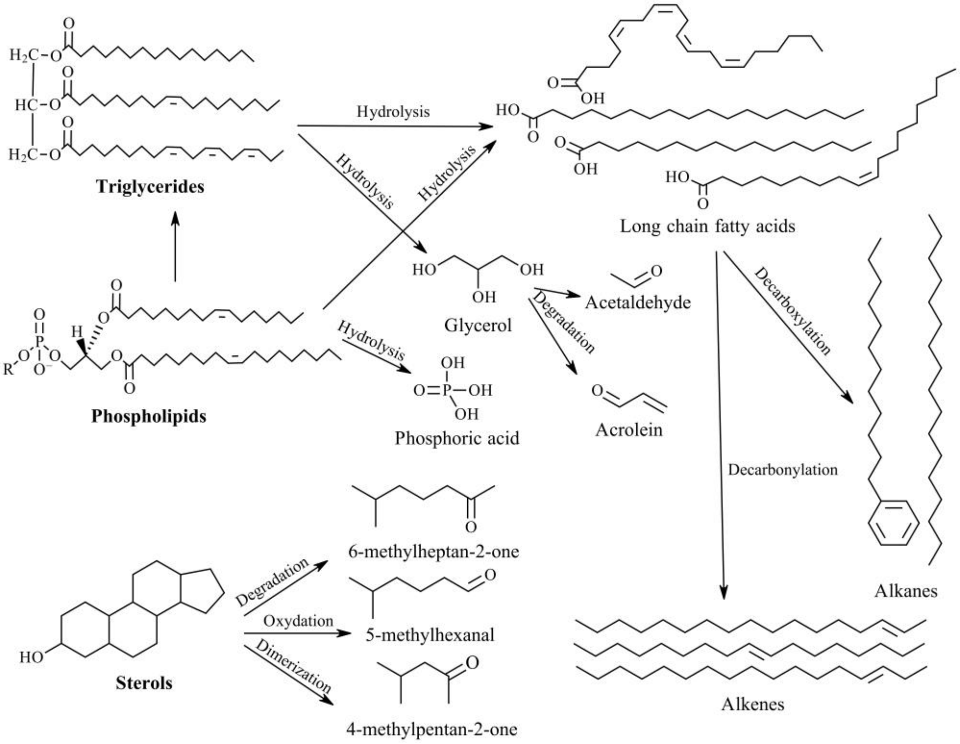


Figure 7. Lipid decomposition reactions[27,106–110]

2.2.3 Recombination

Various reactive fragments formed by the decomposition reactions start to recombine (repolymerize) above 300°C into bio-crude compounds[35]. Large molecules formed in these reactions contribute to bio-crude formation. Basic molecules, on the other hand, stay in the aqueous phase. Most of the organic molecule groups in bio-crude, such as aromatics, ketones, amides, amines, and esters, form in the recombination reactions of long-chain fatty acids. Also, complex alcohol molecules of bio-crude come from the hydration and cyclization reactions of alkenes. Examples of recombination pathways and products are given in Figure 8.

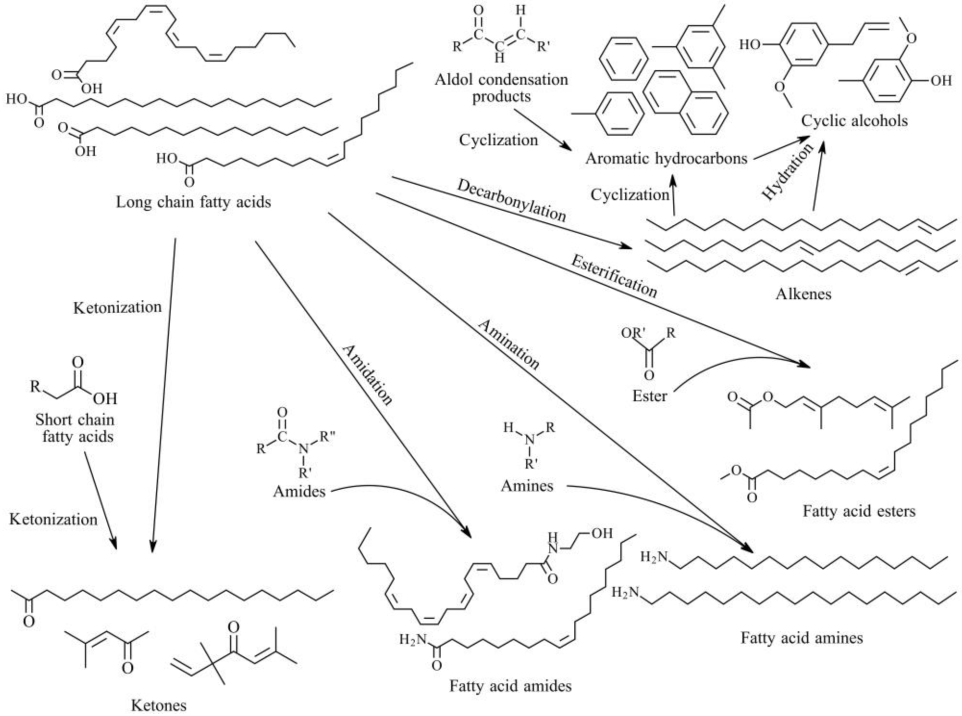


Figure 8. Recombination reaction examples in HTL[111–117]

One of the most important recombination reactions is the Maillard reaction taking place between reducing sugars and amino acids. In these reactions, reducing sugar's aldehyde group reacts with amino groups via the formation of Schiff's base and Amadori rearrangement[118]. Although it is referred to as one reaction, the Maillard reaction is actually a combination of reactions with complex pathways[119]. Although Maillard products, O and N heterocyclic compounds, decrease the quality of bio-crude due to the oxygen and nitrogen in their structures, the reaction is essential in terms of achieving higher carbon recovery in the bio-crude phase. The impurity caused by the Maillard reaction products can be treated in refineries prior to the distillation process. Studies performed on model compounds revealed that if Maillard reaction is not occurring in an HTL process, bio-crude yields obtained from carbohydrates and proteins were in the 7-18% range, while bio-crude yields up to 40% were reported when carbohydrates and proteins are used together in the HTL process[45,46]. Maillard reaction pathways are summarized in Figure 9.

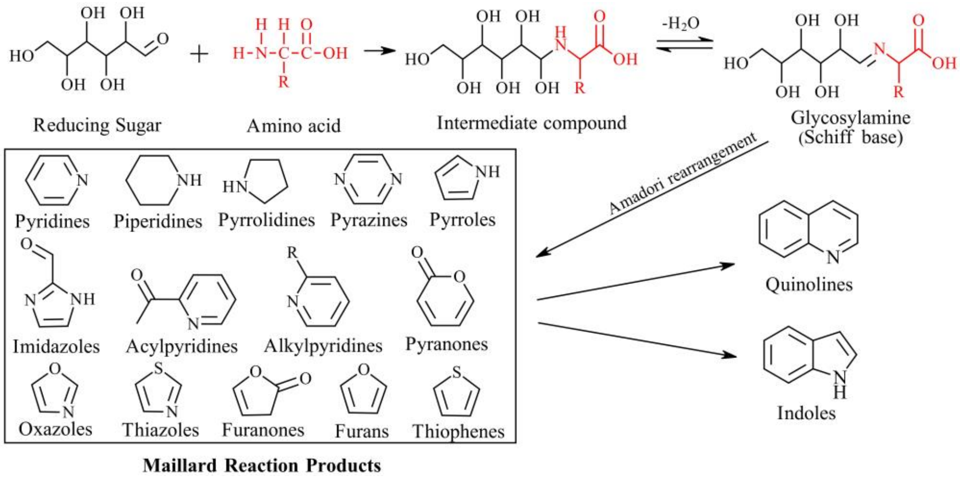


Figure 9. Maillard reaction pathway and products[120–123]

Recombining fragments also include some of the bio-crude compounds which form coke and contribute to hydrochar[124]. Coke formation can be minimized with the application of high pressurized H_2 during the recombination step[125]. At this point, severe HTL conditions can start secondary cracking of bio-crude and decrease the process efficiency.

3 HTL products

3.1 Bio-crude

Bio-crude is a dark brown, free-flowing[126], hydrocarbon-rich liquid obtained in the HTL process as the primary fuel product. When produced from renewable or waste biomass sources, it is accepted as a suitable and sustainable energy source replacement for fossil fuels[127]. Bio-crude contains saturated fatty acids, alkanes, alkenes, aromatic hydrocarbons, N and O heterocyclic compounds, ketones, alcohols, esters, amines, and amides. Concentrations of these organic compound groups in the bio-crude are highly dependent on carbohydrate, protein, and lipid composition of the HTL substrate, HTL process conditions, and bio-crude separation method. Examples for the compound groups that form bio-crude are presented in Figure 10.

Bio-crude is a renewable fuel that can be upgraded and used as a replacement for crude oil. It can be distilled into gasoline, jet fuel, diesel, naphtha[128], fuel oil, and a heavy fraction that can be used in engine lubricant production[129]. Contrary to fossil fuels, bio-crude based fuels lower the greenhouse gas emissions[130] owing to the carbon fixation occurring during the growth of biomass.

Therefore, it can be said that fuels obtained from bio-crude are environmentally friendly, whereas they are also renewable and sustainable due to their source, biomass.

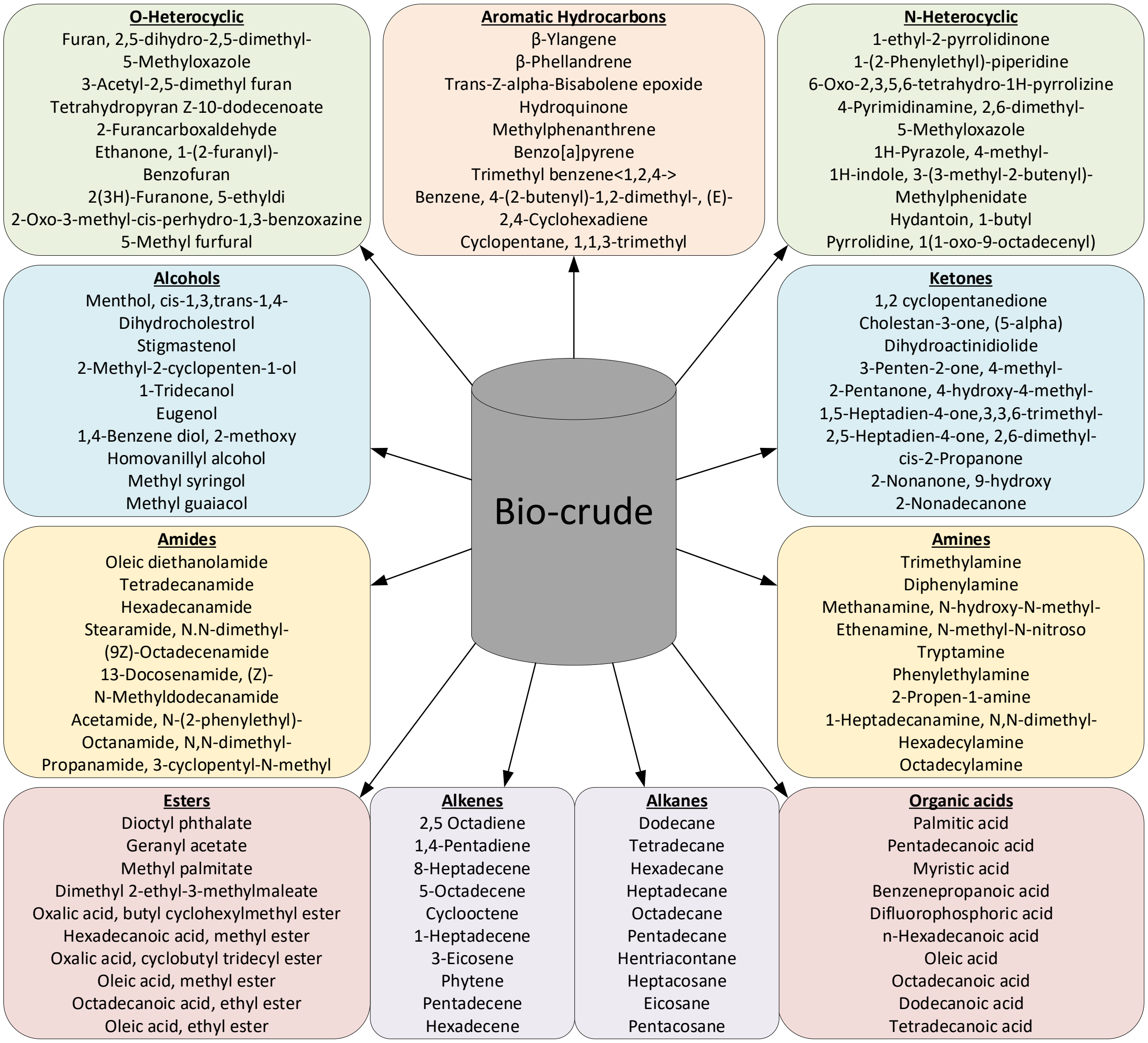
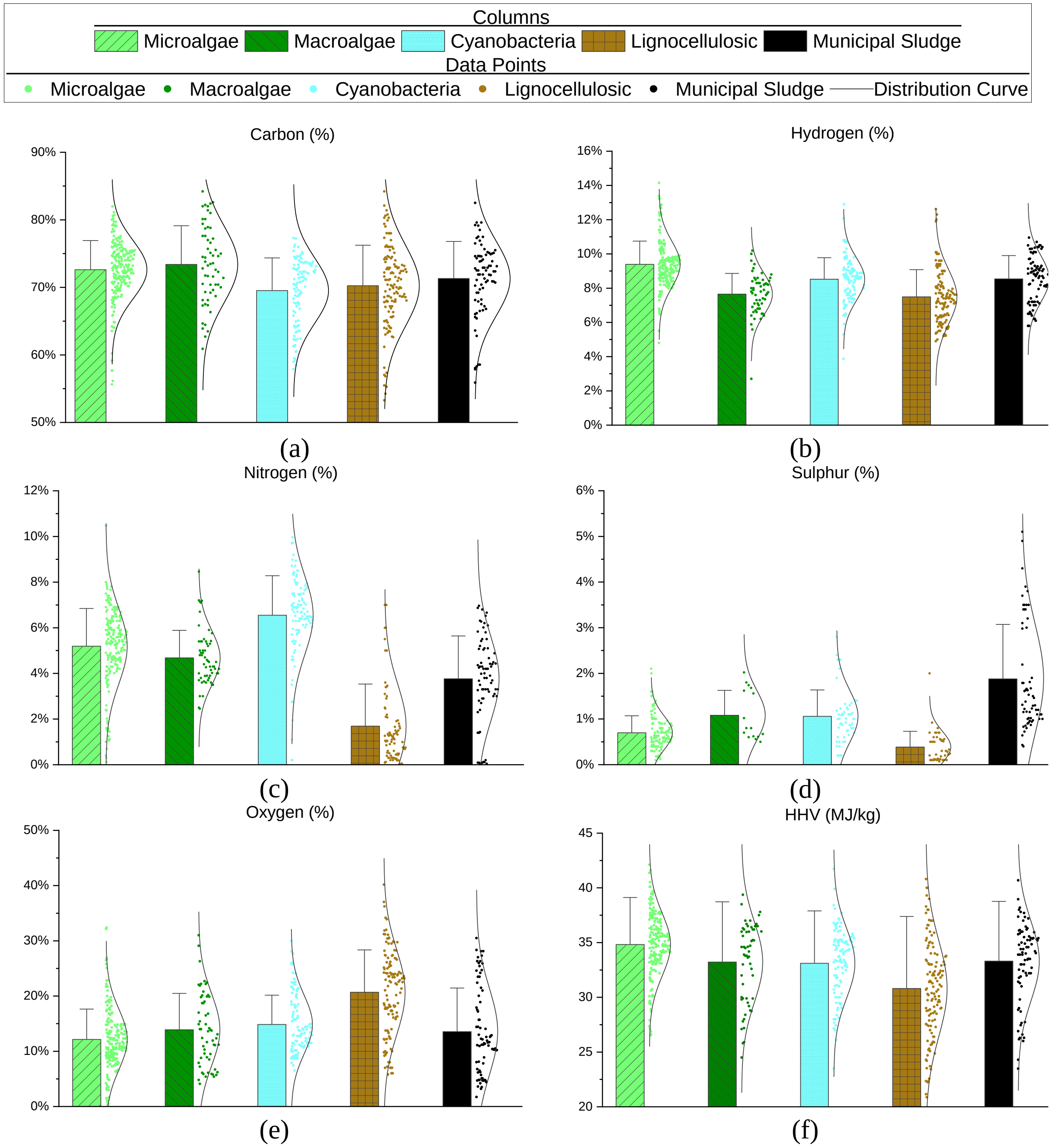


Figure 10. Organic compound groups that form bio-crude and example compounds[31,131–141]

Bio-crude is physically quite similar to crude oil; however, chemically it has some impurities which decrease its fuel quality, such as O-heterocyclic and N-heterocyclic compounds. In the HTL process, to achieve the best fuel quality possible, carbon and hydrogen are aimed to be maximized, whereas oxygen and nitrogen are to be minimized. The typical elemental composition for bio-crude is 60-78% carbon, 6-12% hydrogen, 2-6% nitrogen, 0-2% sulfur and 8-20% oxygen. The elemental distribution of bio-crudes derived from different substrates is presented in Figure 11 (a-e). One of the most important parameters for measuring bio-crude quality is the higher heating value (HHV), which can either be measured with a bomb calorimeter or calculated by the Dulong equation (Equation 1). In Equation 1, C, H, and O represent carbon, hydrogen, and oxygen content of bio-crude in percentage unit, respectively.

$$\mathrm{HHV}\left(\frac{\mathrm{MJ}}{\mathrm{kg}}\right) = 0.338\ \mathrm{C} + 1.428\ (\mathrm{H} - \frac{\mathrm{O}}{8}) \tag{1}$$



(a)

(b)

(c)

(d)

(e)

(f)

Figure 11. Distribution of (a) carbon, (b) hydrogen, (c) nitrogen, (d) sulfur, (e) oxygen, and (f) higher heating value of bio-crudes produced from various substrates[15,17,20,21,31,33,45,48,49,52,53,56,59,63,132,134–140,142–226]

The efficiency of HTL process can be calculated by the amount of bio-crude obtained at the end of the process by Equation 2. Although biomass to bio-crude conversion percentage is mostly used as an efficiency measurement in the literature, in some cases, this parameter can be misleading. Bio-crude yield may decrease as a result of recombination reactions above 300°C; however, reactions can lower the oxygen percentage of bio-crude and increase its HHV. On the other hand, energy recovery (ER) parameter, which can be calculated using Equation 3, represents both quality and quantity of bio-crude, which makes it more representative for the process efficiency measurement. ER should be used as the response of the process, especially for HTL modeling studies. HHV distribution of bio-crudes reported in the literature is given in Figure 11(f).

$$\text{Bio-crude yield } (\%) = \frac{\text{Dry mass of bio-crude}}{\text{Dry mass of substrate used}} \times 100 \tag{2}$$

$$\text{Energy recovery } (\%) = \frac{\text{Dry mass of bio-crude } \times \text{ HHV of dry bio-crude}}{\text{Dry mass of substrate } \times \text{ HHV of dry substrate}} \times 100 \tag{3}$$

There are five major substrate groups that were extensively studied as an HTL substrate in the literature: microalgae, macroalgae, cyanobacteria, lignocellulosic biomass, and municipal sludge. When the elemental composition of bio-crudes produced from these groups is evaluated in terms of carbon and hydrogen, it can be seen that they all have similar characteristics, which makes them valuable fuels with high HHV. According to nitrogen content, cyanobacteria bio-crudes visibly have a higher N profile, and lignocellulosic bio-crudes have a lower N profile. For oxygen, on the other hand, lignocellulosic bio-crudes have significantly high levels compared to other bio-crudes. Those nitrogen and oxygen content variations are directly related to the biochemical and elemental compositions of substrates. Most of the impurities in bio-crude caused by N and O are due to the heteroatoms being formed during HTL[227]. Although sulfur contents were found to be low for all bio-crudes, municipal sludge bio-crudes were found to have higher levels and large standard deviation due to the varying characteristics of substrates in the studies. This sulfur content may cause catalyst fouling in downstream processes, such as hydrodeoxygenation bio-crude upgrading[228].

The average HHV values indicate that microalgae is the most suitable HTL substrate in terms of bio-crude quality (Figure 11(f)). In contrast, lignocellulosic bio-crudes were found to have a vast diversity of HHV and, on average, the lowest fuel quality. Macroalgae, cyanobacteria, and municipal sludge bio-crudes were reported to have similar HHV. However, difficulties in growing and harvesting of microalgae and cyanobacteria[229] along with macroalgae being a food source make municipal sludge the best substrate for HTL. This is the main driver for the HTL conversion of municipal sludge to bio-crude in recent years.

In the literature, pyrolysis oil is also mentioned as bio-crude in some studies. Pyrolysis oil is another thermochemically produced renewable fuel that can replace fossil fuels[230]. However, compared with HTL bio-crude, pyrolysis oil has a higher water content (15-30%), higher oxygen percentage, and ignition complications[231]. Typical properties of pyrolysis oil and HTL bio-crude are given in Table 1.

Table 1. Fuel quality comparison of HTL bio-crude and pyrolysis oil

Parameters	Hydrothermal Liquefaction Bio-crude	Pyrolysis Oil[232,233]
Drying	Not required	Required
C%	46.1-84.2	32-49
H%	2.7-14.2	6.9-8.6
O%	1.7-40.2	44-60
N%	0-10.5	0-0.2
S%	0-5.1	0-0.05
HHV (MJ/kg)	16.5-42.5	16-19

After the HTL process, bio-crude can be separated either by physical methods or solvents. The most utilized method in the literature (mostly in batch-fed HTL studies) is to dissolve bio-crude in dichloromethane (DCM), separate it by centrifugation, and then evaporate the solvent for reuse. Bio-crude that is dissolved and separated from the liquid fraction and hydrochar are called light oil and heavy oil, respectively. Valdez et al.[234] investigated the solubility of bio-crude by different polar and non-polar solvents. They reported that the highest fraction of bio-crude dissolved was 39% by hexane or decane solvents, whereas it was only 30% for DCM. However, DCM solved bio-crude was found to have the highest carbon and hydrogen among seven solvents. Overall, decane was found as the best solvent to separate bio-crude. A similar study was done by Yan et al.[219] to investigate the efficiency of ten different solvents on bio-crude extraction. According to their findings, isopropanol was slightly more successful than DCM in extraction. Xu et al.[216] studied the effect of centrifugation and solvent extraction order on bio-crude recovery. They found that 43.7% bio-crude can be extracted if DCM is directly added to HTL effluent. However, a higher yield of 44.2% was reached by centrifuging the effluent first and then using solvent on both liquid and solid fractions separately. Mujahid et al.[191] also reported that the centrifugation-first approach increased the bio-crude extraction yield from 47% to 64%.

3.2 Hydrochar

Hydrochar is the solid co-product in HTL, and it is the main product of hydrothermal carbonization (HTC) process, which typically utilizes lower temperatures (150-280°C). Hydrochar in HTL process, also called solid residue, is formed by the recombination reactions of compounds in the aqueous phase and bio-crude. Along with recombination products, hydrochar also contains insoluble inorganics. Similar to bio-crude, hydrochar characteristics vary depending on the substrate and HTL conditions, and can consist of up to 80% inorganics[33]. Since bio-crude and hydrochar are formed from the same carbon sources, their yields are inversely proportional. According to the studies in the literature, hydrochar can be directly combusted for energy production, applied to soil for amendment and carbon sequestration, or activated for adsorption purposes[235]. Hydrochar also contains a decent amount of trace elements and phosphorus, which can be extracted for commercial use[236]. The valorization and/or safe disposal of hydrochar is one of the requirements to facilitate the sustainable development of HTL.

3.3 HTL aqueous

HTL aqueous stream contains both organic and inorganic residue compounds. Major organic compound groups in aqueous phase are carboxylic acids, alcohols, ketones, glycerol, aldehydes, phenolics, esters, ethers, amides, pyrazines, pyridines, and N&O-heterocyclic compounds[140,237,238]. Percentages of organic compound groups in HTL aqueous phases obtained from different types of substrates are presented in Figure 12.

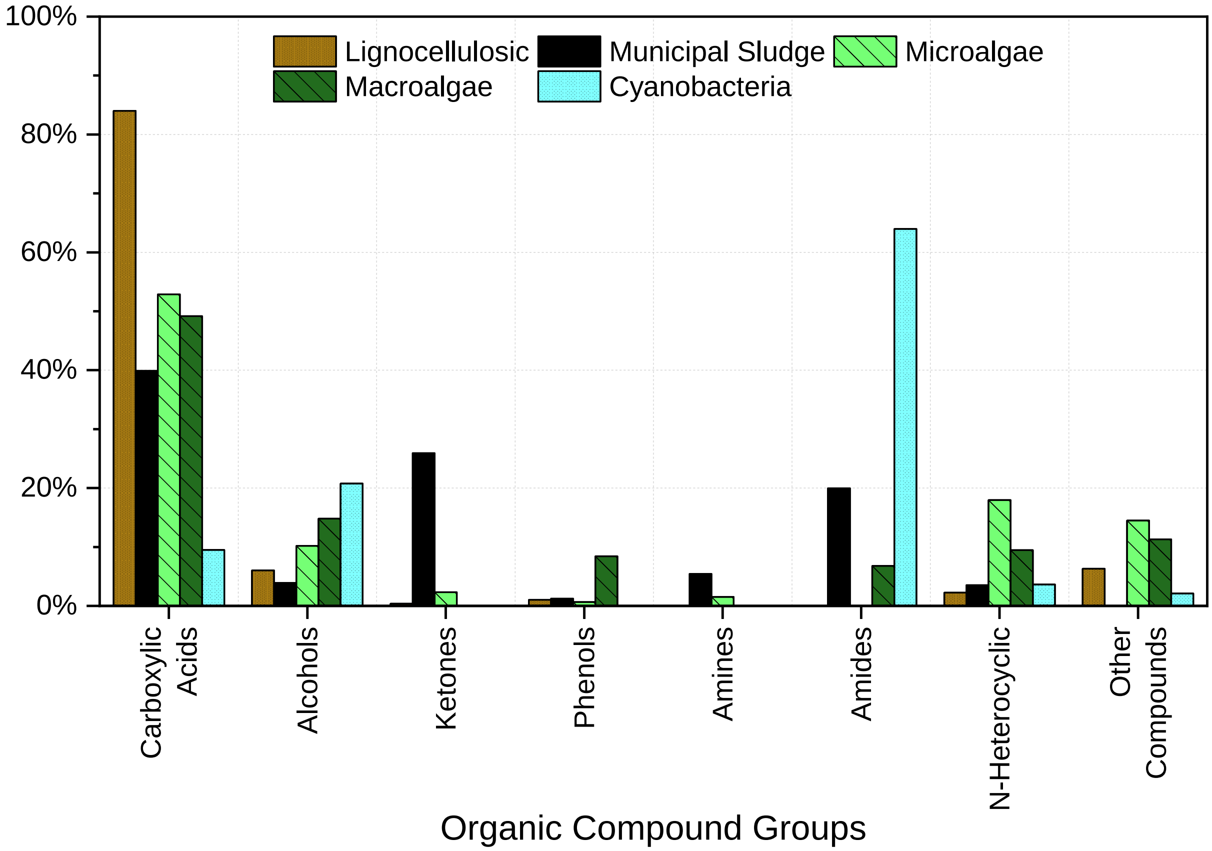


Figure 12. Distribution of organic compounds in HTL aqueous phase of microalgae[239], macroalgae[145], cyanobacteria[240], municipal sludge[241], and lignocellulosic biomass[242]

According to Figure 12, the most abundant organic compound group in the HTL aqueous phase is carboxylic acids, except for HTL aqueous of cyanobacteria. The amount of carboxylic acids in HTL aqueous is directly proportional with carbohydrate percentage of the biomass type due to HTL reaction pathways presented in Figure 2. Therefore, lignocellulosic biomass HTL aqueous was found to have the highest carboxylic acids due to its carbohydrate-rich cellulose and hemicellulose structure. For the same reason, HTL aqueous of macroalgae and some microalgae species also have high amounts of carboxylic acids. Cyanobacteria-based HTL aqueous, on the other hand, was found to be rich in amides as a result of the HTL reactions of lipids and proteins in its structure. HTL aqueous of municipal sludge has the most balanced distribution with carboxylic acids, ketones, amines, and amides as major compound groups. Substrates with high protein content cause an abundance of amides in the aqueous phase. A high amide amount in the aqueous phase indicates that the substrate can be co-liquefied with a carbohydrate-rich substrate to promote the Maillard reactions. Likewise, a substrate with a high carboxylic acid concentration in the aqueous phase can be co-liquefied with a protein-rich substrate to obtain a higher bio-crude yield.

Due to deamination reactions of proteins, ammonia concentration is also high in the aqueous phase. Similar to hydrochar, HTL aqueous is also a suitable medium for nutrient recovery. Ovsyannikova et al.[243] reported that the authors reached 99% P, 79.4% NH_4-N, and 66.5% P, 19.4% NH_4-N recovery by precipitation from HTL aqueous of municipal sludge and *Spirulina*, respectively. On the other hand, Garcia Alba et al.[239] investigated *Desmodesmus* sp. growth in HTL aqueous phase and reported growth reduction in HTL aqueous. Chen et al.[244] also found that even in 100 times diluted HTL aqueous, *Chlorella vulgaris* growth was reduced by 47% due to toxicity. In the study by Das et al.[245], they found that it is possible to grow *Tetraselmis* sp. in HTL aqueous if it is diluted enough to provide 50% of nutrients.

Anaerobic digestion is another valorization method for the HTL aqueous stream. However, according to the study by Zhou et al.[246], HTL aqueous (104 g chemical oxygen demand (COD)/L) inhibits the batch anaerobic digestion process in mesophilic conditions (37°C) when its volume exceeds 13.3% of the reactor liquid volume. Chen et al.[247] reported that in up-flow anaerobic sludge blanket systems that were being fed with HTL aqueous (2.5 g COD/L d), 61.6% and 45% of the COD caused by HTL aqueous (10 g COD/L) were digested under mesophilic and thermophilic conditions, respectively. They also emphasized that it was not possible to digest phenolic compounds, furans, and pyrazines in up-flow anaerobic sludge blanket system. On the other hand, it is known that digesting low concentrations of those compounds in batch anaerobic reactors is possible[248,249]. Elliott et al.[164,165,185] suggested catalytic hydrothermal gasification (CHG) treatment for converting organic compounds in HTL aqueous into combustible gasses. Xu et al.[250] also followed the same approach and found that some N-containing compounds are difficult to be gasified. According to the study by Cherad et al.[251], it is possible to produce sufficient H_2 gas from CHG of HTL aqueous for hydrodeoxygenation fuel upgrading of bio-crude. Recycling HTL aqueous back to HTL process or headworks of a wastewater treatment plant is another option. Ramos-Tercero et al.[201], Biller et al.[157], and Shah et al.[205] found that recycling aqueous phase up to six times in HTL increases energy recovery of the process. However, Shah et al.[205] also stated that the nitrogen content of bio-crude was increased by 55% after the sixth recycle.

Treatment of HTL aqueous with a microbial fuel cell is another topic of research interest. The valorization alternatives of aqueous phase were reviewed in detail by Watson et al.[81].

In terms of widely available and sustainable feedstock and bio-crude yield, one of the best options for the HTL process is to use municipal sludge as substrate by coupling the HTL plant with a wastewater treatment plant. In this configuration, HTL aqueous can be treated by returning it to the headworks of wastewater treatment plant. However, the exact effects of inhibitory aromatic compounds and high concentration of ammonia in the HTL aqueous on wastewater treatment processes are still unclear. Although carboxylic acid concentration can be tolerated due to the dilution with incoming wastewater, high nitrogen concentration of HTL aqueous can affect the biological treatment processes applied in the mainstream by bringing an extra load to the nutrient removal process. If the nutrient removal capacity of the biological treatment process is not sufficient for treating that extra load, nitrogen accumulation may occur in the plant. Zhuang et al.[252] reported that in the HTL aqueous of municipal sludge, organic nitrogen is converted into ammonium (NH_4^+) by increasing the temperature, whereas no significant change was observed on nitrite (NO_2^-) and nitrate (NO_3^-) concentrations. In their study, the ammonium concentration in the aqueous phase was found to be 2500 mg/L at 300°C and 30 minutes HTL condition. Xu et al.[139] also reported a 2210 mg/L ammonia concentration in HTL aqueous phase of municipal sludge processed at 340°C. Ammonia is mostly formed in the deamination reactions of amino acids. Therefore, compared to the HTL aqueous of primary sludge, secondary (biological) sludge HTL aqueous has a higher ammonia concentration due to its higher protein content. In a continuous-flow HTL system working at 350°C, Maddi et al.[241] found 3680 mg/L and 5700 mg/L ammonia concentrations in HTL aqueous of primary sludge and secondary sludge, respectively.

Besides the aerobic or anaerobic treatability of HTL aqueous, its possible effects on settling and UV disinfection units when it is returned to headworks of wastewater treatment plant should also be considered. In the literature, there are no studies investigating the effect of blending HTL aqueous to wastewater on settling and UV disinfection processes. As mentioned above, HTL aqueous contains a wide variety of organic molecules. Many of the organic compounds in HTL aqueous was reported to be inhibitors for anaerobic consortium[246], microalgae[155,253], or even mammal cells[254]. These inhibitors might also change the microbiological structure of wastewater and cause a decrease in settling efficiency. Furthermore, an increase in the concentration of some compounds, which has a high adsorption capacity at 254 nm, such as phenol[255] or melanoidins, can lower the UV disinfection process yield.

3.4 Gases

Gases in the HTL process are mainly produced in decarboxylation, decarbonylation, and deamination reactions. At reaction temperatures over 350°C and 340°C, respectively, water-gas shift[256,257] and methane forming reactions[73,258] also occur and produce H_2 and CH_4. The gaseous phase contains mainly CO_2, which is around 80-95%[200,204]. Typical HTL gas composition is given in Figure 13. The CO_2 content of the gaseous phase can be as high as 97%. Zhang et al.[259] suggested that HTL gaseous phase can be used in algae growth due to the high CO_2 content.

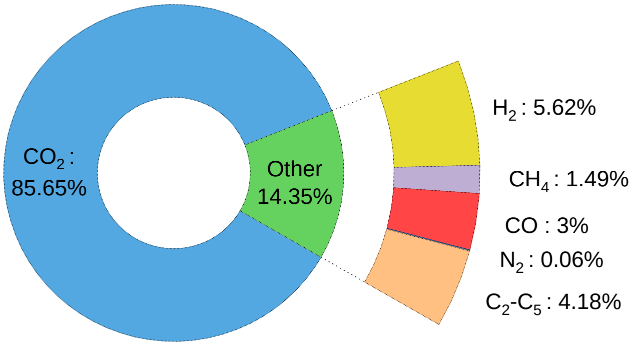


Figure 13. Typical composition of HTL gaseous phase at 350°C[134,179,251]

HTL gaseous phase can also include small quantities of light hydrocarbons, such as ethane, ethylene, propene[58], isobutane, n-butane, 1-butane, isopentane, and 1-pentene[187]. Although these gases are generally in low concentrations, Wagner et al.[58] reported that in HTL of a polyhydroxy butyrate (PHB) producing cyanobacteria, *Synechocystis cf. salina*, it is possible to generate propylene gas with a 2.6% yield along with bio-crude.

4 Effect of process parameters on bio-crude yield and quality

Product yield and quality vary in HTL processes, mainly depending on the reaction temperature, retention time, heating rate, type of biomass, solid content, type of solvent, catalyst type, and catalyst concentration. This product variation is caused by the effect of reaction contents and conditions on the complex kinetics of HTL reactions presented in Section 2.2. In order to evaluate the parameter effect on HTL, studies in the literature using different reaction temperatures, retention times, substrate types, and solid contents are summarized in Table 2.

Table 2. Batch HTL studies performed with water as solvent and without catalyst

HTL contents		HTL conditions			
Substrate	Substrate to solvent ratio (w:w)	Reaction temperature	Retention time	The highest bio-crude yield (%wt)	Reference
L. digitata *L. hyperborea* *L. saccharina* *A. esculenta*	8:30	350°C	15 min	17.6% 9.8% 13% 17.8%	151
Dried sewage sludge	1:2	250-400°C	60 min	52% at 350°C	133
Food waste	3:20	240-295°C	0-30 min	27.5% at 240°C, 30 min	260
C. vulgaris *S. dimorphous* *S. platensis* *C. fritschii*	1:10	300, 350°C	60 min	46.6% at 300°C 35.8% at 350°C 35.5% at 300°C 38.6% at 300°C	155
Nannochloropsis sp.	1:20	200-500°C	60 min	43% at 350°C	134
Eight types of green landscaping waste	1:10	300°C	30 min	Leaves: 41% for *D. racemosum* Branches: 51% for *C. camphora*	261
Microwave pretreated municipal sludge	3:20	340°C	30 min	35.4%	159
Mixed-culture algal biomass	1:4	260-320°C	0-90 min	49.9% at 300°C, 60 min	33
N. salina *G. sulphuraria*	1:20-1:10	310-350°C	5-60 min	59.1% at 310°C, 60 min, 1:20 ratio 31% at 350°C, 30 min, 1:20 ratio	55
G. sulphuraria 5587.1 *G. sulphuraria* SOOS	1:20-1:10	310-350°C	5-60 min	18.2% at 330°C, 60 min, 1:20 ratio 23% at 350°C, 5 min, 1:20 ratio	262
Arthrospira platensis rsemsu 1/02-P	3:10	270-330°C	0 min	45.7% at 330°C	263
Mixed culture of *C. sorokiniana, C. minutissima,* S. bijuga	7:32	350°C	60 min	26.7%	160
Tetraselmis sp.	3:17	325, 350°C	30-60 min	51.2% at 350°C, 30 min	245
Natural hay, oak wood, walnut shell, cellulose	1:5	240, 320°C	30 min	25% for walnut shell	161
Spirulina sp. *Tetraselmis* sp.	4:25	300-350°C	5 min	42% at 350°C 58% at 350°C	163
Desmodesmus sp.	3:40	300°C	5 min	40%	239
Desmodesmus sp.	2:25	175-450°C	5-60 min	49.4% at 375°C, 5 min	167
Mixture of *C. sorokiniana* DBWC2 *Chlorella* sp. DBWC7 *K. pneumoniae* ORWB1 *A. calcoaceticus* ORWB3	3:20	310°C	55 min	15%	264
Chlorella sp. FC2	1:10	350°C	60 min	14.72%	265
Arthrospira platensis	3:10	270°C	80 min	34.6%	169
Cyanophyta	1:20-3:10	320-370°C	10-70 min	39.54% at 370°C, 50 min, 1:10 ratio	170
Oil Mill Wastewater	3:25	240-300°C	15-45 min	58% at 280°C, 30 min	137
Nannochloropsis sp. *Sargassum* sp.	3:20	260-340°C	30 min	54.11% at 320°C 9.49%. at 340°C	30

Raw empty fruit bunch Palm mesocarp fiber Palm kernel shell	1:10	330-390°C	30-240 min	38.24% at 390°C, 120 min 34.32% at 390°C, 60 min 38.53% at 390°C, 60 min	266
Nannochloropsis sp.	3:20	100-400°C	0.16-60 min	Model prediction: 46% at 230°C	267
Chlamydomonas reinhardtii	7:50	220-310°C	60 min	58.7% at 310°C	175
Cyanobacteria sp., *Bacillariophyta* sp.	1:10	250-350°C	15-90 min	21.10% at 325°C, 45 min 18.21% at 325°C, 60 min	176
Spirulina platensis	1:5	350°C	60 min	40.7%	178
Animal by-products	1:1-1:5	150–290°C	5-15 min	74% at 250°C	268
Nannochloropsis sp., *Chlorella* sp.	3:20-1:4	220–300°C	30-90 min	55% at 260°C, 60 min, 1:4 ratio 82.9% at 220°C, 90 min, 1:4 ratio	184
Manure from six different animal species	1:5	310–340°C	30 min	30.85% at 340°C for swine manure	269
N.gaditana *S.almeriensis*	1:10	350°C	15 min	60% 57.7%	138
Spirulina platensis Miscanthus Primary municipal sludge	1:20-1:4	250-350°C	5-31 min	Model predictions: 40% at 300−320°C, 16−18 min, 1:5 46.9% at 330°C, 10 min, 3:20 42.3% at 320°C, 18 min, 3:20	270
α-cellulose Xylan Soy protein Sunflower oil Starch Lignin Food waste Garden waste Paper waste	1:1	260-300°C	20 min	3% at 300°C 97% at 300°C 22% at 300°C 95% at 260°C 3% at 300°C 34% at 300°C 79% at 280°C 33% at 300°C 74% at 280°C	271
Chlorella sorokiniana	1:12-1:3	Direct HTL: 220-300°C Sequential HTL: 220-320°C	5-60 min	30% at 240°C, 20 min, 1:9 ratio	188
Domestic sewage sludge (DSS) *Monoraphidium* sp. (KMC4) Mixture of KMC4 to DSS (3:1 ratio)	1:10	275-350°C	15-60 min	22% at 350°C, 30 min 33% at 325°C, 30 min 39.6% at 325°C, 45 min	190
Dewatered sewage sludge	13:100	300-400°C	30-120 min	64% at 325°C, 30 min	191
Four species of marine and two species of freshwater microalgae	1:15	330-341°C	5 min	Freshwater species: 26.2% for *Oedogonium* Marine algae species: 19.7% for *Derbesia*	194
Lipid Carbohydrate Lignin Protein	3:10	250-350°C	0-60 min	100% at 250°C. 0 min 42.83% at 350°C, 0 min 37.27% at 300°C, 0 min 4.4% at 250°C, 0 min	272
Mixture of lipid, carbohydrate, lignin, and protein	3:10	250-350°C	5-60 min	~30% at 350°C, 30 min	141
Gracilaria gracilis	1:10	350°C	15 min	15.7%	196

Cladophora glomerata				16.9%	
Chlorella vulgaris	11:100	220-265°C	30 min	42.2% at 240°C for the sixth time recycling of HTL aqueous	201
Nannochloropsis gaditana *Chlorella* sp.	1:10	180-330°C	30 min	47.5% at 300°C 32.5% at 275°C	54
1:1 Water hyacinth-Para grass mixture	1:6	260-300°C	15 min	13.34% at 280°C	273
Lipid extraction residue of of *Dunalliela* sp.	4:25	350°C	60 min	11.81%	274
Rice straw	1:6	280-320°C	15 min	17% at 280°C	275
Spirulina *Chlorella* *Enteromorpha prolifera* *Nannochloropsis* sp. *Dunaliella salina* *Euglena* *Cyanophyta*	1:4	280-350°C	30 min	32.5% at 350°C 37.5% at 350°C 27% at 280°C 37% at 280°C 17% at 350°C 29% at 350°C 30.5% at 280°C	52
Nannochloropsis *Spirulina*	1:10	220-300°C	60 min	41% at 280°C 33.3% at 260°C	208
Mixed algae	1:10-1:5	260-340°C	30-90 min	8.4% at 300°C, 60 min, 1:5 ratio	209
Corn straw Peanut straw Soybean straw Rice straw	3:8	320°C	60 min	7.9% 14.6% 15.8% 15.1%	276
Nannochloropsis salina *Spirulina platensis*	1:3	220-375°C	10-30 min	46% at 310°C, 30 min 38% at 350°C, 30 min	53
Nannochloropsis sp.	1:20-7:20	250-400°C	10-90 min	50% at 300°C, 10-20 min	277
Spirulina Swine manure Digested anaerobic sludge	1:5	300°C	30 min	32.6% 30.2% 9.4%	59
Raw *Scenedesmus,* Defatted *Scenedesmus* *Spirulina*	1:5	300°C	30 min	45.4% 36.5% 31.2%	211
Arthrospira platensis	3:10	270-300°C	80 min	32.6% at 330°C	212
Amphora sp. *Spirulina* sp. *Tetraselmis* sp.	4:25	350°C	5 min	55% 50% 66%	213
Spirulina, *Synechococcus/Anabaena* *Synechocystis* Soybean Rapeseed oil Cornflour Polyhydroxy butyrate	4:25	300-360°C	0 min	36.9% at 340°C 31.2% at 340°C 16.6% at 340°C 28% at 360°C 100% at 320-360°C 3% at 340°C 8% at 300°C	58
Secondary sewage sludge	1:10	260-350°C	10 min	22.9% at 340°C	139
Nannochloropsis sp.	7:50	350°C	20 min	43.9%	216
Chlorella Sewage sludge Mixture (1:3,1:1,3:1)	1:10	340°C	30 min	22% 24% 26.8% for 1:1 mixing ratio	217
Duckweed (*Lemna minor*)	1:3	350°C	30 min	26% by isopropanol extraction 24% by dichloromethane extraction	219
Animal carcass	1:20-1:5	230-350°C	10-80 min	55.6% at 320°C, 60 min, 1:10 ratio	221
Spend coffee grounds	1:20-1:5	200-300°C	5-30 min	35.29% at 275°C, 10 min, 1:5 ratio	222
Chlorella pyrenoidosa	1:5	100-300°C	0-120 min	39.5% at 280°C, 120 min	278
Spirulina platensis	1:10	280-350°C	10-60 min	19.74% at 315°C, 35 min	143

Lemon peel Mixture (0-4:0-4)				7.24% at 315°C, 35 min 26% at 336°C, 35 min, 4:1 blending	
Enteromorpha prolifera	3:17	300°C	30 min	17.8%	279
Swine manure Sewage sludge 11 algae species	1:5	280°C	30 min	33% 32% 35% for *Chlamydomonas*	259
Dunaliella tertiolecta	1:40-7:40	300-380°C	10-90 min	36.9% at 360°C, 30 min, 1:10 ratio	148
Sargassum tenerrimum	1:6	260-300°C	15 min	16.33% at 280°C	280
Macroalgal mix	1:5	305-350°C	0 min	16% at 345-350°C	281
Sargassum tenerrimum	1:6	260-300°C	15 min	16.33% at 280°C	282
Ulva prolifera	1:6	200-310°C	10-30 min	12% at 290°C, 10 min	283
Human feces	1:20-1:4	260-340°C	10-50 min	34.44% at 340°C, 10 min, 1:4 ratio	284
Corn stover	1:6	250-375°C	0-60 min	42.61% at 300°C, 0 min	285

According to the result summary of HTL studies performed without catalyst in Table 2, in varying HTL conditions, the average bio-crude yields for microalgae, macroalgae, cyanobacteria, lignocellulosic and municipal sludge were 35.3%, 17.5%, 28.7%, 26.9%, and 39.4%, respectively. The two lowest average bio-crude yields, which belong to lignocellulosic and macroalgae substrates, indicate that due to the HTL pathways of carbohydrate-rich biomasses, the application of an alkaline catalyst is crucial to reach higher bio-crude yields. In HTL of carbohydrate-rich biomasses, volatile fatty acids can accumulate and decrease pH. As indicated by Elliot et al.[286], acidic conditions in HTL favors hydrochar generation instead of bio-crude.

Due to different reactor types, ramping times and substrates used in these studies, it is not possible to determine an optimum HTL condition for maximum biocrude yield. For the determination of optimum conditions, substrate-specific studies with a wide-range experimental design are required. In Table 2, it can be clearly seen that the optimum HTL conditions and biocrude yield results are highly dependent on the substrate type. Among the most investigated five substrate types, municipal sludge studies reported the highest bio-crude yields. This trend is consistent with biochemical compositions and HTL reaction pathways, as discussed in Section 2.2.

4.1 Type of biomass

As one of the most significant advantages of the HTL process, there is no limitations or pretreatment requirement for the types of substrate that are processed. Regardless of the moisture content and structure of organic substrate, it is possible to produce bio-crude with diverse quality and quantity. In the literature, microalgae, macroalgae, cyanobacteria, lignocellulosic biomass, and municipal sludge are the most studied HTL substrates. There are also studies that investigated the

HTL of manure, food waste, slaughterhouse waste, and organic fraction of municipal solid waste[59,195,221,225,242,260,268,269,287].

To compare the bio-crude quality obtained from the five most promising HTL substrates, a van Krevelen diagram was created from the reported bio-crude data and presented in Figure 14. According to the diagram, macroalgae have the closest bio-crude quality to crude oil, assessed by hydrogen to carbon (H/C) and oxygen to carbon (O/C) atomic ratios. However, as shown in Figure 16, macroalgae substrates also have the lowest bio-crude yield. When both bio-crude quality and quantity are evaluated, it can be seen that municipal sludge and microalgae are the most promising substrates. Figure 14 also reveals that, regardless of the substrate type, application of a bio-crude upgrading process can be necessary to lower the oxygen percentage of bio-crude and reach the fuel quality of crude oil.

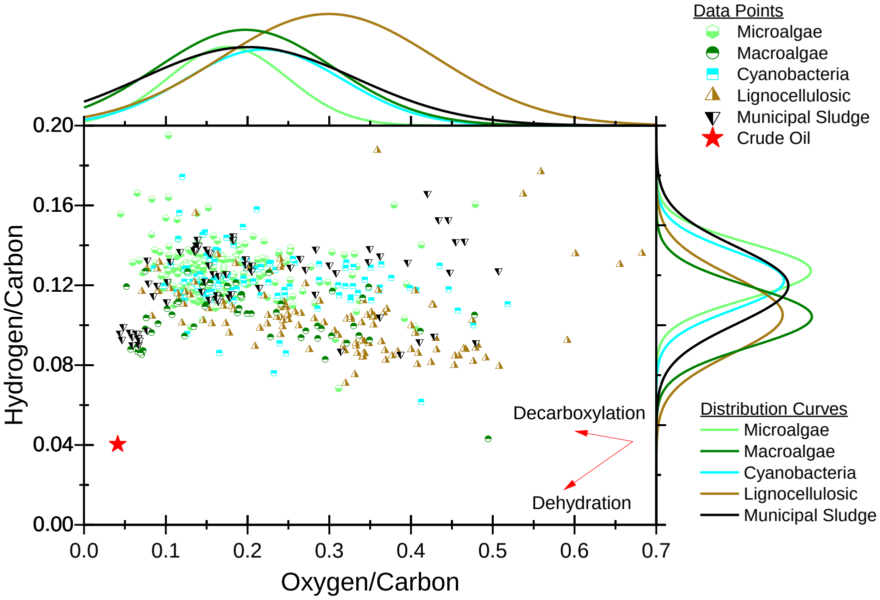


Figure 14. van Krevelen diagram of bio-crudes produced from different substrates in the literature[15,17,20,21,31,33,45,48,49,52,53,56,59,63,132,134–140,142–226]

In the literature, comparative studies on HTL of cyanobacteria, lignocellulosic biomass, and municipal sludge were performed to determine the effect of substrate type on bio-crude yield. For HTL at 350°C and 20 min conditions, Huang et al.[63] found 39.46%, 34.51%, and 21.14% bio-crude yields for municipal sludge, *Spirulina*, and rice straw, respectively. In a similar study, Anastasakis et al.[15] reported yields of 32.9% for *Spirulina*, 26.2% for *Miscanthus*, and 24.5% for municipal sludge in a continuous-flow HTL system. Furthermore, by using the same substrates, Madsen et al.[270] found 40%, 46.9%, and 42.3% bio-crude yields for *Spirulina*, *Miscanthus,* and municipal sludge, respectively, by optimized process conditions using a statistical method.

4.2 Reaction temperature, retention time, and pressure

Undoubtedly, reaction temperature and retention time have the most significant effect on HTL products. In the HTL process, high temperatures cause water to be a potent solvent by decreasing its dielectric constant. Improved solvent properties allow water to hydrolyze organic matter and allow further HTL reactions to take place. Also, water acts as a catalyst during HTL due to its dissociation into H^+ and OH^- ions[190]. After hydrolysis, increasing temperatures cause decomposition and, in severe conditions, repolymerization reactions. To reach the highest bio-crude yield, reaction temperature should be optimized to minimize the repolymerization reactions. The typical temperature range for HTL is 200-374°C. The optimum HTL temperature and the end-product distribution is biomass composition specific. The required temperature for the optimum bio-crude production can also be decreased by utilizing the correct catalyst type and amount.

Since the reaction temperature is the most effective parameter in the HTL process, many studies investigated its effect on the end products. Garcia Alba et al.[167] investigated the effect of HTL temperature on energy recovery for *Desmodesmus* sp. and reported energy recovery of 60%, 67%, and 75% for 325, 350, and 375°C, respectively. For HTL of mixed algal culture, Chen et al. [33] studied reaction temperatures between 260-320°C. They found that although the best bio-crude quality can be obtained at 320°C, the highest energy recovery of 52% can be reached at 300°C due to higher bio-crude yield. Madsen et al.[270] built a response surface model for *Spirulina platensis*, *Miscanthus,* and primary sewage sludge substrates at HTL temperatures of 250-350°C. They reported that according to their model, the highest bio-crude yields were at 300, 330, and 320°C for *Spirulina platensis*, *Miscanthus*, and primary sewage sludge, respectively.

Most studies agree that the optimum HTL reaction temperature is under the water's critical point (i.e., ≤374 °C). Over the water's critical temperature, bio-crude yield decreases due to syngas forming reactions[288] and secondary cracking of bio-crude. Lowering bio-crude yields were reported at temperatures over water's critical temperature[133,134,148,167,170,191,277]. As an exception, increasing bio-crude yields were reported at supercritical conditions (390°C) for oil palm biomass[266,289] due to the substrate's high lipid content.

The reaction temperature is also the parameter that controls another important HTL parameter, the reaction pressure. Pressure in HTL is autogenous, varying between 15.51 and 222.4 bars for temperatures of 200 and 374°C, respectively. High pressure in the HTL process allows for the existence of liquid water until the critical point. Therefore, the large energy loss due to phase change is avoided[290]. Since high pressure comes with high temperatures in the HTL process, it would not be economical to increase the pressure further for better process efficiency. Qian et al.[291] revealed the effect of pressure change between 200-400 bar in their study and stated that once the critical pressure (221 bar) is reached, the pressure has no significant effect on bio-crude yield. Sangon et al.[292], on the other hand, investigated coal liquefaction in toluene-tetralin and found that increasing pressure from 75 to 120 bar resulted in 30% higher bio-crude yield. Another important consideration for pressure is the feeding pump costs and effluent pressure regulators in continuous-flow systems. Application of the correct catalyst can decrease the required temperature and pressure, and lower the feed pumping costs significantly.

Retention time (reaction, holding, or residence time) is the second most crucial HTL process parameter. Yu et al.[278] studied retention times of 0 to 120 minutes and found that increasing retention time affects bio-crude yield positively for all reaction temperatures between 100-300°C. Both temperature and retention time parameters directly contribute to the HTL process severity. Changing the retention time allows for fine adjustment in process severity. HTL severity can be calculated by Equation 4[293,294] where n is the number of treatment stages; t_i is retention time (minutes); T_i is reaction temperature (°C); T_b is the base temperature (100°C), and ω is the fitted parameter which is assigned the value of 14.75. Variation of HTL severity by temperature and retention time is presented in Figure 15.

$$\mathrm{Severity} = \log\left[\sum_{i=1}^{n} t_i \times e^{\left(\frac{T_i - T_b}{\omega}\right)}\right] \tag{4}$$

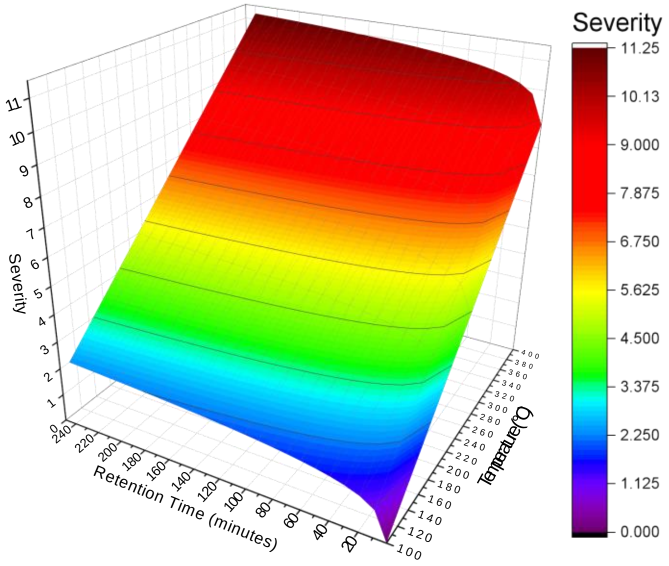
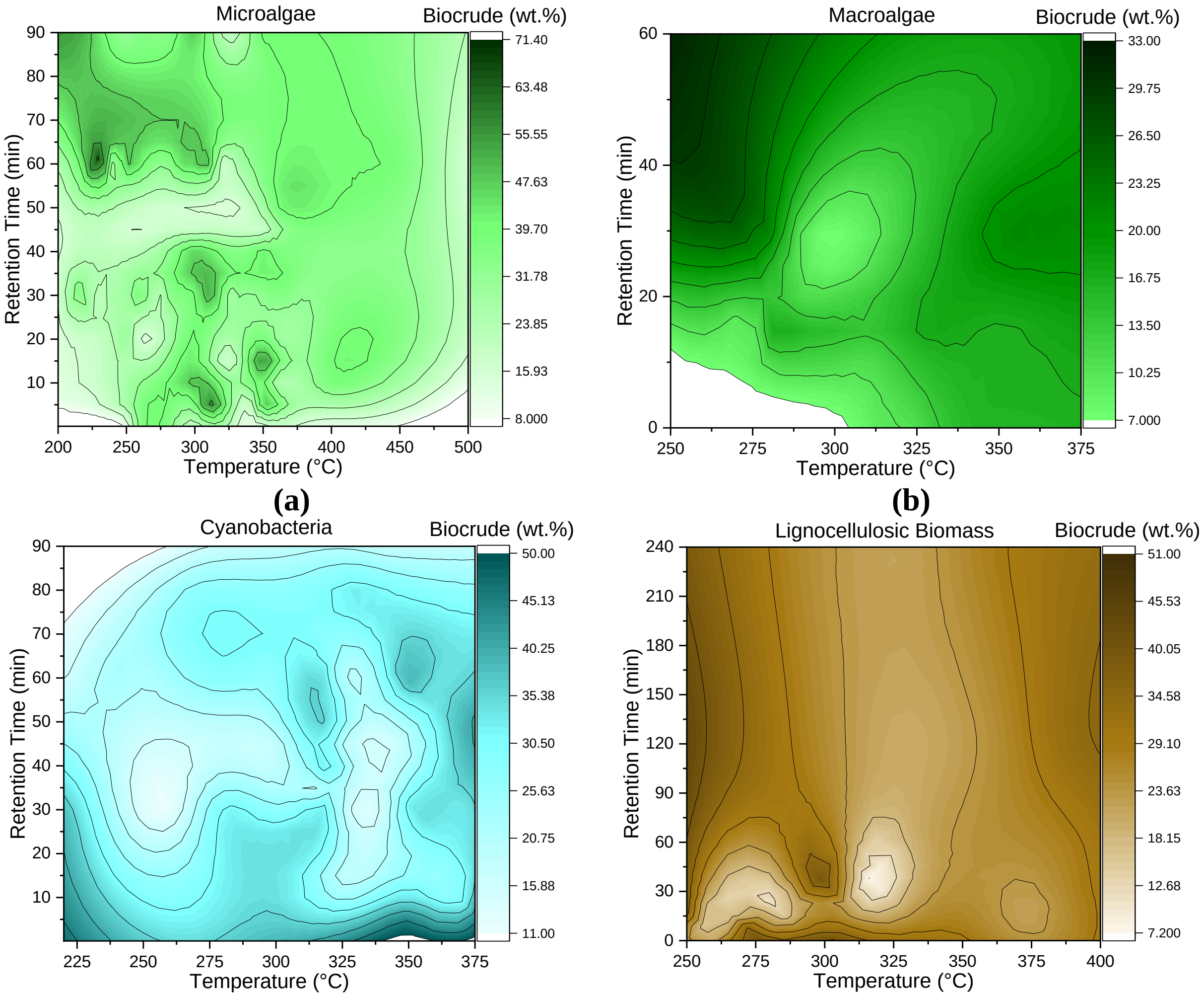


Figure 15. Effect of temperature and retention time on HTL severity

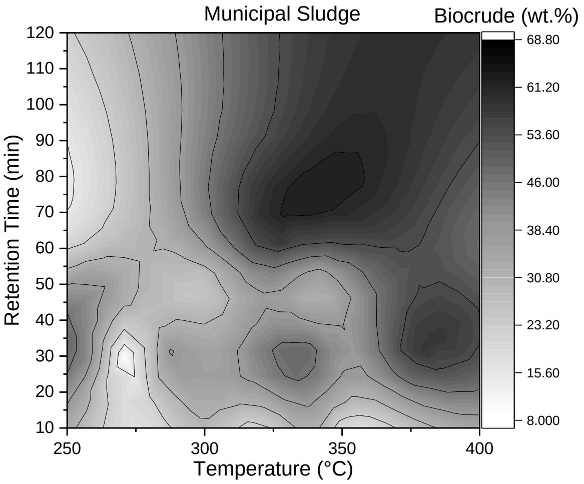
The effect of severity can be seen in the study of Guo et al.[170]. They reported a 38.46% bio-crude yield at 350°C and 60 minutes (severity: 9.14) and 39.54% bio-crude yield at 370°C and 50 minutes (severity: 9.6). Some of the literature findings indicate that the effect of temperature rise can also be achieved by increasing retention time. However, longer retention times in the HTL process can cause bio-crude to repolymerize into hydrochar and coke. Therefore, although the severity is an important parameter for hydrothermal processes, it can be said that it is not directly related to the biocrude yield due to the HTL process's complexity.

Bio-crude yields observed at different HTL temperatures and retention times for different substrates in the literature are presented in Figure 16. According to the results reported for HTL of microalgae given in Figure 16(a), bio-crude yield was low for temperatures under 275°C and 0-50 min retention time. High yields were obtained at 200-300°C and 55-90 min or 300-350°C and 0-40 min HTL conditions. The highest bio-crude yield of 71.4% from microalgae was obtained at 230°C, 60 min. Bio-crude yields of macroalgae, given in Figure 16(b), were lower compared to the other substrates. The highest yields reported for macroalgae were reached at 250-275°C and 40-60 min conditions. For cyanobacteria substrate, on the other hand, the highest yields were at 325-375°C and 0-5 min. There were also some high bio-crude yield results for lipid-rich cyanobacteria liquified at 220°C reaction temperature. Similar to macroalgae, lignocellulosic biomass bio-crude yields were also low except for one point. The highest yield of 51% was obtained at 300°C and 45 min. The most evident HTL condition to bio-crude yield pattern was found for municipal sludge due to less variation in substrate characteristics among studies. The highest bio-crude yields from municipal sludge were reported to be obtained at 325-360°C and 70-85 min conditions.



(a) **(b)**

(c) **(d)**



(e)

Figure 16. Bio-crude yields reported in different HTL conditions for (a) microalgae[30,33,52–55,134,138,143,148,155,160,163,167,175,176,184,188,190,194,201,211,213,217,245,277,295,296], (b) macroalgae[52,151,152,259,280–283,297], (c) cyanobacteria[52,53,59,143,155,163,170,176,209,211–213,253,263,296], (d) lignocellulosic biomass[143,222,261,266,273,276,285], and (e) municipal sludge[133,139,159,190,191,259,284]

4.3 Ramping time

In HTL processes, long reaction times, including the ramping time, increase char and coke formation by promoting the repolymerization reactions of bio-crude forming compounds. Therefore, higher heating rates (allowing for shorter reaction time) are beneficial in terms of bio-crude yield. Getting inspiration from the fast pyrolysis process, a study on a fast HTL process was performed by Faeth et al.[166] on *Nannochloropsis.* They performed their experiments in a preheated sandbath to 300-600°C by allowing 1-5 minutes of ramping time for fast HTL and 250-400°C reaction temperature and 10-60 minutes retention time for conventional HTL. According to their findings, the HTL reactor temperature reached around 275°C for 1 min ramping time in 600°C preheated environment, and it resulted in the highest bio-crude yield of 66% reported for *Nannochloropsis* sp. They also calculated 91% energy recovery for fast HTL conditions. In another study, Faeth et al.[298] also reported an increased bio-crude yield for *Botryococcus* in fast HTL and found that the fast HTL process is more effective at low solid loadings (0-10 wt% total solids). The effect of fast HTL process on chitin was studied by Gollakota and Savage[168]. For 1 minute ramping time, they reported that the maximum bio-crude yield was observed at the HTL condition with the highest heating rate (350°C/min). They also found that fast HTL bio-crude contains aldehydes and a double amount of nitrogenous compounds compared with the conventional HTL bio-crude. The effectiveness of fast HTL was also evaluated with kinetic modeling by Hietala et al.[267]. Their model predicted a 46% bio-crude yield at 400°C and 1-minute ramping time (reaching 230°C) conditions.

Short ramping times are applicable for continuous-flow HTL reactors[299]. However, stronger heating systems and requirements for reactor material due to higher temperatures can increase capital costs drastically. On the other hand, higher energy recovery and shorter reaction times can be beneficial in the long run. In continuous-flow systems, decreasing coke and char formation by fast HTL can also lower the risk of clogging the plug-flow reactors[300]. This type of continuous-flow fast HTL reactor is suitable for coupling with a wastewater treatment plant, where the substrate supply is sustainable.

The behavior of municipal sludge under fast HTL conditions was investigated by Xu et al.[139]. They reported that the maximum bio-crude yield of 22.9% was observed at 340°C and 2-3 minutes ramping time under fast HTL conditions. Qian et al.[291] also reported that it is possible to reach ~25% bio-crude yield in 500°C preheated sandbath with 1-minute ramping time HTL conditions. According to their results, the highest bio-crude yield from isothermal HTL (400°C – 60 minutes retention time) was 26.8%, whereas it was 27.5% from the fast HTL process.

4.4 Solid content

Water in HTL processes behaves like a solvent at high temperatures and hydrolyzes biomass. Therefore, the solid content can also be defined as a solute-to-solvent ratio by mass. Since hydrolysis is the first step of the HTL process, and the other processes only occur with hydrolyzed compounds, solid content affects all subsequent reaction kinetics. The solid content at which the highest bio-crude results in HTL process can vary depending on the type of substrate, type of solvent and process severity. For this reason, the determination of optimum solid content needs to be performed specific to substrate and solvent.

In the literature, most of the studies used a fixed 1:10 substrate to solvent ratio. There are also many studies that investigated the effect of different ratios. Arun et al.[131] investigated the effect of substrate to solvent ratio of 1:40-4:40 on bio-crude yield for the macroalgae *Sargassum tenerrimum*. They revealed that, for their substrate, at 300°C and 60 minutes conditions, the maximum bio-crude yield can be produced at 3:40 substrate to solvent ratio. For another macroalga

Laminaria saccharina, Anastasakis et al.[152] examined the bio-crude yield for 1:20-5:20 substrate to solvent ratios and reported that the highest bio-crude was produced at 1:10 ratio. Jazrawi et al.[177] studied ratios between 1:100-1:10 on microalgae *Chlorella* and found the most efficient ratio as 1:10.

For the economy of the process, in other words, in order to maximize net energy generation per kg of substrate, the highest solid content possible should be used without lowering the bio-crude production efficiency. Therefore, dewatering of substrate can be considered prior to HTL process. For substrates like municipal sludge, anionic or cationic polymers can be used in order to lower the zeta potential to reach higher dewatering. There are continuous-flow HTL systems that can utilize biomass with up to 20% solids[301]. In terms of pumping, current commercial vendors offer pumps for HTL systems that can pump up to 40% solid containing organic materials[302].

4.5 Type of solvent

The HTL process is suitable for using different solvents instead of water. By using alcohol or acetone as solvent, it is possible to reach supercritical conditions at lower temperatures. The most common solvents used in HTL process ethanol, methanol, isopropanol, and acetone have critical points of 241°C, 240°C, 235.6°C, and 235°C, respectively. Although better hydrolysis conditions can be reached with the utilization of different solvents, taking advantage of the catalytic effect of the H^+ and OH^- water ions at high temperatures is not possible. Therefore, in some studies, decreasing bio-crude yields were reported. Using solvents along with water, as co-solvent to take advantage of both, is also a good strategy for increasing bio-crude yield[303]. In addition, the use of solvents avoids repolymerization reactions and increases bio-crude stability during the process[304]. Results from the studies that used different solvent than water in the HTL process are presented in Table 3.

Table 3. Summary of HTL studies using different solvent than water

Substrate	HTL process conditions and reactor type (Temperature, retention time, substrate to solvent mass ratio, reactor type)	Bio-crude yield in water (%)	Bio-crude yield in solvent (%) and percentage of change with respect to water as solvent	Reference
Black pine wood and Kukersite oil shale mixture (2:1)	300°C, 30 min, 1:15 Batch	10.24%	Methanol: 31.86% (+211%)	149
Eremurus spectabilis	310°C, 75 min, 2:15 Batch	N/A	Methanol: 41.6% Ethanol: 53.8% Acetone: 64.3%	132
Datura stramonium L.	325°C, 75 min, 2:15 Batch	N/A	Isopropanol: 42.5% Acetone: 56%	153
Nannochloropsis oceanica	240°C, 30 min, 6:25 Batch	36%	50% Ethanol: 58% (+61%) 50% Methanol: 48% (+33%)	158
Rice straw	280°C, 15 min, 1:6 Batch	23%	Ethanol: 25% (+8.7%) Methanol: 23% (+0%)	136
Tetraselmis sp.	350°C, 30 min, 1:10 Batch	31%	10% Ethanol: 30.7% (-1%) 10% Isopropanol: 35.4% (+14.2) 10% Ethylene glycole: 30.4% (-1.93%) 10% Glycerol: 39% (+25.8%)	172
Oedogonium intermedium strain TSV2	350°C, 3 min, 1:20 Continuous-flow	24%	10% N-heptane: 20% (-20%) 10% Toluene: 21% (-12.5%) 10% Anisole: 28% (+16.66)	21
Rice straw	350°C, 20 min, 2:25 Batch	N/A	Ethanol: 21.14%	63
Spirulina			Ethanol: 34.51%	
Sewage sludge			Ethanol: 39.46%	
Cryptococcus curvatus	240°C, 30 min, 1:10 Batch	N/A	50% Isopropanol: 56.38%	180
Birchwood	243°C, 60 min, 1:15 Batch	N/A	Ethanol: 19%	305
Concentrated acid hydrolysis lignin	300°C, 60 min, 1:20 Batch	24.8	Ethanol: 20.1% (-18.95) Isopropanol: 21.2% (-14.5%)	182
	350°C, 28 min, 1:33 Continuous-flow	51%	Ethanol: 52% (+1.96%) Isopropanol: 60% (+17.64%)	
Kenaf	300°C, 60 min, 1:2 Batch	N/A	Tetralin: 77.2%	306
Sorghum			Tetralin: 75.1%	

Wheat straw			Tetralin: 72.1%	
Waste activated sludge, Rubberwood sawdust	310°C, 10 min, 3:25 Continuous-flow	N/A	30% Ethanol: 31.9%	192
Wheat straw	300°C, 120 min, 1:60 Semi-continuous flow	27%	Ethanol: 43% (+59.26%)	307
Pinewood sawdust	300°C, 30 min, 1:10 Batch	11.35%	50% Ethanol: 47.63% (+319%)	198
White pine sawdust	300°C, 15 min, 1:10 Batch	40%	50% Ethanol: 66% (+65%) 100% Ethanol: 71% (+77.5%) 50% Methanol: 33% (-17.5%) 100% Methanol: 24% (-40%)	308
α-Cellulose	350°C, 350 min, 1:30 Batch	N/A	Ethanol: 2.82% Methanol: 1.3% Acetone: 2.78%	309
Lignite, wheat straw, and plastic waste mixture	300°C, 30 min, 1:8 Batch	14%	Tetralin: 19% (+35.71%)	310
Eucalyptus	260°C, 30 min, 1:10 Batch	30%	Ethanol: 27% (-10%)	311
Pinus banksiana	260°C, 60 min, 1:13 Batch	N/A	Ethanol: 35%	215
Dunaliella salina	200°C, 60 min, 1:9 Batch	N/A	Ethanol: 34.8%	220
Dewatered secondary sludge	340°C, 40 min, 3:40 Batch	N/A	75% Methanol: 23.7	223
Macroalgae	300°C, 45 min, 1:10 Batch	14%	75% Ethanol: 45% (+221%)	142
Chlorella pyrenoidosa	280°C, 120 min, 3:10 Batch	46%	50% Ethanol: 57% (+23.91)	312
Corn straw	300°C, 15 min, 1:4 Batch	28%	15% Methanol: 32% (+14.28%) 100% Methanol: 20% (-28.57%) 100% Ethanol: 14% (-50%) 100% Isopropanol: 11% (-60.71%)	303

When the HTL results of different solvents are evaluated, it can be seen that the positive effect of solvents decreases when the HTL conditions become more severe. In terms of bio-crude yield, from the most to least effective, solvents can be sorted as acetone, isopropanol, ethanol, and methanol. Overall, organic solvents were found to be more effective when used as co-solvents.

Using pure solvents either caused a decrease or an insignificant increase in bio-crude yield. On the other hand, no noteworthy change for the HHV of bio-crude was reported for varying solvents. Like the other HTL parameters, the effect of solvent also varies depending on the substrate structure.

The most significant increases were reported for lignocellulosic substrates, including macroalgae. This increase was caused by the reaction of organic solvents with the decomposition products. For lignocellulosic substrates and macroalgae, carboxylic acids are the major decomposition products in HTL. These carboxylic acids are known to react with alcohols in hydrothermal conditions and form esters[313]. The esterification reaction is given in Figure 17. Esterification reaction of carboxylic acids and alcohols. As a result of this reaction, molecules that would normally stay in the aqueous phase can form longer chain hydrocarbons and contribute to bio-crude formation. The esterification reaction yield can be significantly increased with catalysts, such as sulphuric acid and ZSM-5 (zeolite socony mobil catalyst)[314].

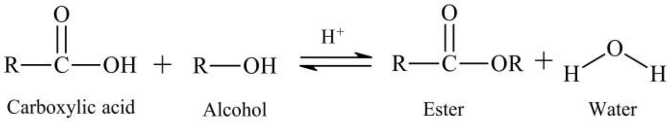


Figure 17. Esterification reaction of carboxylic acids and alcohols

The highest bio-crude yield increase, 221%, was achieved by using 50% ($v/v_{solvent}$) ethanol as solvent[142]. In this study, macroalgae was used as the substrate, which is known to produce high amounts of organic acids in the HTL process. The use of ethanol as solvent caused formation of esters with organic acids. With 25.95%, esters were reported as the most abundant group in the bio-crude in this study. By applying the ZSM-5 catalyst, esterification reactions were promoted, and the bio-crude's ester content was increased to 43.5%. Along with lignocellulosic biomass and macroalgae, organic solvents were also found beneficial at 240°C on microalgae[158] and yeast[180] substrates.

4.6 Headspace purging

Headspace purging is another HTL process variable applicable only for batch systems. It is performed before closing the reactor to avoid liquid loss[278,279] and to get rid of the oxygen[188,272,315], which can reduce the bio-crude quality in the HTL process. The most common purging method is to use inert gases like nitrogen or a noble gas[56,70,199]. To determine the effect of purging with different gases on bio-crude yields, Yin et al. [225] used air, CO, H_2, and N_2. They reported that the effect of purging was the most apparent at 310°C. According to their results, purging with CO, H_2, N_2, and air resulted in 48.76%, 44.72%, 38.49%, and 27.97% bio-crude yields, respectively, and revealed the necessity of purging in batch systems.

Another important hypothesis tested related to purging is, "can a partial hydrotreating effect be achieved by purging the reactor with H_2?" Jogi et al.[305] reported bio-crude yields of 13% for Ar purged, and 19% for H_2 purged HTL experiments. They also reported that H_2 purging caused a significant increase of phenolics in the aqueous phase. Xu and Etcheverry[215] studied the effect of 20, 50, and 100 bar initial H_2 pressurizing of the HTL system at 220 and 300°C. They reported only minor bio-crude yield increases proportional to H_2 pressure for both temperatures. Malins et al.[186] also carried out a detailed study to reveal the effect of H_2 purging at 300°C and 40 minutes reaction conditions with the addition of 5% $FeSO_4$. For 20 to 110 bar initial H_2 pressure, they found no significant change in terms of calorific value and yield of bio-crude. According to the results of these studies and safety concerns, it can be said that H_2 purging is not advantageous in the HTL process.

4.7 Catalysts used in HTL

HTL is a suitable process for the application of various catalyst types. Utilization of correct type and concentration of catalyst has the potential to decrease required HTL temperature and pressure while increasing bio-crude yield. Furthermore, the use of milder process conditions can lower energy and capital costs significantly. However, since catalysts work by altering the reaction kinetics, their effects are substrate-specific. This effect can be seen in the study of Shakta et al.[56], where they studied catalytic effect of Na_2CO_3 on three different microalgae at 350°C, and reported bio-crude yield decreased for *Nannochloropsis sp*, increased for *Pavlova* sp. and not affected for *Isochrysis* sp. On the other hand, the effect of different catalyst types was revealed in the study of Nazari et al.[193]. They used seven different catalysts, including alkaline, alkali salt, mineral, and metal-based types, and reported varying bio-crude yield and quality for every catalyst.

4.7.1 Alkaline catalysts

Alkaline catalysts are well-known and widely used in HTL processes due to their char formation inhibiting behavior[258] by avoiding repolymerization of bio-crude forming compounds.

Therefore, depending on the substrate, alkaline catalysts can significantly increase bio-crude and decrease hydrochar yields. Strong alkaline solutions can promote lignin decomposition and increase bio-crude yield[26,316], especially in HTL of lignin-rich biomass. Alkaline catalysts are mostly effective on high-carbohydrate containing biomass types, such as lignocellulose. In HTL process, carbohydrate-rich substrates tend to produce organic acids due to the pathways presented in Section 2.2. In the presence of an alkali catalyst, the pH changes can be neutralized during the HTL process; thus, the process favors bio-crude formation instead of repolymerization reactions. Also, keeping the pH at alkaline conditions avoids corrosion risk in the reactors. The varying effect of alkaline catalysts linked to the substrate type is presented in the literature summary in Table 4.

Table 4. Summary of HTL studies using alkaline catalyst

HTL contents			HTL conditions and reactor type (Temperature, retention time, substrate to solvent mass ratio, reactor type)	Bio-crude yield w/o catalyst (%)	Bio-crude yield with catalyst (%) and effect of catalyst to yield (%)	Reference
Substrate	Solvent	Catalyst type and amount (% reactor volume)				
L. Saccharina	Water	5% KOH	350°C, 15 min, 1:10 Batch	19.30%	10% (-48%)	152
S. obliques	Water	2.5% NaOH	300°C, 60 min, 3:40 Batch	27%	27% (-9%)	131
Eremurus spectabilis	Ethanol	10% NaOH	310°C, 75 min, 2:15 Batch	7.80%	9.5% (+22%)	132
Datura stramonium L.	Acetone	10% $Ca(OH)_2$	325°C, 75 min, 2:15 Batch	42%	46% (+9.5%)	153
Laminaria saccharina	Water	0.5% KOH	350°C, 15 min, 1:10 Batch	65%	67% (+3%)	154
Corn straw	Water	4% NaOH	230°C, 60 min, 1:10 Batch	N/A	17.02%	317
Nine different lignocellulosic biomass	Water	20% KOH	302°C, 30 min, 1:15 Batch	31.20%	63.7% (+104%)	318
Black cumin seed	Water	10% $Ca(OH)_2$	350°C, 0 min, 1:12 Batch	36.24%	28.85% (-20%)	319
Beech wood	Water	0.9% NaOH	300°C, 60 min, 3:20 Batch	14%	28% (+100%)	171
Korean native kenaf	Water	1% NaOH	350°C, 30 min, 1:8 Batch	17.09%	23.74% (+39%)	181
Waste activated sludge	Water	0.5% KOH	310°C, 10 min, 1:10 Batch	N/A	23.10%	192

Waste activated sludge	15% Ethanol	0.13% KOH	310°C, 10 min, 1:10 Continuous-flow	N/A	29.99%	[192]
Waste activated sludge, birch wood sawdust	Water	0.35% KOH	320°C, 20 min, 7:100 Batch	N/A	33.60%	[320]
Miscanthus giganteus	Water	1.4% KOH	350°C, 5.6 min, 3:20 Continuous-flow	N/A	26.20%	[15]
Pinewood sawdust	Water	0.5% NaOH	300°C, 30 min, 1:10 Batch	11.35%	26.73% (+135%)	[198]
Chlorella vulgaris *Spirulina*	Water	5.6% KOH	350°C, 60 min, 1:10 Batch	N/A	22.4% 15.2%	[202]
Blackcurrent pomace	Water	0.45% NaOH	300°C, 60 min, 1:20 Batch	26.50%	32% (+20%)	[203]
Scenedesmus abundans	Water	NaOH	300°C, 60 min, 1:20 Batch	N/A	35.50%	[207]
Eucalyptus	Water	0.5% NaOH 0.5% KOH	260°C, 30 min, 1:10 Batch	31.50%	60% (+90%) 57% (+81%)	[315]
Spirulina platensis	Water	0.056% KOH	300°C, 35 min, 1:10 Batch	29.70%	30.1% (-1.35%)	[240]
Tomato plant waste	13% Ethanol	0.5% KOH	250°C, 30 min, 1:20 Batch	30%	45% (+50%)	[321]
Swine carcass	Water	0.04% NaOH	250°C, 60 min, 1:20 Batch	58%	62% (+6.9%)	[144]
Water hyacinth	Water	5.6% KOH	280°C, 15 min, 1:6 Batch	16%	23% (+43.75%)	[322]
Cattle manure	Water	2% NaOH	310°C, 15 min, 1:4 Batch	N/A	48.76%	[225]
Birchwood	Water	0.5% KOH	300°C, 30 min, 1:10 Batch	18.90%	39.5% (+109%)	[193]

In HTL of lignocellulosic substrate studies[171,193,198,315,318,321], an increase in bio-crude yield by 50-135% was observed by the addition of an alkaline catalyst. For other types of substrates, on the other hand, this effect was minor or even negative. Anastasakis et al.[152] reported that the negative effect of alkaline catalysts is caused by the increased solubility of organics, including bio-crude, in the aqueous phase.

Alkali salts can also be classified as alkaline catalysts due to their chemical behavior. The most used alkali salts, Na_2CO_3 and K_2CO_3, form a strong base and carbonic acid with a pK_b of 3.75[323] when they are dissolved. Carbonic acid further decomposes into water and CO_2 gas. Chemical equations occurring are given in Reactions 1, 2, and 3.

$$Na_2CO_3 + 2\ H_2O \rightarrow H_2CO_{3\ (aq)} + 2\ NaOH_{\ (aq)} \tag{1}$$

$$K_2CO_3 + 2\ H_2O \rightarrow H_2CO_{3\ (aq)} + 2\ KOH_{\ (aq)} \tag{2}$$

$$H_2CO_{3\ (aq)} \rightarrow H_2O_{\ (aq)} + CO_{2\ (g)} \tag{3}$$

Due to the reactions that alkali salts and alkaline catalysts undergo, it is not possible to recover and reuse them. However, if considered for full-scale HTL applications, they are not expensive and are easy to obtain. When the summary of alkali salt catalyst studies in Table 5 evaluated, it can be seen that the effect of alkali salts on bio-crude yield shows a similar pattern to alkaline catalysts. According to the studies, by the addition of alkali salt catalysts, bio-crude yield can be significantly increased for cellulose[258] and lignocellulosic biomass[147,193,198], whereas it shows fluctuating results for other types of biomass[156,291,324].

Table 5. Summary of HTL studies using alkali salts as catalyst

HTL contents			HTL conditions and reactor type (Temperature, retention time, substrate to solvent mass ratio, reactor type)	Bio-crude yield w/o catalyst (%)	Bio-crude yield with catalyst (%) and effect of catalyst to yield (%)	Reference
Substrate	Solvent	Catalyst type and amount (% reactor volume)				
C. vulgaris	Water	10.5% Na_2CO_3	350°C, 60 min, 1:10 Batch	42%	31.6% (-25%)	49
Spirulina				26.6%	18.3% (-31%)	
N.occulta				20%	15.8% (-21%)	
P.cruentum				32%	13.3% (-58%)	
Sewage sludge	Water	2% K_2CO_3	340°C, 20 min, 1:5-1:3 Batch	35.4%	30.7% (-13%)	156
Miscanthus				21.2%	24.1% (+13.6%)	
Switchgrass				26.5%	22.1% (+3.5%)	
willow				25.1%	26% (-25%)	
Pine flakes				28.6%	23.6% (-17.5%)	
Dried distillers grains with solubles	Water	2% K_2CO_3	340°C, 20 min, 3:4 Batch	34%	40% (+17.6%)	157
Herb pasture	Water	K_2CO_3	340°C, 20 min, - Batch	26.6%	24.1% (-9.4%)	242
Bog myrtle				21.6%	23.1% (+6.9%)	
Molinia pasture				22.2%	26.3% (+18.5%)	
Sedge pasture				22.8%	19.4% (-14.9%)	
Rush pasture				22.8%	23.8% (+4.4%)	
Heather				25.6%	30.4% (+18.8%)	
Bracken				20.8%	24.2% (+16.3%)	
Timothy/wclover				23.3%	23.7% (+1.7%)	
Ryegrass/wclover				22%	24.5% (+11.4%)	
Lucerne				28.9%	30.1% (+4.2%)	
Reed canary				26%	24% (-7.7%)	
Triticale				26.1%	22.5% (-13.8%)	
Oats				25.1%	23.3% (-7.2%)	
Rye				24.7%	24.5% (-0.8%)	
Beet				20.3%	20.3% (+0%)	
Maize				27.6%	23.4% (-15.2%)	

Botryococcus braunii	Water	0.3% Na_2CO_3	300°C, 60 min, 3:50 Batch	56%	63% (+12.5%)	325
Botryococcus braunii	Water	5% Na_2CO_3	300°C, -, - Batch	54%	75% (+38.9%)	326
Cryptococcus curvatus	Water	5% Na_2CO_3	300°C, 30 min, 1:10 Batch	49.11%	52.61% (+7.1%)	180
Sargassum patens C. Agardh	Water	5% Na_2CO_3	340°C, 15 min, 1:10 Batch	32%	28% (-12.5%)	183
Anglerfish waste	Water	10.6% Na_2CO_3	250°C, 60 min, 3:20 Batch	68.25%	49.53% (-27.4%)	324
Grape pomace	Water	1% Na_2CO_3	350°C, 30 min, 3:20 Continuous flow	N/A	39-40%	185
Sewage sludge	Water	1% Na_2CO_3	300°C, 40 min, 1:5 Batch	40%	39% (-2.5%)	186
Dunaliella tertiolecta	Water	1% Na_2CO_3	300°C, 60 min, 1:5 Batch	34.3%	42% (+22.5%)	189
Cellulose	Water	0.8% Na_2CO_3	300°C, 0 min, 1:6 Batch	20%	44% (+120%)	258
Mixture of aspen wood, glycerol, carboxymethyl cellulose (16.9:15.7:0.8)	Water	4.2% K_2CO_3	400°C, 43 min, 2:3 Continuous flow	N/A	20-31%	197
Glucose xylose lignin Aspen wood sorbitol xylitol glycerol ethylene glycol	Water	2% K_2CO_3	400°C, 15 min, 1:5 Batch	N/A	30% 28% 14% 42% 26% 23% 18% 14%	327
Pinewood sawdust	Water	0.5% Na_2CO_3	300°C, 30 min, 1:10 Batch	11.35%	29.89% (+154%)	198
Sewage sludge	Water	1.5% Na_2CO_3 1.5% K_2CO_3	300°C, 60 min, 3:20 Batch	26.8%	20.9% (-22%) 21.6% (-19.4%)	291
Chlorella vulgaris *Spirulina*	Water	10.6% Na_2CO_3	300°C, 60 min, 1:10 Batch	N/A	9% 6.6%	202
Douglas fir wood	Water	0.1% Na_2CO_3	335°C, 100 min, 1:10 Continuous	N/A	56.8%	11
Sewage sludge	Water	2.5% K_2CO_3	350°C, 15 min, 7:25 Batch	25%	28% (+12%)	205
Nannochloropsis sp. *Pavlova* sp. *Isochrysis* sp.	Water	0.7% Na_2CO_3	300°C, 60 min, 1:6 Batch	45% 38% 35%	39% (-13.3%) 44% (+15.8%) 40% (+14.3%)	56
Dunaliella tertiolecta	Water	5% Na_2CO_3	360°C, 50 min, 1:10 Batch	21%	25% (+19%)	206

Water hyacinth	Water	13.8% K_2CO_3 27.6% K_2CO_3	280°C, 15 min, 1:6 Batch	16%	18% (+12.5%) 22% (+37.5%)	322
Litsea cubeba seed	Water	10% Na_2CO_3	290°C, 60 min, 1:10 Batch	56.9%	49.6% (-12.8%)	214
Microcystis viridis	Water	5% Na_2CO_3	300°C, 30 min, 1:20 Batch	22%	26% (+18.2%)	224
Raw sewage sludge	Water	5% Na_2CO_3	300°C, 0 min, 1:4 Batch	20%	48% (+140%)	226
Corn straw	Water	2.5% Na_2CO_3 2.5% K_2CO_3	300°C, 15 min, 1:4 Batch	32%	35% (+9.4%) 36% (+12.5%)	303
Enteromorpha prolifera	Water	5% Na_2CO_3	300°C, 30 min, 2:15 Batch	21%	22.5% (+7.1%)	145
Barley straw	Water	1.5% K_2CO_3	300°C, 15 min, 3:20 Batch	N/A	35%	146
Barley straw	Water	1.5% K_2CO_3	300°C, 15 min, 3:20 Batch	17.88%	34.85% (+94.9%)	147
Spirulina platensis	Water	1% Na_2CO_3	300°C, 0 min, 1:5 Batch	39.9%	51.6% (+29.3%)	179
Birch wood	Water	0.5% K_2CO_3	300°C, 30 min, 1:10 Batch	18.90%	38.5% (+104%)	193
A. platensis *Tetraselmis* sp.	Water	5% Na_2CO_3	350°C, 30 min, 1:5 Batch	N/A	35% 40%	127

4.7.2 Acid catalysts

Acidic conditions in the HTL process were reported to favor repolymerization[12] and condensation[185] reactions and decrease bio-crude yields. However, adding organic acids, which are also produced by HTL, can change reaction kinetics and increase bio-crude yield. Also, small chain organic acids can decompose into hydrogen and carbon monoxide, and hydrogen can act as a proton donor, increasing bio-crude yield. There are only a few studies regarding beneficial use of acid catalysts in the literature. Lou et al.[324] and Shah et al.[205] reported that by the addition of acetic acid, a minor bio-crude increase was observed from seafood waste and sewage sludge, respectively. The summary of acid catalyst studies is presented in Table 6.

Table 6. Summary of HTL studies using acid catalyst

HTL contents			HTL conditions and reactor type (Temperature, retention time, substrate to solvent	Bio-crude yield w/o catalyst (%)	Bio-crude yield with catalyst (%) and effect of catalyst to yield (%)	Reference
Substrate	Solvent	Catalyst type and amount (%				

		reactor volume)	mass ratio, reactor type)			
Chlorella vulgaris *Spirulina* *N. occulta* *P. cruentum*	Water	4.6% HCOOH	350°C, 60 min, 1:10 Batch	42% 26.6% 20% 32%	25.6% (-39%) 18.3% (-31%) 15.8% (-21%) 13.3% (-58%)	49
Concentrated acid hydrolysis lignin	50% Ethanol	5% HCOOH	300°C, 60 min, 1:20 Batch	40.9%	61.9% (+51%)	182
		3% HCOOH	350°C, 28 min, 1:33 Continuous	51.47%	59.22% (+15%)	
Anglerfish waste	Water	6% CH_3COOH	250°C, 60 min, 3:20 Batch	68.25%	76.4% (+12%)	324
Chlorella vulgaris	Water Water	4.6% HCOOH 6% CH_3COOH	300°C, 60 min, 1:10 Batch	N/A	HCOOH: 22% CH_3COOH: 23.5%	202
Spirulina			230°C, 60 min, 1:10 Batch	N/A	HCOOH: 11.75% CH_3COOH: 13.2%	
Sewage sludge	Water	2.5% CH_3COOH	350°C, 15 min, 7:25 Batch	24%	26% (+8.3%)	205
Enteromorpha prolifera	Water	0.2% H_2SO_4 1.2% CH_3COOH	290°C, 20 min, 1:3 Batch	18%	14% (-22%) 12.5% (-30%)	140
Spirulina platensis	Water	0.34% CH_3COOH	300°C, 35 min, 1:10 Batch	29.7%	28% (-5.7%)	240
Tomato plant waste	13% Ethanol	0.5% H_2SO_4	250°C, 30 min, 1:20 Batch	N/A	44.95%	321
Sewage sludge	Water	10% HCOOH 10% CH_3COOH	400°C, 60 min, 3:20 Batch	26.8%	20.7% (-23%) 20.8% (-22%)	291

4.7.3 Metal-based catalysts

Metal oxides, metal salts, pure metals, and other metal-based catalysts can also be used in the HTL process. Due to their charges, they adsorb organic reactant molecules; then, they release the molecule after the reaction is completed[328]. Adsorbed molecules by metal-based catalysts require less activation energy for HTL reactions. Therefore, high bio-crude yields in lower process temperatures can be achieved. Unlike acidic and alkaline ones, metal-based catalysts are heterogeneous. This gives important advantages to metal-based catalysts in terms of handling, separation, recovery, and regeneration[329]. Metal-based catalysts are also widely used for activating H_2 molecules[330] in bio-crude upgrading processes, such as hydrodeoxygenation[331]. HTL studies investigating metal-based catalysts, which are presented in Table 7, reported mostly increased bio-crude yield regardless of substrate type.

Table 7. Summary of HTL studies using metal-based catalyst

HTL contents			HTL conditions and reactor type (Temperature, retention time, substrate to solvent mass ratio, reactor type)	Bio-crude yield w/o catalyst (%)	Bio-crude yield with catalyst (%) and effect of catalyst to yield (%)	Reference
Substrate	Solvent	Catalyst type and amount (% reactor volume)				
Eremurus spectabilis	Ethanol	10% $FeCl_3$	310°C, 75 min, 2:15 Batch	53.8%	64.5 (+19.9%)	[132]
Datura stramonium L.	Acetone	10% ZnO	325°C, 75 min, 2:15 Batch	42%	56% (+33.3%)	[153]
Corn straw	Water	2% CuO	230°C, 60 min, 1:10 Batch	N/A	11.77%	[317]
Oak wood	Water	10% Ni powder 10% nano-spiked Ni	330°C, 10 min, 1:5 Batch	32.88%	35.05% (+6.6%): 36.63% (+11.4%)	[161]
Oak wood	Water	2% Fe 2% Fe_2O_3 2% Fe_3O_4	320°C, 15 min, 1:5 Batch	26%	38% (+46.2%) 27% (+3.85%) 31% (+19.2%)	[162]
Rice straw	Water	10% Al/SBA-15 10% Ni/SBA-15 10% Ni-Al/SBA-15	280°C, 15 min, 1:6 Batch	23%	36% (+56.5% 33% (+43.5%) 44% (+91.3%)	[136]
Nannochloropsis sp.	Water	3% Pd/C 3% Pt/C 3% Ru/C 3% Ni/SiO_2-Al_2O_3 3% CoMo/γ-Al_2O_3	350°C, 60 min, 3:50 Batch	35%	57% (+62.9%) 48% (+37.1%) 50% (+43%) 50% (+43%) 53% (+51%)	[332]
Black cumin seed	Water	10% Al_2O_3 10% $SnCl_4$ $5H_2O$	300°C, 0 min, 1:12 Batch	20.34%	39.88% (+96%) 26% (+27.9%)	[319]
Sugarcane bagasse	Water	1.38% 1:1 Fe/Co	250°C, 120 min, 1:28 Batch	35%	57.6% (+64.6%)	[333]
Red grape seeds	Water	0.74% $MgCI_{2,}$ $TiCI_4$	300°C, 30 min, 1:10 Batch	39%	48% (+23%)	[173]
Pinus ponderosa Derived Acid Hydrolysis Residue	Water	5% $Ni(NO_3)_2$	300°C, 0 min, 1:30 Batch	N/A	25%	[334]
Spirulina platensis	Water	1% NiO 1% $Ca_3(PO_4)_2$	300°C, 0 min, 1:5 Batch	39.9%	30.2% (-24.3%) 34.5% (-13.5%)	[179]
Birch wood	Ethanol	Fe-beta zeolite Fe-SiO2	243°C, 60 min, 3:20 Batch	19%	25% (+31.6%) 17% (-10.5%)	[305]

Spirulina platensis	Water	0.4% CeO_2	250°C, 30 min, 1:10 Batch	16%	26% (+62.5%)	31
Spirulina platensis	Water	1.5% Fe_3O_4	320°C, 37 min, 1:10 Batch	N/A	32.33%	335
Chlorella	Water	1.5% Zr/Al_2O_3 1.5% Ti/Al_2O_3 1.5% Sn/Al_2O_3 1.5% $Zr/Al_2O_3.SO_4$ 1.5% $Ti/Al_2O_3.SO_4$ 1.5% $Sn/Al_2O_3.SO_4$	300°C, 60 min, 3:10 Batch	27.6%	28.3% (+2.5%) 31.6% (+14.5%) 31.2% (+13%) 32.7% (+18.5%) 31.7% (+14.9%) 32.1% (+16.3%)	336
Anabaena variabilis	Water	1% SnO 1% $TiO.Al_2O_3$ 1% $ZrO.Al_2O_3$ 1% $SnO.Al_2O_3$ 1% TiO-kaolin 1% ZrO-kaolin 1% SnO-halloysite 1% TiO-clay 1% ZrO-nanotubes	300°C, 30 min, 3:10 Batch	N/A	37% 36% 34% 26% 16% 20% 26% 21% 30%	337
Sewage sludge	Water	5% Raney nickel 5% $FeSO_4$ 5% MoS_2	300°C, 40 min, 1:5 Batch	40%	40% (+0%) 46% (+15%) 42% (+5%)	186
Cellulose	Water	6.6% Ni catalyst	300°C, 0 min, 1:6 Batch	20%	0% (-100%)	258
Birch wood	Water	0.5% $FeSO_4.7H_2O$ 0.5% MgO	300°C, 30 min, 1:10 Batch	18.9%	32% (+69.3%) 30.3% (+60.3%)	193
Wheat straw	50% Ethanol	1.66% Ru/H-Beta	300°C, 20 min, 1:11 Semi-continuous	26%	24% (-7.7%)	307
Chlorella vulgaris	Water	1% $NiMo/Al_2O_3$ 1% $CoMo/Al_2O_3$	325°C, 30 min, 1:10 Batch	32%	29% (-9.4%) 35% (+9.4%)	199
Sewage sludge	Water	13.8% K_2CO_3 27.6% K_2CO_3	280°C, 15 min, 1:6 Batch	27%	24% (-11.1%) 21% (22.2%)	
Sewage sludge	Water	1.5% MoO_3-CoO/γ-Al_2O_3 1.5% Ru/C	400°C, 60 min, 3:20 Batch	26.8%	21.7% (-19%) 18.9% (-29.5%)	291
Nannocloropsis gaditana	Water	5% CaO 5% CeO_2 5% La_2O_3 5% MnO_2 5% Al_2O_3	320°C, 10 min, 1:10 Batch	42.6%	49.73% (+16.7%) 43.8% (+2.8%) 42.66% (+0.1%) 44.11% (+3.5%) 44.22% (+3.8%)	204

Pine wood	Water	5% $Ni(NO_3)_2.6H_2O$	250°C, 120 min, 1:10 Batch	N/A	22.14%	338
		5% $Fe(NO_3)_3.9H_2O$			15.29%	
		5% $Co(NO_3)_2.6H_2O$			24.8%	
		5% $Ca(NO_3)_2.4H_2O$			16.1%	
Lignite, wheat straw, plastic waste mixture	Water	Fe_2O_3+S	300°C, 30 min, 1:8 Batch	14%	10% (-28.6%)	310
		FeS+S			12% (-14.3%)	
		FeS			5% (-64.3%)	
Pinus banksiana	Ethanol	0.38% $FeSO_4.7H_2O$	300°C, 40 min, 1:13 Batch	44%	53% (+20.5%)	215
		0.38% FeS			43% (-2.3%)	
Dunaliella salina	Ethanol	2.22% REHY	200°C, 60 min, 1:9 Batch	34.8%	51.6% (+48.3%)	220
		2.22% Ni/REHY			72% (+106.9%)	
Malaysian oil palm biomass	Water	1% CaO	390°C, 60 min, 1:10 Batch	11.85%	14.5% (+22.4%)	289
		1% MgO			10.5% (-11.4%)	
		1% MnO			16.4% (+38.4%)	
		1% ZnO			14.2% (+19.8%)	
		1% NiO			13.7% (+15.6%)	
		1% SnO			15.3% (+29.1%)	
		1% CeO_2			16.6% (+40%)	
		1% Al_2O_3			13% (+9.7%)	
		1% La_2O_3			16.2% (+36.7%)	
Chlorella pyrenoidosa	Water	0.5% Ce/HZSM-5*	300°C, 20 min, 1:10 Batch	33.3%	49.87% (+49.76%)	339

*HZSM-5: acid-activated zeolite socony mobil catalyst

4.7.4 Mineral catalysts

Mineral catalysts are another heterogeneous catalyst group that has a broad application in many fields. Mainly acid-activated zeolite socony mobil catalyst (HZSM-5) was investigated for the HTL process due to its selective cracking, alkylation, isomerization, and aromatization properties[142,340]. Zhang et al.[303] observed an 18.8% bio-crude yield increase by the addition of 2.5% HZSM-5, whereas the catalyst had a negative effect on bio-crude yields from microalgae[218] and macroalgae[142]. Also, some promising results for hydrotalcite and colemanite catalysts were reported in the literature[193,341] with a significant bio-crude yield increase in the HTL of lignocellulosic biomass. The studies that utilized mineral catalysts in the literature are summarized in Table 8.

Table 8. Summary of HTL studies using mineral catalyst

HTL contents			HTL conditions and reactor type	Bio-crude yield w/o	Bio-crude yield with catalyst (%)	Reference

Substrate	Solvent	Catalyst type and amount (% reactor volume)	(Temperature, retention time, substrate to solvent mass ratio, reactor type)	catalyst (%)	and effect of catalyst to yield (%)	
Nannochloropsis sp.	Water	3% Zeolite	350°C, 60 min, 3:50 Batch	35%	45% (+28.6)	332
Birch wood	Water	0.5% Hydrotalcite 0.5% Colemanite	300°C, 30 min, 1:10 Batch	18.9%	34.4% (+82%) 36.3% (+92%)	193
Beech wood	Water	1% Colemanite	300°C, 0 min, 1:10 Batch	21%	41% (+95.2%)	341
Lignite, wheat straw, plastic waste mixture	Water	Tourmaline	300°C, 30 min, 1:8 Batch	14%	12.5% (-10.7%)	310
Chlorella pyrenoidosa	Water	HZSM-5*	300°C, 20 min, 1:10 Batch	33.3%	34.02% (+2.2%)	339
Microalgae	Water	0.28% HZSM-5*	300°C, 20 min, 1:10 Batch	15.8%	12.5% (-20.9%)	218
Macroalgae	50% Ethanol	15% HZSM-5*	300°C, 45 min, 1:10 Batch	45%	44.5% (-1.1%)	142
Corn straw	Water	2.5% HZSM-5*	300°C, 15 min, 1:4 Batch	32%	38% (+18.8%)	303
Rice straw	Water	10% SBA-15**	280°C, 15 min, 1:6 Batch	23%	24.5 (+6.5%)	136

*HZSM-5: Acid zeolite socony mobil catalyst, **SBA-15: Mesoporous silica

4.7.5 Other additives and mixed catalysts

Along with typical catalyst applications, there are also studies in the literature that investigated the effect of other additives or the synergistic effect of two catalysts on the HTL process. Chen et al. [317] studied the effect of NaOH, CuO, and their mixture as catalysts on corn straw. According to their results, CuO + NaOH catalyst resulted in the highest bio-crude yield of 26.6%, whereas the yield was 11.77% for CuO and 17.02% for NaOH. This result indicates that catalyst studies should be performed at different pH values to identify the ideal pH conditions. Other studies reported that the pH is effective on catalysts product selectivity[342]. The mixture of Fe with Pd/Al_2O_3, Ru/Al_2O_3, Pt/Al_2O_3, Cu/SiO_2, and Ni/kieselguhr as HTL catalysts were investigated on cellulose by Hirano et al.[343]. They reported that the combination of metal catalysts enhanced decomposition reactions and converted all bio-crude into smaller molecules in the aqueous phase. Zhang et al.[303] used a fixed-bed cracking catalyzer produced by Nankai University (NKC-11) and reported an increase of 25% in bio-crude yield.

Alhassan and Kumar[287] researched the effect of chloromethylene (ChCl) based deep eutectic solvents (DES) addition to HTL of food waste. They reported that 4% DES loading as catalyst was the most effective process. In a similar study conducted on *Jatropha curcas*, Alhassan et al.[150] tested different DES by mixing ChCl with KOH, p-toluenesulfonic acid, glycerol, or $FeCl_3$. According to their findings, all DES additions increased bio-crude yield. The highest yield increase of 89% was observed in the presence of ChCl-KOH.

4.7.6 Substrate-specific overall catalyst performance

The effect of catalyst varies in the HTL process, depending on the type of catalyst and substrate. Catalytic effect is achieved by altering the complex HTL reaction pathways or kinetics. However, due to the complexity of the process, catalytic effect can also be negative in terms of bio-crude yield. Therefore, catalyst type and concentration, which are specific for the substrate type, need to be selected carefully to enhance bio-crude yield and quality. To determine the substrate-specific catalyst performances, the overall effects of catalysts used by the studies summarized in Tables Table 4-Table 8 were calculated and presented in Figure 18.

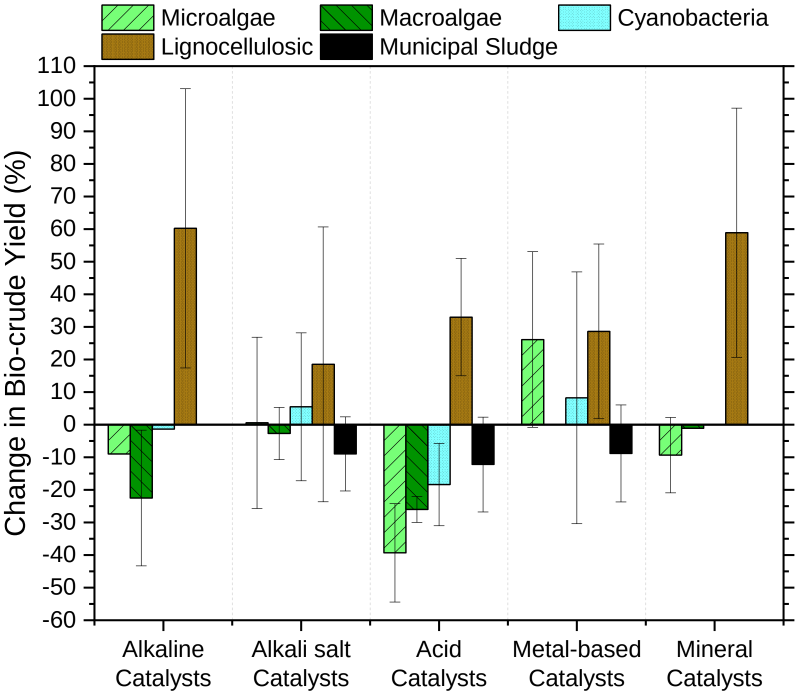


Figure 18. The overall catalyst performance on different HTL substrates

According to the results presented in Figure 18, it can be seen that lignocellulosic biomass is the most suitable biomass type for a catalytic HTL process. A high bio-crude yield enhancement for lignocellulosic biomass is reported for all five catalyst types, especially for alkaline and mineral catalysts. Due to the carbohydrate-rich structure of lignocellulosic biomass, the majority of the HTL reactions that can be catalyzed are based on carbohydrates. In uncatalyzed HTL of lignocellulosic biomass, carbohydrates are converted into organic acids. The accumulation of organic acids causes HTL reactions to favor hydrochar formation due to low pH. However, when the process is catalyzed, this pH change is avoided either by neutralizing pH or enhance degradation of organic acids. Although low pH during the HTL process is not favored, adding an acid catalyst in low concentrations initially can enhance the hydrolysis step and increase bio-crude yield for lignocellulosic biomass.

For the substrates that are balanced in terms of carbohydrate and protein, catalysts are less effective compared to lignocellulosic biomass. Except for metal-based catalysts, mostly negative results were reported for microalgae, macroalgae, cyanobacteria, and municipal sludge. Particularly acid catalysts caused a significant loss in bio-crude yield for these substrates. Some promising results were reported for HTL of microalgae and cyanobacteria with a metal-based catalyst. The development of a reusable heterogeneous metal-based HTL catalyst can positively affect the process's energy balance by decreasing the required reaction temperature while increasing the bio-crude yield. Therefore, it can be said that catalyst development will be an important step in the transition to full-scale applications.

5 HTL systems

HTL process can be performed both in batch and continuous-flow systems. Although most of the studies were performed with batch systems due to limitations, the ultimate goal for full-scale applications is to use continuous-flow systems, particularly for biomass available on a continuous basis, such as municipal sludge. Both reactor systems have their advantages and disadvantages. To determine the effect of reactor type on bio-crude yield and quality, Biller et al.[238] performed HTL assays using the same substrate in both types of reactors, which were set to 350°C. They reported 34.5% and 44.3% bio-crude yields for batch and continuous-flow testing, respectively. The difference was caused by lower temperature in the batch reactor, which was able to reach 340°C, and better mixing in the continuous-flow system. According to their results, while the batch reactor bio-crude had better quality, continuous-flow system bio-crude had higher energy recovery due to higher bio-crude yield.

Kristiano et al.[182] also investigated the effect of reactor type on the HTL of concentrated acid hydrolysis lignin. They used 50% ethanol and formic acid as solvent and catalyst, respectively, at a reaction temperature of 300°C for batch, and 350°C for the continuously stirred-tank reactor (CSTR). They reported a 61.9% bio-crude yield with an 896.5 g molecular weight in the batch reactor. On the other hand, the bio-crude yield was 59.92%, with a molecular weight of 614.7 g in the continuous-flow HTL system.

5.1 Batch HTL systems

Batch HTL systems are widespread in laboratory-scale applications all over the world. Compared to continuous-flow systems, controlling and monitoring the process parameters in batch systems are much easier. This makes them ideal for research purposes. However, to expand research to higher heating rates to maximize bio-crude yield as previously discussed in Section 4.2, small reactors, or a batch reactor with a powerful heater is required. High ramping time in standard batch reactors can cause an increase in repolymerization reactions and decrease the bio-crude yield. Therefore, it is not possible to determine the true bio-crude potential of a substrate with batch reactors with a low heating rate[344]. Another disadvantage of the batch systems is the headspace purging requirement to avoid liquid loss and to get rid of oxygen. This is not a major problem at lab-scale; however, at full-scale, purging would increase operational costs significantly.

Batch HTL systems are also able to utilize not pumpable substrates with higher solid content. Due to their simplicity, major continuous-flow HTL system problems, such as clogging, do not develop in batch systems[18]. Since the substrate in the continuously stirred batch reactor stays homogenous during the process, it is also possible to obtain samples from both slurry and gas. On the other hand, as a drawback, batch reactor stirring systems are not so efficient as continuous-flow conditions. Batch studies in the literature reported agitation speeds ranging between 50 rpm[322] to 1300 rpm[338] depending on the reactor volume and stirring equipment. Among batch studies in the literature, no study considered agitation as a significant HTL parameter. A potential full-scale batch HTL system is presented in Figure 19.

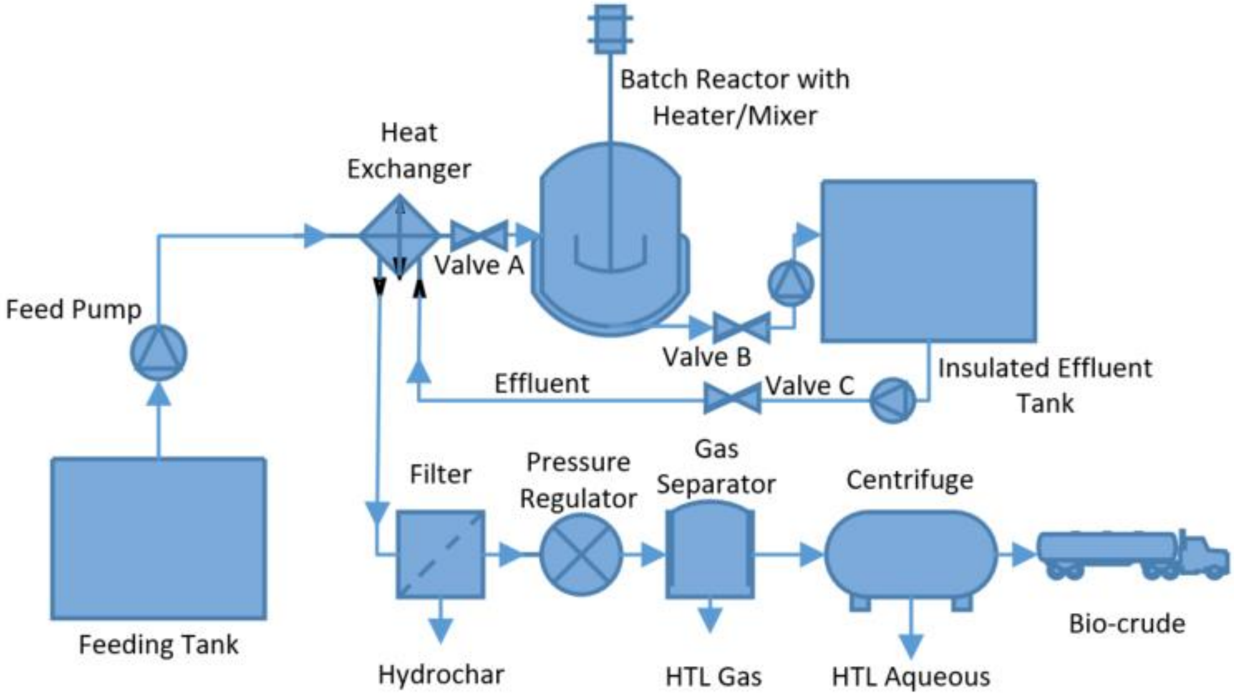


Figure 19. A potential full-scale batch HTL reactor system

In this design, after the HTL reaction is complete, in order to achieve heat recovery, this system needs to send the effluent to an insulated tank. After emptying the reactor, valve B is closed, and the hot effluent collected in the insulated tank is pumped to the heat exchanger along with feed being pumped into the reactor. The preheated substrate can be further heated to the desired temperature in the batch reactor. However, pumping the effluent into another tank after the reaction and waiting for the reactor to be drained entirely result in a considerable amount of energy loss. For that reason, in terms of heat recovery, batch HTL systems are inefficient and can not be applied at full-scale. Also, due to the filling and draining times of the batch reactor, the reactor volume can not be used efficiently throughout the operation. Continuous-flow HTL systems can overcome all the limitations mentioned above and issues that a full-scale batch HTL reactor would face.

5.2 Continuous-flow HTL systems

Continuous-flow systems are the best option for pilot- and full-scale applications. Although a high-pressure pumping, up to 220 bar, is required for feeding the reactor, the higher heat recovery rate makes these systems effective. Anastasakis et al.[15] reported heat recovery rates between 66.5-79.9% in their continuous-flow HTL system. Another major advantage of these systems is the high heating (ramping) rate, which was reported in the literature as 100°C/min[15,17] or even 200-400°C/min[197]. HTL conditions with lower ramping times lead to a higher bio-crude yield[139,267,291] and decrease the required reactor volume significantly. HTL reactors need to be built from expensive, heat and corrosion-resistant alloys due to the high temperatures that they are operated. Therefore, smaller reactor volumes can lower the capital costs drastically and make continuous-flow HTL systems more affordable. The main units of a full-scale continuous-flow HTL system are feeding pump, heat exchanger, electric heater, a plug flow reactor and a pressure regulator, presented in Figure 20.

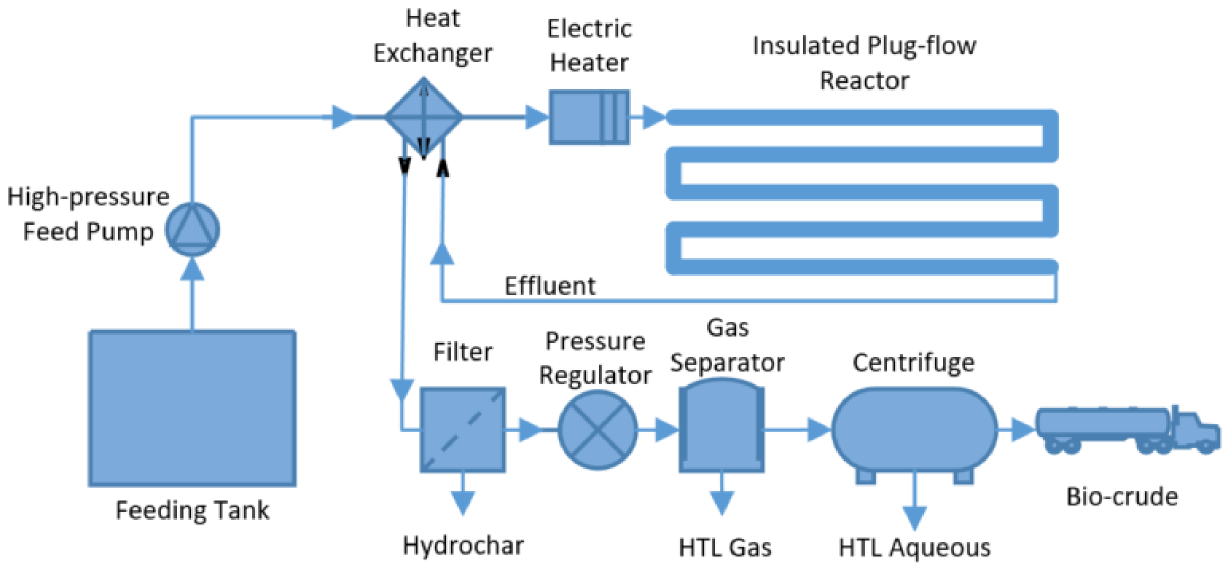


Figure 20. A typical full-scale continuous-flow HTL reactor design

The primary purpose of the electric heater and plug flow reactor is to reach the desired temperature and provide retention time; therefore, they can also be combined and designed as a CSTR reactor[345]. The order and design of phase separation units can vary depending on the type of substrate and budget.

Research on continuous-flow HTL systems can be conducted with both lab-scale continuous-flow reactors and fast heating batch reactors. However, building a lab-scale continuous-flow system is challenging due to the complexity of system, safety concerns, and scaling down limitations, such as acquiring a lab-scale high-pressure pump[346]. Therefore, most of the studies on continuous-flow HTL systems have been conducted with reactors between lab- and pilot-scale. In their study, Wagner et al.[344] described the design of an inexpensive lab-scale continuous-flow HTL system by using high-pressure N_2 for feeding. Mørup et al.[346] also published a very detailed study that describes the design and construction of a continuous-flow HTL reactor used in Aarhus University. This study includes the mechanical properties of selected units and acquisition of reactor with LabVIEW software. Details of current continuous flow HTL studies around the globe are summarized in Table 9.

Table 9. Summary of continuous-flow HTL studies

HTL conditions					Bio-crude yield from HTL (% wt)	Reference
Substrate	Catalyst(s)	Substrate to solvent ratio (w:w)	Reaction temperature	Retention time		
Pine *Miscanthus* *Spirulina* Sewage sludge	-	Pine 1:5 Miscanthus 3:20 Spirulina 4:25 Sewage sludge 1:25	350°C	6 min	38.2% 26.2% 32.9% 24.5%	17
Dried distillers grains with solubles	2% K_2CO_3	1:5	340°C	20 min	38.9% daf[a]	157
Blend of sewage sludge and scum from primary settling	-	N/A	350°C	10-30 min	50%	347
G. sulphuraria 5587.1 *G. sulphuraria SOOS*	-	1:20	350°C	5 min	16.9% 23%	20
Saccharina spp.	-	1:5	364°C	40 min	27.7% daf	164
Algae: Solix LEA, NB238, Cellana LL[b], Cellana HL[c]	-	Solix LEA: 1:6 NB238: 1:5 Cellana LL: 7:20 Cellana HL: 1:3	344-362°C	27-40 min	53.2% daf 38% daf 60.8% daf 63.6% daf	165
Oedogonium intermedium strain TSV2	-	1:20	300°C	5 min	25% daf	21
Dewatered sludge	-	1:5	290-300°C	260 min	48% daf	348
Chlorella	-	1:10	350°C	3 min	41.7% daf	177
Concentrated acid hydrolysis lignin	3% HCOOH	1:3	350°C	28 min	59.92%	182
Douglas fir wood	-	1:5	340°C	60 min	33%	14
Grape pomace	1% Na_2CO_3	3:25-17:100	350°C	30 min	Montepulciano: 39% daf Cabernet sauvignon: 41% daf	185

PS[e], SS[f], DS[g]	-	PS 3:25 SS 1:10 DS 4:25	350°C	PS 18 min SS 19 min DS 30 min	PS: 37.3% daf SS: 24.8% daf DS: 34.4% daf	187
WAS[h], Rubber wood sawdust	0.14% KOH	1:36	310°C	10 min	25.31% daf 31.9% daf	192
Swine manure	-	1:5	305°C	80 min	70% daf	195,349
Miscanthus *Spirulina* Sewage sludge	*1.4% KOH only for Miscanthus*	*Miscanthus* 3:20 *Spirulina* 4:25 Sewage sludge 1:25	350°C	5.6 min	26.2% 32.9% 24.5%	15
1:1 Aspen wood and glycerol	4.2% K_2CO_3	7:20	400°C	43 min	~31%.	197
Acid treated or untreated Douglas fir wood	0.1% Na_2CO_3	3:25	332°C	100 min	56.8% daf	11
Nannochloropsis salina	-	1:5	350°C	N/A	64% daf	350
Kraft lignin	5% NaOH	1:20	240°C	2 min	N/A	351
SL[d] and HL[c] *Chlorella*	-	SL: 3:20 HL: 1:5	350°C	27 min	SL: 35% daf HL: 71% daf	352
Kraft lignin	$NaOH/Na_2CO_3$, KOH/K_2CO_3	1:20	350°C	6 min	37.60%	353
Kraft lignin + 2-10% phenol	0.3% KOH 1.6% K_2CO_3	1:20	350°C	6 min	61%	354
Kraft lignin	1.6% KOH 1.6% K_2CO_3	1:20	350°C	12 min	44%	355
Chlorella	-	1:10	350°C	1.4 min	39.7% daf	356
Bioshell slurry Eucalyptus	-	Bioshell slurry: 3:41 Eucalyptus: 1:33	350°C	6 min	42.5% daf 48.6% daf	357
S. cerevisiae	0.9% K_2CO_3	7:25	400°C	2 min	51.40%	358
S. cerevisiae Apple pomace	0.9-1.6% K_2CO_3	*Saccharomyces cerevisiae*: 1:4 Apple pomace: 1:5	400°C	2 min	47.4% 39.8%	359
Food waste	1.5% K_2CO_3	3:25	330°C	10 min	13%	360
Distiller dried grains with solubles	2% K_2CO_3	1:5	350°C	15 min	39%	346
Primary sewage sludge	5% Na_2CO_3	1:5	275°C	261 min	36.3% daf	361
Kraft lignin	4.1% Phenol 1.6% K_2CO_3	1:20	290°C	10-13 min	6.6%	362
Sewage sludge	-	1:5	350°C	N/A	45%	301

Nannochloropsis sp.	-	N/A	380°C	0.5 min	38%	[363]
Rhizopus oligosporus	-	1:25	400°C	12 min	60.9% daf	[364]
Distilleries dried grains with solubles	2.5% K_2CO_3 ZrO_2	1:4	350°C	N/A	33.9%	[365]
Scenedesmus sp.	-	1:20	350°C	30 min	35% daf	[366]
Scenedesmus and *Chlorella*	-	1:20	344°C	N/A	21.2%	[344]
Sugar beet pulp	-	N/A	350°C	15 min	~67% daf	[367]
Any type of biomass	K_2CO_3 ZrO_2	-	341°C	30 min	45%	[368]

[a]daf: Dry ash-free, [b]LL: Low lipid, [c]HL: High lipid, [d]SL: Standard lipid, [e]PS: Primary sludge, [f]SS: Secondary sludge, [g]DS: Digested sludge, [h]WAS: Waste activated sludge

The literature indicates that continuous-flow HTL systems have, on average, shorter reaction times and higher bio-crude yields compared to batch HTL reactor results. Although there have been many projects and large investments from the industry, there is a lack of information regarding process performance failures and challenges revealed during design, construction, start-up, and operation in the industry. This situation creates a major obstacle to the development and scale-up of HTL technology as a reliable process at full-scale. Future studies in partnership with industry and research institutions should allow for dissemination of results to general public that would help to overcome these challenges.

6 Techno-economical analysis of the HTL process

The major operating expenses in a full-scale HTL process are caused by substrate production or supply, dewatering, pumping, heating, phase separation, chemicals (solvents, catalysts), and waste management for product streams (aqueous and hydrochar). Among the major expenses, if algae or agricultural sources biomass is used, substrate supply would constitute the majority of the total cost[369]. Hence, the most economical option is to couple HTL plants with waste-producing facilities, such as wastewater treatment plants. As an important advantage among biomass valorization methods, HTL does not require a biomass dying process, which is an energy sink[12]. The bottleneck of the HTL process is the energy consumption for heating the substrate to the desired temperature. However, by incorporating a heat exchanger and efficient heat insulation, this energy consumption can be lowered. Furthermore, the application of the right catalyst to the HTL process can decrease the process temperature and input energy costs significantly. Energy consumption points and amounts of a continuous-flow HTL system are given in Figure 21. Calculations were done by assuming a 15% solid content of substrates and 50% (daf) bio-crude yield in the HTL process.

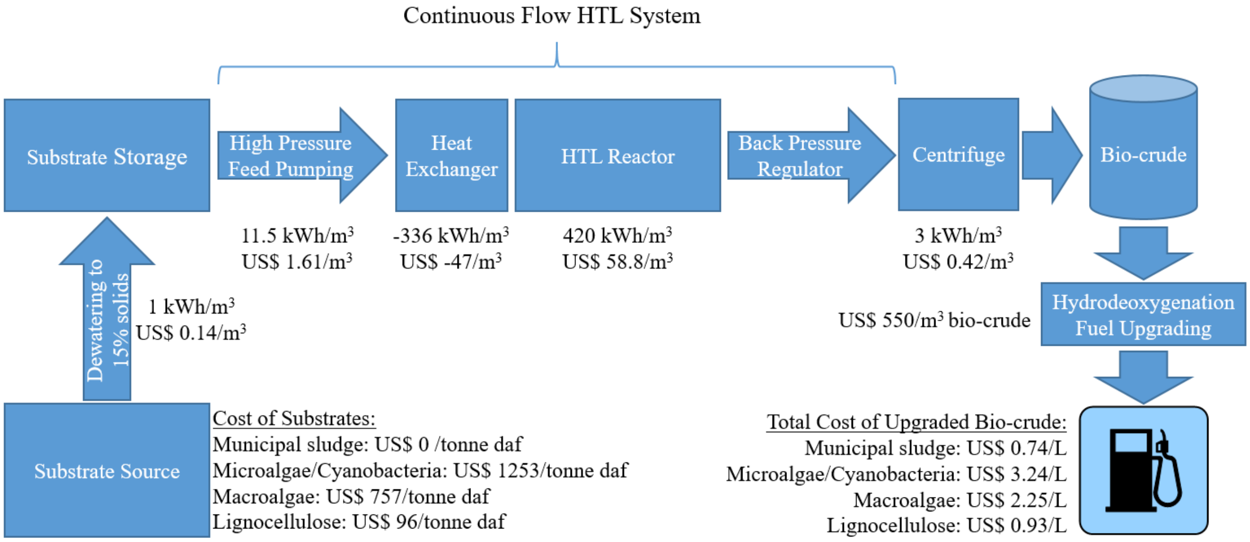


Figure 21. Summary of costs in the HTL process (data obtained from[15,370–373])

In the literature, production costs of microalgae/cyanobacteria, macroalgae and lignocellulose were reported as US$ 1253 /tonne (daf)[374], US$ 757 /tonne (daf)[375] and US$ 96 /tonne (daf)[376], respectively. Since it is a waste, and it is assumed that the HTL plant will be coupled with a wastewater treatment plant, the cost of municipal sludge production was assumed as US$ 0 /tonne (daf). Since the substrate cost is the main cost in the total operational cost, municipal sludge-based bio-crude was found to be cheaper than the other bio-crudes. For the substrate of municipal sludge, microalgae or cyanobacteria, macroalgae, and lignocellulose, the cost of producing a liter of upgraded bio-crude by HTL was found to be US$ 0.74, US$ 3.24, US$ 2.25, and US$ 0.93, respectively. Results indicate that elimination or reduction in substrate costs plays a major role in the final product's price. Funkenbusch et al.[377] investigated coupling an HTL plant with a Kraft pulping process and found that Kraft lignin-based bio-crude can be produced for US$ 0.41-0.43 /L if the hydrodeoxygenation process for fuel upgrading is performed on-site. Zhu et al.[378] reported a US$ 1.29 /L bio-crude cost produced from lignocellulosic sources, whereas Ramirez et al.[379] found the minimum selling price of wood-based bio-crude as US$ 1.17 /L. Also, Perkins et al.[380] underlined that with current production costs, the minimum bio-crude selling price should be US$ 0.92-1.10 /L.

These cost calculations do not include valorization or treatment of HTL aqueous, hydrochar, and gases. Among those co-products, HTL aqueous has the potential to affect bio-crude costs considerably. One of the most efficient ways of valorizing HTL aqueous is to use it in anaerobic hydrogen or methane production due to presence of soluble organics. Although producing hydrogen seems to be the right approach to decrease the cost of hydrodeoxygenation fuel upgrading process, HTL aqueous may not be an ideal substrate for biochemical hydrogen or methane production due to its high concentrations of inhibitory and recalcitrant compounds[381,382]. Si et al.[383] found that in an up-flow anaerobic sludge blanket reactor, by the addition of 8 g COD/L equivalent HTL aqueous, biohydrogen fermentation and subsequent methane fermentation were inhibited 100% and 50%, respectively. Another alternative is to dilute HTL aqueous and utilize it in an anaerobic digestion process. Produced methane from this process can be converted to electricity and heat on-site and used in HTL or hydrodeoxygenation processes. Coupling an HTL plant with an anaerobic digestion process was also found beneficial in terms of energy recovery[384,385]. However, adding an anaerobic process for hydrogen or methane production increases capital costs. Davidson et al.[386] calculated that if co-products are processed on-site, waste disposal would only increase the bio-crude cost by US$ 4 /L. If the HTL aqueous is used in a treatment process instead of valorization, capital investments required for condensed phase ketonization, dual-bed steam reforming, and catalytic hydrothermal gasification processes were reported as US$ 34.1M, US$ 34.1M[386] and US$ 16.8M[387], respectively.

The handling cost of the HTL aqueous phase from an HTL utilizing lignocellulosic biomass with low moisture would be lower since it can be recirculated in the HTL process. Knorr et al.[388] also stated that direct aqueous phase recirculation increases heat recovery significantly. They found that an HTL aqueous recirculating plant has the lowest operating cost with US$ 22.5M/year. However, it was also reported in the literature that over six times of recirculation of the HTL aqueous phase could lower bio-crude yield and quality[157,201,205]. Furthermore, recirculation causes the accumulation of inhibitors and recalcitrant substances, which increases the treatment cost of the aqueous phase. If the substrate is municipal sludge in the HTL process, the aqueous phase might be returned to the treatment plant to not to add an extra treatment cost to the process. However, the effect of the inhibitory compounds in the aqueous phase, mainly nitrogen-containing organics and aromatic compounds[389], on wastewater treatment processes is unknown.

HTL gas and hydrochar are the other co-products that need handling. Hydrochar can be landfilled, combusted, or valorized by the application of further processes. Generally, hydrochar amount produced in the HTL process is so low (<20% on a dry basis) that its effect on total process cost is negligible. The only concerns about hydrochar are its heavy metal and persistent organic pollutant concentrations. However, Li et al.[269] reported that HTL reduced the high environmental risk due to the immobilization of heavy metals in the raw substrate (animal manures) to medium for hydrochar. Therefore, it is even possible to use hydrochar in soil amendment safely. Some studies also showed that HTL can destroy most persistent organic pollutants present in the substrate[390]. On the other hand, since the major fraction of HTL gas is CO_2 and it does not contain any dangerous compounds, it can be released into the atmosphere. However, to make the HTL process more environmentally friendly, greenhouse gases, including CO_2, can be captured by adsorption[391]. The addition of the gas adsorption process would cause an extra operating cost of US$ 60-190/tonne of CO_2 captured[392].

7 Conclusion and recommendations for future research

As one of the most efficient ways of converting biomass into biofuels, the development of the HTL process is both economically and environmentally crucial. This review is aimed to be a source study for HTL researchers by summarizing the key design and operational parameters to optimize process performance and energy/product recovery. The key findings of this review are presented below.

- Optimum HTL process conditions for bio-crude production require short ramping (high heating rate) and retention times. Optimum values of other HTL conditions, on the other hand, differ depending on the substrate type.
- Among the five most studied substrate types, municipal sludge was found to be the most suitable feedstock for HTL due to its availability and biochemical composition.
- In the techno-economical analysis, bio-crude upgrading was found as the highest operating cost.
- The effect of catalysts was found to be substrate-specific. Therefore, it is not possible to define a common catalyst for all substrate types.

- Catalysts can decrease the required HTL severity for the bio-crude generation. Utilization of the right catalyst type in the right concentration can lower the operation cost.

- In HTL of lignocellulosic substrates and macroalgae, bio-crude yields were found lower compared to the other substrates due to the accumulation of organic acids. Therefore, to reach higher bio-crude yields, alkaline catalysts should be used for these substrates.

- HTL substrates should have a balanced carbohydrate to protein ratio to take advantage of Maillard reactions in the HTL process. Carbohydrate-rich and protein-rich substrates were found to have high amounts of organic acids and amides in HTL aqueous, respectively.

- Alcohol solvents were found beneficial on the HTL of carbohydrate-rich biomasses. They increase the bio-crude yield by undergoing an esterification reaction with carboxylic acids. This reaction can be catalyzed by zeolite or acid catalysts for further increase.

Although this promising technology has come a long way, there is still much room for development. Once the research gaps of HTL are filled, it has the potential to minimize our dependence on fossil fuels without changing our current fuel utilizing infrastructure. Hereof, there is still much to explore for researchers and the industry. Recommendations for future research are given below.

- There are still unknown HTL pathways due to the vast number of organic molecules involved in the process. Revealing the unknown pathways and reaction kinetics would be beneficial to provide a deeper understanding of the process and product optimization.

- To the best of our knowledge, there is no published study focusing on the HTL parameter of pressure, possibly to difficulties in logistics to separate temperature from the pressure affect at the lab- or pilot-scale. Studies differentiating the effect of temperature and pressure on bio-crude yield are required.
- More studies regarding producing higher quality bio-crude that does not require an upgrading process and research on more economical upgrading processes are needed.

- There are still important research gaps for the utilization/safe disposal of co-products of HTL, aqueous phase, and hydrochar. For the co-products, more research towards valorization, treatment, and environmental impact of disposal is required.

- Catalysts are crucial in the HTL process in order to decrease reaction severity and costs while increasing bio-crude yield and quality. Although many studies investigated the use of catalysts, their specific effect on pathways and kinetics are generally not reported. Hence, more studies focusing on the catalytic effects are needed for the development of HTL technology at full-scale.

- Studies that investigate optimum HTL conditions are limited. More substrate-specific optimization studies that use more comprehensive experimental designs and statistical methods are required.

- For future studies, it would be beneficial if the results were reported in the energy recovery (ER) unit instead of bio-crude yield (wt %). This way, both the quality and quantity of bio-crude can be included in the comparison of results.

- HTL technology is both costly and scientifically complex. Therefore, long-term interdisciplinary collaborations in partnership with academia and key industry are essential for process development at full-scale and sharing/dissemination of knowledge.

- The majority of the studies do not provide sufficient information regarding mechanical issues encountered with continuous-flow HTL systems. Further studies assessing continuous-flow HTL systems using various substrates are needed.

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