



Article

Sub-Supercritical Hydrothermal Liquefaction of Lignocellulose and Protein-Containing Biomass

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Abstract: Hydrothermal liquefaction (HTL) is an emerging technology for bio-crude production but faces challenges in determining the optimal temperature for feedstocks depending on the process mode. In this study, three feedstocks—wood, microalgae spirulina (*Algae Sp.*), and hydrolysis lignin were tested for sub-supercritical HTL at 350 and 400 °C through six batch-scale experiments. An alkali catalyst (K₂CO₃) was used with wood and hydrolysis lignin, while *e* (*Algae Sp.*) was liquefied without catalyst. Further, two experiments were conducted on wood in a Continuous Stirred Tank Reactor (CSTR) at 350 and 400 °C which provided a batch versus continuous comparison. Results showed *Algae Sp.* had higher bio-crude yields, followed by wood and lignin. The subcritical temperature of 350 °C yielded more biocrude from all feedstocks than the supercritical range. At 400 °C, a significant change occurred in lignin, with the maximum percentage of solids. Additionally, the supercritical state gave higher values for Higher Heating Values (HHVs) and a greater amount of volatile matter in bio-crude. Gas Chromatography and Mass Spectrometry (GCMS) analysis revealed that phenols dominated the composition of bio-crude derived from wood and hydrolysis lignin, whereas *Algae Sp.* bio-crude exhibited higher percentages of N-heterocycles and amides. The aqueous phase analysis showed a Total Organic Carbon (TOC) range from 7 to 22 g/L, with *Algae Sp.* displaying a higher Total Nitrogen (TN) content, ranging from 11 to 13 g/L. The pH levels of all samples were consistently within the alkaline range, except for Wood Cont. 350. In a broader perspective, the subcritical temperature range proved to be advantageous for enhancing bio-crude yield, while the supercritical state improved the quality of the bio-crude.

Keywords: sub-supercritical HTL; lignocellulosic biomass; microalgae; bio-crude



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1. Introduction

The decline in the use of fossil fuels has led the world to explore new resources and embrace renewables. Biomass, a renewable source, can be harnessed for energy production [1]. The European Union (EU) is making significant efforts to become the first climate-neutral region globally by 2050, emphasizing sustainable transportation with green fuels [2]. For energy production in the form of biofuel or biogas, biomass can be treated in two ways, through biochemical and thermochemical routes. The thermochemical process has an edge over the biochemical due to its rapid conversion and short duration of reaction time [3]. Hydrothermal liquefaction (HTL) is a type of thermochemical process which converts any type of biomass into high-energy bio-crude under temperature from 280 to 400 °C and pressure from 15 to 25 MPa [4]. HTL utilizes the basic thermodynamic property of water at sub and near-critical state where reactions such as depolymerization, bond

breaking, rearrangement, and decarboxylation take place to decompose the solid structure of biomass into oily components (bio-crude) [5].

Over the years, various studies have been published on the treatment of mainly lignocellulosic and high-proteinaceous biomass like wood [6–10], microalgae [11–14], and lignin [15,16]. Lignocellulosic biomass is a ubiquitous natural resource, with lignin ranking as the second most abundant compound in plants [17]. Moreover, the paper industry produces a significant amount of lignin as a by-product, known as Kraft lignin (cellulose extracting process) [18]. Approximately 55 million tons of lignin have been produced annually by the pulping processing industry, contributing significantly (80%) to the global production. However, despite being one of the most abundant biopolymers in nature and industry, lignin has not been effectively utilized, as it is only being used for chemical production and heating sources. Exploring bio-crude production presents a promising option to extract the maximum energy potential from lignin [19]. Yang et al. conducted a liquefaction test at 290 °C on five model components: xylan (hemicellulose), crystalline cellulose, alkaline lignin, soya protein, and soybean oil. Their findings revealed the bio-crude yield trend from highest to lowest as lignin, hemicellulose, cellulose, protein, and lipids. [20]. Mathanker et al. conducted a parametric study on corn stover, exploring temperatures of 250, 300, 350, and 375 °C, along with initial pressures set at 300 and 600 psi, and retention times of 0, 15, 30, and 60 min. The highest conversion and yield of Heavy Oil were achieved at 300 °C, with values of 82.62 wt.% and 29.25 wt.%, respectively. Notably, the Heavy Oil yield decreased with temperatures rising beyond 300 °C [21]. Pinkowska et al. carried out a sub-supercritical liquefaction (279 to 379 °C) of alkali lignin, examining its impact on the yield of primary compounds. The highest yields for guaiacol, catechol, phenol, and cresol isomers were observed at approximately 11.23% (553K, 0 min), 11.11% (653K, 0 min), 4.21% (663K, 240 min), and 7.00% (663K, 240 min), respectively [22]. Belkheiri et al. explored the impact of phenol as a capping agent on HTL of lignin to inhibit char formation. Various feed concentrations of phenol (2–10%) were examined, revealing that even at low concentrations, phenol partially hinders repolymerization. The bio-crude yield remained stable at 61% across varying phenol concentrations. Regarding catalyst-induced char formation, the char yield exhibited a modestly decreasing trend (14.6–12.3%) with an increase in the amount of phenol in the feed [23]. Similarly, microalgae are a promising renewable, sustainable, and economical resource for biofuels and chemicals due to their good adaptability, high conversion rate, and environmental friendliness. The majority of researchers have reported their results in the range from 280 to 370 °C [24–27]; for example, Biller et al. studied the effects of acid and alkaline catalysts on microalgae (*Chlorella*, *Nannochloropsis oculata*, *Porphyridium*, and *Spirulina*) and some modal compounds at 350 °C. The results showed the trend of lipids > proteins > carbohydrates for bio-crude yield. Both proteins and lipids were converted to bio-crude most efficiently without the use of catalysts, while carbohydrates were best processed using Na₂CO₃ [14]. Whereas Vo et al. observed 51% bio-crude yield while liquifying microalgae (*Aurantiochytrium* sp.) under supercritical temperature (400 °C) for 10 min [28].

However, a comparative study of wood, *Algae* Sp., and hydrolysis-lignin at sub- and supercritical states (particularly at 400 °C) and its characterization is still missing in the literature. In this context, three different feedstocks (Wood, *Algae* Sp., and *Hydrolysis lignin* (by-product of bioethanol)) were selected for the sub-supercritical HTL. This study was conducted to assess the liquefaction behavior of different varieties of feedstocks (lignocellulosic and high-protein-containing biomass) in sub- and supercritical water and to examine its effect on bio-crude yield and properties. Moreover, some continuous HTL experiments were also performed using the Continuous Stirred Tank Reactor (CSTR) on wood at same conditions to have a comparative information of batch and semi continuous plant. In the last section, the identified challenges with suitable recommendations are discussed to pave the way for feasible HTL in the future.

2. Materials and Methods

2.1. Collection of Feedstocks and Their Analysis

Pine wood powder was collected from Aalborg South, Aalborg Denmark, while *Algae* Sp. was purchased commercially from Norway, the Cellunolix[®] hydrolysis lignin was obtained from St1 Norge AS. The proximate analysis of the feedstocks was carried out. The moisture content was determined by a moisture analyzer. The volatile matter (VM) was detected through thermogravimetric analysis (TGA, TA instrument Discovery) at 800 °C under nitrogen gas, whereas the ash content was measured through furnace method by heating the biomass at 775 °C for four hours. Temperature ranges for ash and volatile fractions were selected on the basis of previous studies [29,30]. Elemental composition of all feedstocks was analyzed through elemental analyzer (Perkin Elmer, 2400 Series II CHNS/O), operated on CHN mode. HHV of biomass were calculated through C2000 basic Calorimeter (IKA, Staufen, Germany).

2.2. HTL Experiments

All HTL experiments were carried out at SINTEF Energy Research's lab facilities, Trondheim Norway, whereas all the characterization of HTL products was carried out in Advanced Biofuel Lab, at Aalborg University, Denmark. At SINTEF Energy Research, the batch experiments were conducted in Continuous Stirred Tank Reactor (CSTR)—operated on batch mode with the following features: internal volume 1000 mL, internal diameter 80 mm, internal height 200 mm, feed capacity 0.5–2 L/h, and maximum design range of temperature 500 °C. For continuous scale experiments, the same system was used with complete CSTR mode, slurry feeding with dual pumps at 350 and 400 °C, at a pressure of 350 bar as demonstrated in Figure 1.

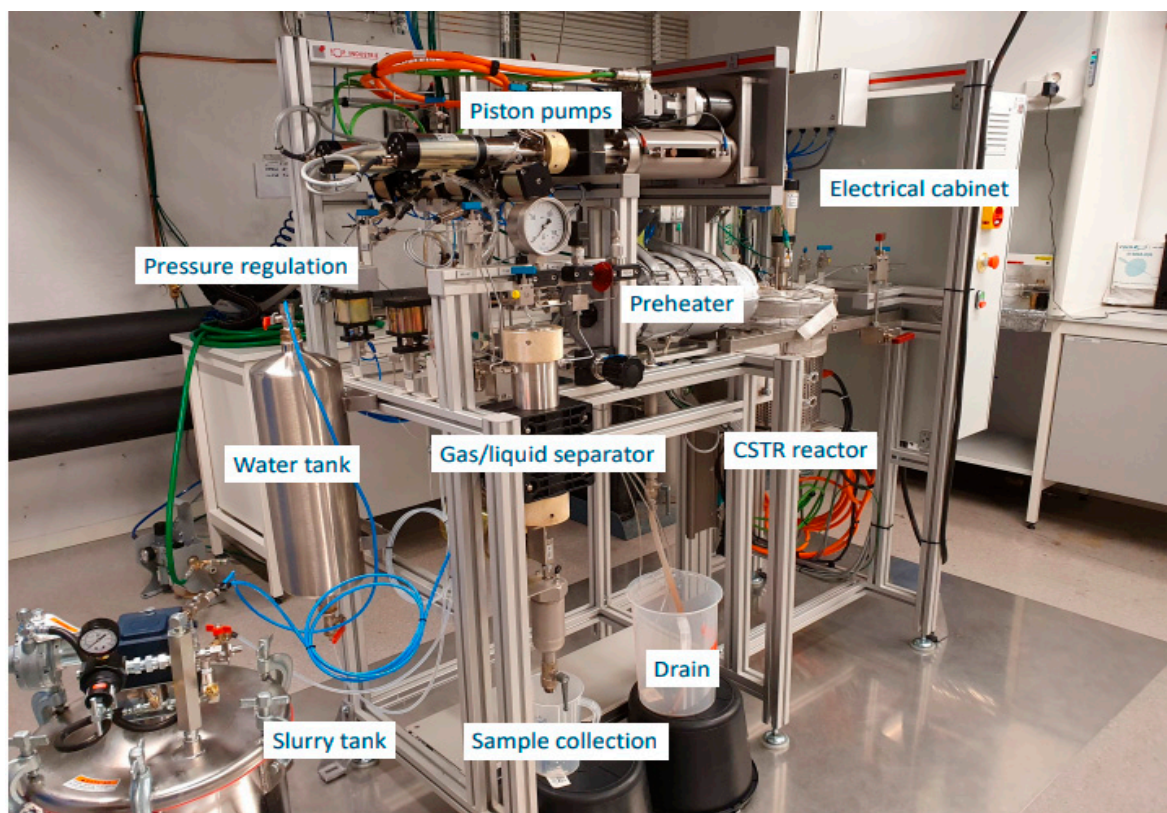


Figure 1. CSTR system at SINTEF Bio-Lab, Trondheim, Norway.

For batch experiments, 550 mL and 330 mL of slurries were prepared with 10% dry matter from all feedstocks at temperatures of 350 and 400 °C under the retention time of 1 h. The 2% catalyst (K_2CO_3) was applied to wood and hydrolysis lignin, whereas *Algae* Sp.

slurry was prepared without catalyst, after a literature survey that alkali catalysts do not prove useful for high-proteinaceous biomass [14,25]. The different volume of slurries was kept by keeping in mind the expected volume of gases to be produced at higher temperature. The slurry was poured into the reactor, the reactor was tightened, the temperature was allowed to increase up to the desired level, and continuous readings of temperature and pressure were recorded at screen monitors.

After the reaction, the reactor was allowed to cool down to room temperature. Firstly, the upside valve was opened, and the gas was vented out. Then, the reactor was opened, and the aqueous phase was collected by a syringe. The reactor was washed with acetone, and then the mixture underwent vacuum filtration to collect the solid phase. The remaining mixture of acetone and bio-crude was slowly heated at 40 °C to evaporate the acetone, and, in last bio-crude, it was weighted to report the final yield on a dry ash-free (daf) basis. All experiments were performed in duplicate to maintain consistency in results.

The two experiments were carried out at a semi-continuous scale on wood at temperatures of 350 and 400 °C, with a 2% catalyst concentration corresponding to 10% dry matter. Unfortunately, the *Algae Sp.* slurry proved to be too thick and fluffy, hindering interaction with water. Consequently, only water drained out of the outlet valve, resulting in inadequate hydrothermal conversion. On a positive note, lignin was efficiently pumped; however, issues arose downstream as the reactor became blocked due to the increased char production under pressure and the system capillaries' incompatible size.

Product separation in the wood experiments followed the same procedure as in the batch experiments, excluding the use of acetone. The gravimetric method was employed to separate bio-crude and water.

2.3. Analysis of HTL Products

The elemental composition of HTL bio-crude and solid phase was determined by elemental analyzer (Perkin Elmer, 2400 Series II CHNS/O), operated in CHN mode. The stability and thermal behavior of bio-crude was detected through TGA under the nitrogen atmosphere at a temperature of 800 °C; simultaneously, the ash content was also determined by keeping the sample on isothermal mode under oxygen gas at 800 °C. Organic compound composition in bio-crude was analyzed by a Gas Chromatograph system coupled with a Mass Spectrometer (GC-MS). The GC oven, equipped with a capillary column, had the temperature raised up to 300 °C. For GCMS, the bio-crude samples were prepared using the DEE and then filtered using the syringe filters before being injected into GC oven. The aqueous phase was also analyzed through indicators of total organic carbon, total nitrogen, and pH. The TOC and TN were through HACH Kits (LCK: 386, 138 respectively) and a spectrophotometer unit (Hach & Lange, DE3900), respectively. The pH was measured through a WTW pH meter 3210. The Higher Heating Value (HHV) for bio-crude was calculated using the Channiwala and Parikh correlation [31].

The bio-crude, solid yield, and energy recoveries were calculated using the following equations.

$$\text{Bio - crude yield}(\%) = \frac{\text{weight of bio - crude}}{\text{weight of grassresidue (daf)}} \times 100 \quad (1)$$

$$\text{Solid residue yield} (\%) = \frac{\text{weight of Solid residue}}{\text{weight of grass residue (daf)}} \times 100 \quad (2)$$

$$\text{HHV (MJ/kg)} = (0.3419) \text{ C} + (1.1178) \text{ H} - (0.1005) \text{ O} - (0.1034) \text{ N} \quad (3)$$

$$\text{Carbon recovery}(\%) = \frac{\% \text{C in Product}}{\% \text{C in grass residue}} \times \text{product yield in } (\%) \quad (4)$$

$$\text{Energy recovery in bio - crude} (\%) = \frac{\text{HHV of bio - crude}}{\text{HHV of grassresidue}} \times \text{bio - crude yield} \quad (5)$$

3. Results and Discussion

3.1. Feedstock Characterization

The feedstocks were characterized to assess their proximate and chemical properties. In the biomass context, the volatile matter content is a key parameter, influencing the combustible fraction, ignition, and combustion characteristics. Volatile matter values were determined for all feedstocks using TGA in the presence of nitrogen gas. Wood exhibited the highest value (91%), followed by *Algae Sp.* (72%), and lignin (60%), all measured at 800 °C. This indicates that, under this temperature, all organic matter involved in forming (biocrude, aqueous phase, and gas) was combusted, leaving behind fixed carbon and ash contents. The thermogravimetric curves are illustrated in Figure 2.

Both wood and lignin showed lower values for ash contents from 0.3 to 0.5, whereas *Algae Sp.* contained 8.92% of ash. Fixed carbon (FC) was calculated by the formula $FC = 100 - (\text{Moisture} + \text{Ash} + \text{VM})$. Lignin showed the highest value for HHV due to the presence of maximum amount of carbon. All feedstock showed promising values for H/C, indicating good prospects for bio-crude production. Here, all values are reported on a dried ash-free basis (Table 1).

Table 1. Characterization of the feedstocks.

Feedstocks	Moisture (%)	Ash ^a	VM ^a	FC ^a	C (%) ^b	H (%) ^b	N (%) ^b	O (%) ^{b,d}	H/C	HHV (MJ/kg)
Wood Powder	9.88	0.40	91.11	8.60	46.09	6.59	0.09	47.24	1.71	18.36
<i>Algae Sp.</i>	5.87	8.92	72.23	19.08	45.80	6.83	10.66	36.72	1.79	18.50
Lignin	4.41	0.20	60.45	39.80	61.85	6.08	0.63	31.45	1.18	24.72

^a Dry basis. ^b Dried ash-free basis. ^d Oxygen calculated by difference.

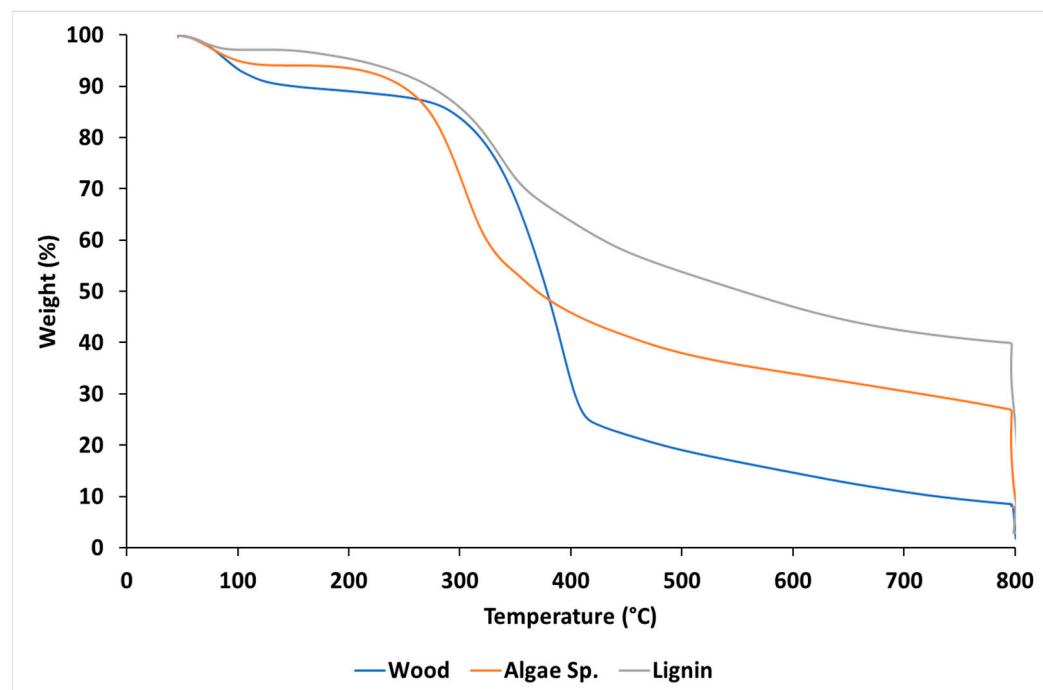


Figure 2. Volatile matter in feedstocks.

3.2. Yield of HTL Products

Eight experiments were carried out in total, with six conducted at batch scale at 350 and 400 °C, and two (Wood cont. 350 and Wood cont. 400) performed at continuous scale, as depicted in Figure 3. The bio-crude yield from three feedstocks (wood, *Algae Sp.*, and

lignin) exhibited temperature-dependent variations. Notably, the highest bio-crude yield (29%) was observed from *Algae Sp.* at 350 °C. Under subcritical conditions, all feedstocks demonstrated higher bio-crude yields with lower solids compared to the supercritical state. Interestingly, at supercritical conditions, both wood and *Algae Sp.* experienced a 6–7% decrease in bio-crude yield, while lignin exhibited a unique behavior, displaying the lowest bio-crude yield of 7% and the highest solids content (35%). Earlier, Yong et al. reported that SCW caused to depolymerize the lignin in a few seconds but resulted in high char yield due to repolymerization of phenolics and aromatic intermediates at high temperatures and long residence time [32]. The temperatures in the sub- and near-critical region cause a decrease in the dielectric constant, density, and polarity of water. This, in turn, accelerates hydrolysis reactions and enhances the solubility of hydrophobic organic fractions. Despite these effects, there was no significant increase observed in bio-crude yield in the supercritical state; however, the bio-crude HHV was improved fairly. This lack of increase in bio-crude yield could be attributed to surpassing the threshold temperature (critical point: 373.74 °C), leading to the conversion of bio-crude components into the aqueous or gaseous phase. Under supercritical conditions, the lower solid yield resulted from the conversion of heavier fragments into lighter ones through cracking reactions.

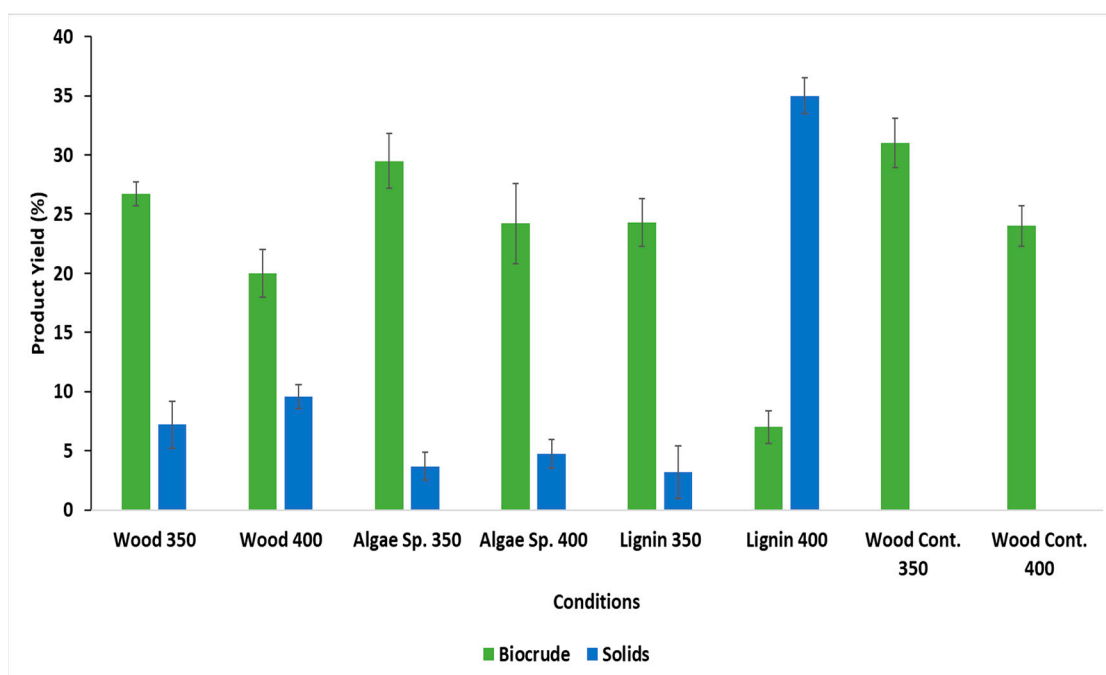


Figure 3. The yield of HTL products.

If we consider bio-crude yield as the focal point of the discussion, it is noteworthy that *Algae Sp.* exhibited the highest bio-crude yields in the subcritical state, potentially attributed to the higher presence of proteins. These proteins undergo facile hydrolysis into water-soluble amino acids under high-temperature conditions. Subsequently, amino acids further degrade into gaseous products, such as carbon dioxide and ammonia, through processes like decarboxylation and deamination, respectively [33]. This outcome aligns with findings by Toor et al., who liquefied microalgae within the temperature range from 300 to 375 °C, noting a peak yield at 350 °C [34]. On the other hand, the lower bio-crude yield at the supercritical state can be attributed to the diminished lipid content. This aligns with the observations made by Vo et al., who reported that 400 °C is an optimal temperature for microalgae with a higher percentage of lipids [28].

Wood exhibited a reasonable yield, attributed to the presence of catalysts (K_2CO_3), which expedited the hydrolysis process by breaking down glycosidic bonds in carbohydrates. In the case of lignin, the catalyst demonstrated effectiveness at 350 °C, while its

impact reversed under supercritical conditions, resulting in an excess of solids and a diminished bio-crude yield (7%). This phenomenon can be attributed to the accelerated repolymerization reactions of phenolic compounds, especially in the presence of higher temperatures beyond the critical point (374 °C) and alkali catalysts.

Further, two sets of experiments were performed at a semi-continuous scale to obtain comparative results between batch and semi-continuous scales. Wood showed slightly higher bio-crude than at a batch scale with yields of 31 and 23% at 350 and 400 °C, respectively. The solids were detected in extremely negligible amounts that could not be measured and hence are not reported here. Upon broader examination, it becomes extremely difficult to compare these results, as batch and semi-continuous scales cannot be identical due to pressure variations, retention times, and product separation techniques. These factors can greatly alter bio-crude and solid yields bio-crude. Secondly, semi-continuous experiments were only conducted on wood, not on *Algae Sp.* and hydrolysis lignin; the details are already provided in Section 2.2.

3.3. Quality of Bio-Crude

In all bio-crudes, reasonable values of carbon were detected from 72 to 83%, as provided in Table 2. Higher carbon content was observed in the wood and lignin bio-crudes under supercritical conditions. This can be supported by lower carbon in wood and lignin aqueous phases as discussed in Section 3.6. This phenomenon can be attributed to the accelerated kinetic reaction rates facilitated by elevated temperature and pressure. These conditions promote a more extensive disintegration of carbon rings, resulting in an increased enrichment of carbon in the bio-crude phase. Earlier, Jensen et al. explored the interaction of supercritical water with lignocellulosic biomass. They found that water's chemical properties are directly linked to density and indirectly affected by pressure and temperature, a phenomenon they named as Hydrofaction [35]. Higher nitrogen around 6% was detected in *Algae Sp.* bio-crude due to the cleavage of peptide linkages and deamination, which imparts substantive nitrogen in the bio-crude. The HHVs across all samples ranged from 33 to 36 MJ/kg. Ash content was determined through Thermogravimetric Analysis (TGA), involving heating the bio-crudes at 800 °C in an oxygen environment. Generally, the bio-crudes exhibited low ash content (from 0.13 to 2.2%), except for those derived from lignin, which displayed higher ash content, specifically 15.30% and 12.65% at sub- and supercritical temperatures, respectively.

In summary, supercritical conditions yielded lower bio-crude quantities compared to subcritical conditions but enhanced the bio-crude quality. The notable H/C ratio (1.15 to 1.56) suggests that the liquefaction process directed a greater amount of carbon and hydrogen to the bio-crude by releasing oxygen to the gas phase through reactions such as decarboxylation and dehydration. However, the H/C values still fell below those of petroleum crude (H/C: 1.84), indicating the need for bio-crude upgrading through hydrotreatment.

Table 2. Elemental composition of bio-crude.

Samples	C (%) ^a	H (%) ^a	N (%) ^a	O (%) ^{a,b}	H/C	HHV (MJ/kg) ^c	Ash (%)	Water Content (%)
Wood 350	77.76	7.45	0.72	14.07	1.15	33.43	2.22	5.93
Wood 400	82.50	7.97	0.75	8.79	1.16	36.15	1.21	4.21
<i>Algae Sp.</i> 350	77.16	10.01	6.06	6.78	1.56	36.26	1.15	4.59
<i>Algae Sp.</i> 400	77.77	9.76	6.45	6.03	1.51	36.22	0.13	6.11
Lignin 350	72.03	7.23	1.15	19.60	1.20	30.62	15.30	5.54
Lignin 400	79.96	7.91	1.07	11.07	1.19	34.95	12.65	6.54
Wood Cont. 350	73.23	7.26	0.44	19.08	1.19	31.19	0.75	9.44
Wood Cont. 400	77.69	7.81	0.65	13.87	1.21	33.83	1.16	8.51

^a Dried ash-free basis; ^b Oxygen calculated by difference; ^c HHV calculated by the Channiwala and Parikh correlation.

Water content in the bio-crudes was determined by Karl Fischer method. On average, from 4 to 6% of water was recovered in bio-crude despite trying best to separate the product. Slightly higher water content was found in both Wood Cont.-derived bio-crude; this is obvious, as no extraction solvent was used to separate the bio-crude and aqueous phase, rather it was carried out through density separation method.

To assess the volatility of bio-crude, Thermogravimetric Analysis (TGA) was conducted under a nitrogen atmosphere, spanning temperatures from 30 to 800 °C, as illustrated in Figure 4. The bio-crudes derived from Lignin 350 and Wood Cont. 350 exhibited the highest heavy residue, measuring 40% and 33%, respectively. Except for Wood 350, Lignin 350, and Wood Cont. 350, nearly all bio-crudes manifested approximately 50% volatile components within the 350 °C temperature range. This interval indicates the presence of valuable compounds that can be converted into gasoline, diesel, and jet fuel through thermal distillation.

In this temperature range, both *Algae Sp.* bio-crudes displayed exceptional volatility, with nearly 70% volatile fragments. At an extreme temperature of 800 °C, supercritical conditions resulted in a lower amount of heavy residue compared to the subcritical state. This phenomenon may be attributed to the elevated temperature causing the disintegration of heavier fragments, which are then transferred to the bio-crude.

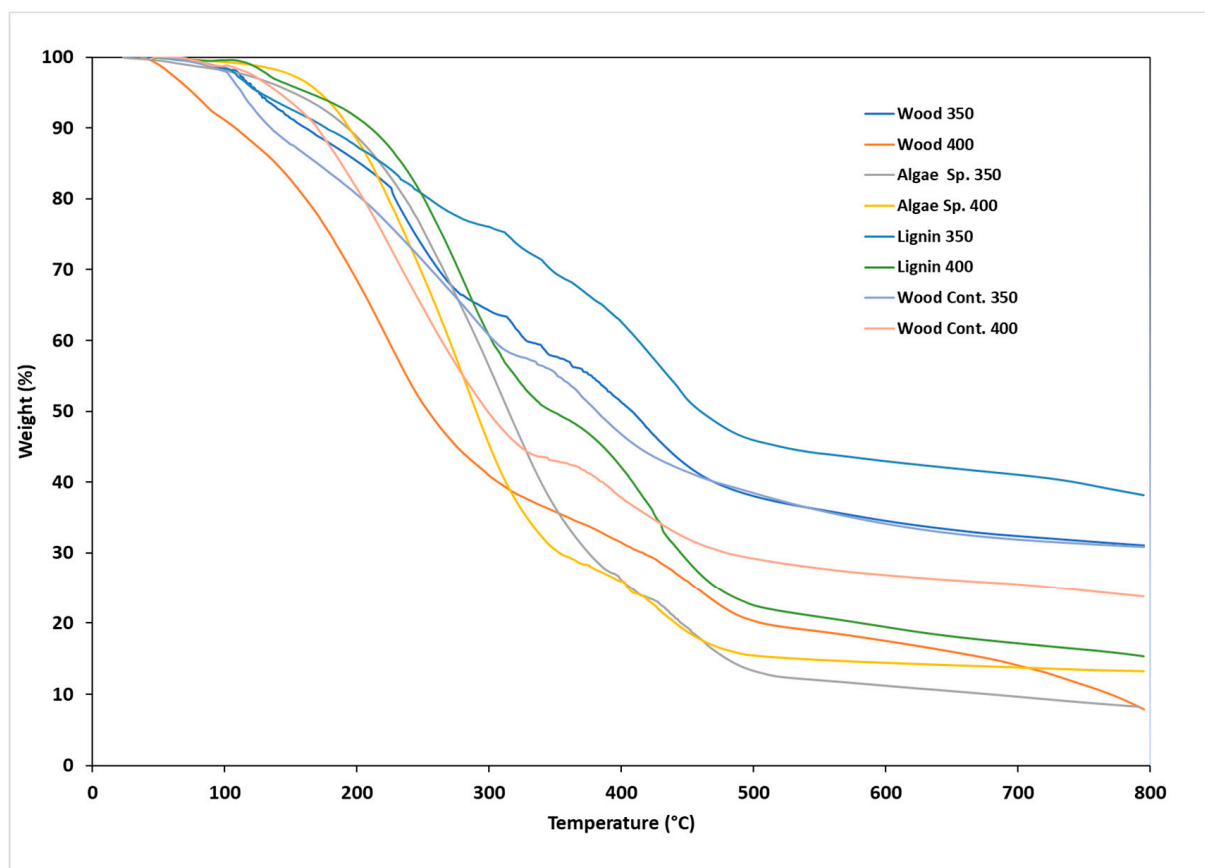


Figure 4. Thermal behavior of bio-crudes.

3.4. Compounds Composition of Bio-Crude

To analyze the organic composition of the bio-crude, GCMS analysis was conducted at a temperature of 300 °C. Due to temperature constraints, GCMS provided partial information compared to TGA. The detected compounds were classified into Ketones, Acids and Esters, Aromatics, Hydrocarbons, N-containing compounds, and Alcohols and Aldehydes, as illustrated in Figure 5. Relative percentages of each compound were calculated based on the total area covered by all compounds in a particular bio-crude sample. Detailed

information, including the retention time and percentage of peak area, can be found in Supplementary Table S1.

No distinct regular trend was observed in the compounds. However, all lignocellulosic feedstocks exhibited a higher percentage of phenolic compounds at both 350 and 400 °C, such as Phenol, 2-methyl-, Phenol, 3-ethyl-, Creosol. This observation can be attributed to the chemical composition of wood and hydrolysis lignin.

Algae Sp.-derived bio-crude at both 350 and 400 °C showed a higher presence of nitrogen-containing compounds, specifically *N*-heterocyclic compounds, and amides. *N*-heterocyclic compounds were formed through the Maillard reaction between amino acids (proteins) and polysaccharides (carbohydrates). On the other hand, amides like dodecanamide, *N*-methyldodecanamide, and 9-octadecenamide- (*Z*) originated from the decarboxylation and amination of the monomers of carbohydrates containing nitrogen in the ring structure [36].

It is always difficult to explore the exact reaction pathway of these compounds due to the occurrence of various reactions at the same time. However, we could speculate through their reaction chemistry as the ketones (2-butanone, 2-pentanone, 4-hydroxy-4-methyl-, 2-cyclopenten-1-one, 2-methyl-) are produced from the hydrolysis and dehydration of polysaccharides. Aromatic compounds like phenols and their derivatives are primarily originated from the lignin and repolymerization of the long-chain compounds from carbohydrates [37]. Acids and esters were placed in a single category like acetic acid, 2,5-octadecadiynoic acid, methyl ester, oleic acid, eicosyl-ester, might be originated from hydrolysis of carbohydrates and subsequent oxidation of ketones or aldehydes [38]. Long-chain hydrocarbons such as (2-octene, octadecane, 3-ethyl-5-(2-ethylbutyl) are produced from the decarboxylation of carboxylic acids [39].

The GCMS results show that the bio-crude contained almost 70–80% of the heteroatoms, specifically the oxygen and nitrogen. Therefore, the removal of these atoms is very important to improve the quality bio-crude via adopting cost-effective hydrotreatment techniques.

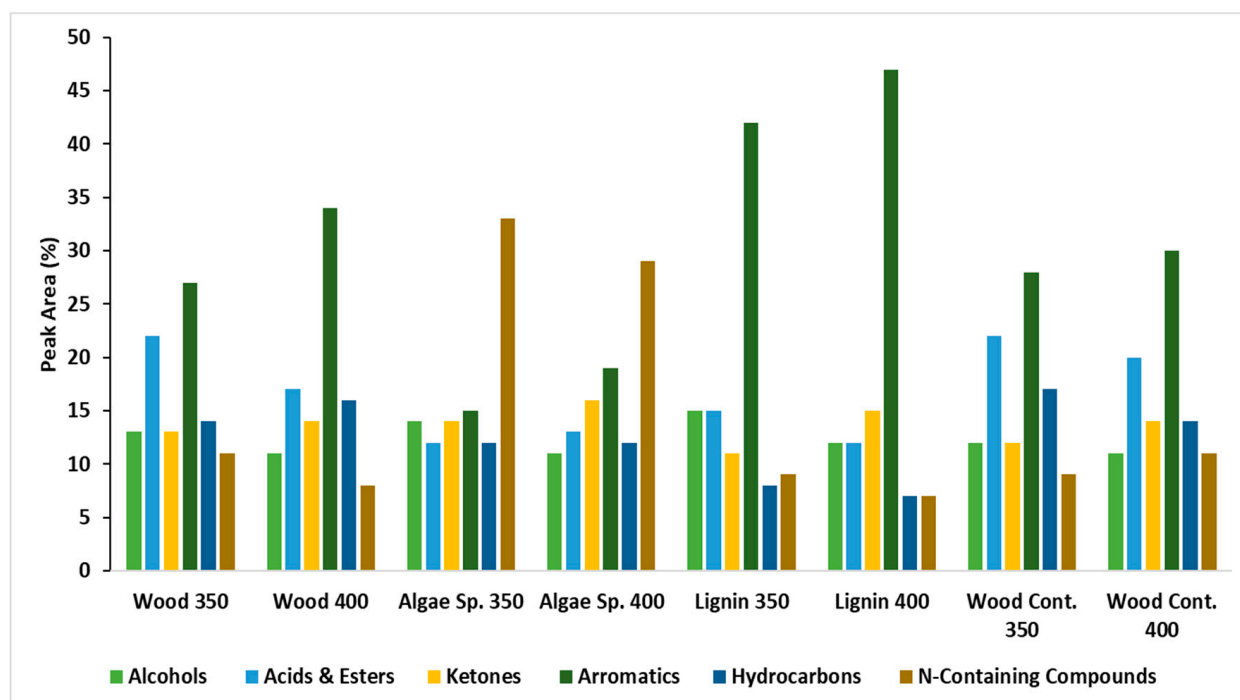


Figure 5. Distribution of organic compounds in bio-crude.

3.5. Analysis of Solid Residue

The elemental analysis was conducted for solid residue as provided in Table 3. Higher values of carbon in the range of 71–83% were noticed in all lignocellulosic samples at both conditions, which resulted in an increase in HHVs of the samples. The ash contents in the solids were detected through furnace method by heating the samples at 750 °C for four hours. A higher amount of oxygen was detected in solid samples of *Algae Sp.* at both conditions; this might have been due to the presence of a higher amount of ashes in the form of oxides. The H/C ratios for solids were lower than bio-crude, which implies that a higher amount of hydrogen transferred to the bio-crude phase. The elemental values for Wood Cont. samples are not mentioned here, as these were not available in sufficient amount for analysis. Higher HHVs from solids of lignocellulosic feedstocks (25 to 31 MJ/kg) showed that these solids have the potential to be used as heating source. Moreover, biochar derived from HTL holds substantial significance due to its diverse applications. Primarily, it functions as a highly effective soil amendment, elevating fertility by enhancing nutrient retention, cation exchange capacity, and water retention [40]. Furthermore, biochar aids in carbon sequestration, offering a stable carbon storage solution in the soil, thereby contributing to climate change mitigation. Its utility extends to livestock management, contaminated site remediation, and water filtration, making it a versatile solution with far-reaching environmental implications [41].

Table 3. Elemental values for solid residue.

Samples	C (%) ^a	H (%) ^a	N (%) ^a	O (%) ^{a,b}	H/C	O/C	HHV (MJ/kg) ^c	Ash (%)
Wood 350	77.15	4.11	0.18	18.58	0.64	0.18	29.08	20.12
Wood 400	83.95	4.01	0.14	11.90	0.57	0.11	31.97	11.27
<i>Algae Sp.</i> 350	32.08	2.58	1.94	63.41	0.97	1.48	7.28	26.15
<i>Algae Sp.</i> 400	28.00	1.01	1.34	69.66	0.43	1.87	3.56	29.37
Lignin 350	71.76	2.92	1.34	23.99	0.49	0.25	25.24	22.76
Lignin 400	79.63	4.48	0.63	15.27	0.67	0.14	30.63	17.34

^a Dried ash-free basis; ^b Oxygen calculated by difference; ^c HHV calculated by the Channiwala and Parikh correlation.

3.6. Analysis of Aqueous Phase

The aqueous phase was characterized through the values of TOC, TN, and pH, as illustrated in Figure 6. The *Algae Sp.* aqueous phase exhibited elevated TOC values at both temperatures. This correlation could be associated with the higher bio-crude yields of these samples. During the hydrolysis of organics, the organic matter initially dissolves in water, transforming into bio-crude through repolymerization at elevated temperatures. Consequently, higher TOC values align with increased bio-crude yields, a phenomenon further supported by the lower carbon content in the solid phase of both *Algae Sp.* samples. Notably, Wood Cont. samples demonstrated elevated TOC levels (12 and 16 g/L) at both temperatures.

This loss of carbon to the aqueous phase decreases the bio-crude yield and overall effectiveness of the HTL processing. Over the years, the researchers have tried to valorize the aqueous phase through different ways: (1) a high TOC-containing aqueous phase can be used as suitable medium for the biogas production through anaerobic digestion [42], or (2) it can be utilized for the syngas production via hydrothermal gasification [43,44]. (3) From the HTL perspective, the recirculation of aqueous phase back to the HTL unit with the slurry is a very popular approach [45–48]. The first and second options require the integration of HTL with other facilities; as a result, they would undermine the sustainability of HTL processing to be stand alone. However, the third option seems to be viable, as it does not require any integration and saves the cost of fresh water in the process of slurry preparation, particularly in the case of lignocellulosic biomass.

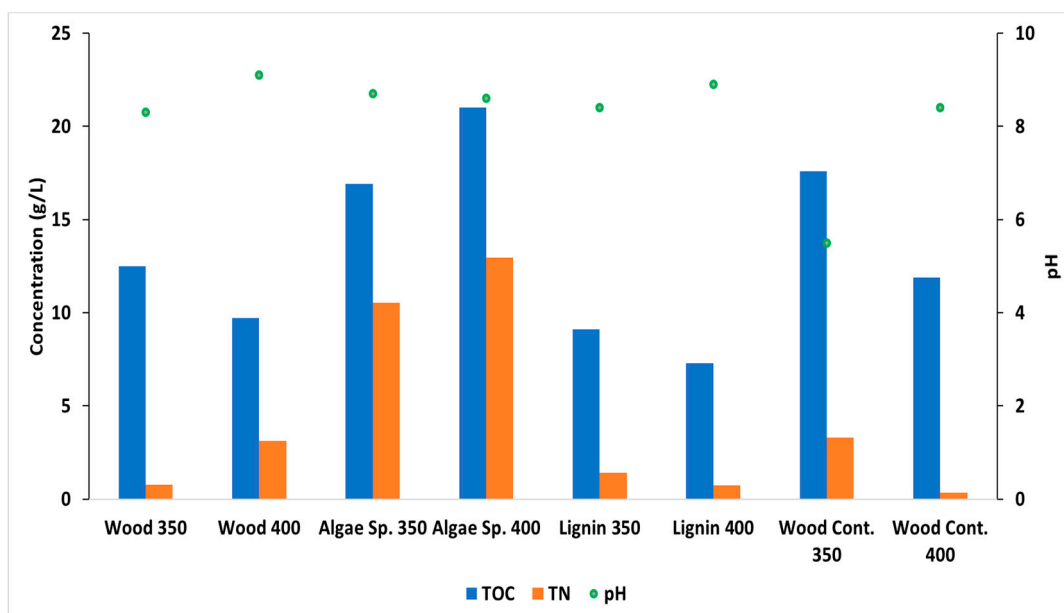


Figure 6. TOC, TN, and pH of the aqueous phase.

The higher amount of TN was noticed from *Algae Sp.* samples (11 and 13 g/L); this was evident due to the hydrolysis of proteins containing nitrogen compounds. Here, the analysis of GCMS of aqueous was not conducted; however, the previous studies have reported that the presence of *N*-heterocyclic compounds is the major reason for the higher nitrogen in the aqueous phase, whereas high-TN-containing aqueous phase often contains nutrients such as nitrogen and phosphorus, which are essential for plant growth. It can be used as a nutrient-rich water source for irrigation in agriculture, providing an environmentally friendly alternative to synthetic fertilizers. This nutrient-rich aqueous phase can be further processed to concentrate and extract valuable nutrients. These concentrated solutions can then be used as biofertilizers, promoting sustainable and organic agricultural practices [49]. The pH levels range from 5.5 to 9.1. In all samples, the presence of an alkali catalyst (K_2CO_3) ensures that pH values remain in the alkaline or neutral range, except for Wood Cont. 350, which has a pH of 5.5. This deviation might be attributed to a higher concentration of H^+ ions in the form of acids and esters.

4. Conclusions

In this study, the HTL of three different feedstocks—wood, microalgae (*Algae Sp.*), and hydrolysis lignin—was conducted at sub-supercritical conditions (350 and 400 °C). Six experiments were conducted on a batch scale. The homogenous catalyst (K_2CO_3) was added with lignocellulosic materials, wood and hydrolysis lignin, whereas *Algae Sp.* was liquefied without catalyst. Results revealed that the subcritical temperature (350 °C) showed higher bio-crude yields from all feedstocks than supercritical conditions. The maximum bio-crude yield was observed by *Algae Sp.* (29.53%) followed by wood (26.76%) and lignin (24.31%). Conversely, higher values for HHVs for bio-crude and higher amount of volatile matter were detected at supercritical temperature (400 °C). To get the comparison between batch and continuous ones, the two experiments were conducted on wood in a Continuous Stirred Tank Reactor (CSTR) at 350 and 400 °C. Wood Cont. experiments showed the same trend of bio-crude yield at both temperatures as that of batch ones. The aqueous phase had a range of TOC from 7 to 22 g/L. A higher amount of TN was measured in *Algae Sp.*, ranging from 11 to 13 g/L. Building on these findings, it appears that opting for subcritical HTL at lower temperatures holds advantages, while supercritical HTL demonstrates elevated HHVs. Therefore, navigating the selection of the optimal condition for bio-crude production presents a considerable challenge. This study could

be proved instrumental for the scale-up of HTL to a commercial level, especially when utilizing aforementioned feedstocks for bio-crude production.

5. Challenges and Recommendations for Future Prospective of HTL

After conducting the above experiments and extensive review of studies, it is evident that HTL is a versatile process for treating diverse types of biomass. Despite its potential, the technology is presently confined to the batch or pilot scale, highlighting the need to address specific gaps hindering its broader technological advancement.

5.1. Temperature

Subcritical temperatures offer the advantage of creating gentler operating conditions and demanding less energy input. However, this approach sometimes leads to incomplete conversion, especially with substances like lipids. In contrast, the supercritical state promotes higher reaction rates, resulting in elevated HHVs and a more detailed comparison of the yields and HHVs under subcritical and supercritical conditions is essential. Nevertheless, the supercritical method has drawbacks, including higher costs, increased energy requirements, and the formation of undesirable by-products. These by-products may involve the transfer of a larger amount of carbon to the aqueous or gaseous phase, consequently diminishing the bio-crude yield and overall economic feasibility of the HTL process. Conducting a comprehensive techno-economic analysis becomes crucial to thoroughly analyze the differences in yields and HHVs under both subcritical and supercritical conditions.

5.2. Feedstock

Lignocellulosic biomass is commonly used in an HTL, but it faces challenges such as high biomass cost, deforestation, and difficulties in pumping. To address this, using waste biomass like wheat straw or rice husks is a solution. Pumping can be improved by adding substances like glycerol or mixing with other biomass like microalgae, it can also be enhanced by reusing HTL-aqueous phase that can save the freshwater cost and increase bio-crude productivity. However, studies present a drawback of recycling of aqueous phase as it imparts higher nitrogen content in the bio-crude particularly from high protein-containing feedstocks. This can pose challenges such as reducing the catalyst lifespan and increasing the cost of hydrogen during hydrotreating [47]. Therefore, further research is needed to assess the cost-effectiveness of bio-crude production through HTL compared to nitrogen removal via hydrotreatment including catalyst cost. To establish a reliable HTL process, it is crucial to precisely define performance parameters, including the HHV of both feedstock and bio-crude, along with the yields of bio-crude on a dry ash-free basis. Developing a distinct model for processing HTL products is highly recommended.

5.3. Process Mode

After analyzing various studies on continuous HTL plants [2,50–53], it is advisable to consider the benefits associated with specific plant reactor configurations. In cases where a tubular configuration is employed, advantages such as the absence of moving parts and ease of scalability become apparent. Additionally, utilizing a combination of reactor types, such as a Continuous Stirred Tank Reactor (CSTR) and Plug Flow Reactor (PFR), can aid in minimizing plugging issues and facilitating faster heat exchange. Implementing oscillating flow can further enhance heat transfer efficiency. In continuous HTL processes involving highly concentrated slurries, maintaining stable pumping is crucial for the technoeconomic viability of the overall process. The choice of reactor material is a critical factor, and careful attention must be given to selecting materials that align with the specific reaction environment. When evaluating reactor materials, considerations for plant operating life and cost should be judiciously assessed. Ghavami et al. [54] and Elhassan et al. [55] compiled some pertinent studies, delving deeper into the operational challenges associated with continuous HTL. The specific issues addressed encompassed process safety, plugging,

corrosion, and catalyst deactivation. HTL product separation technique is also an important aspect for the process economics; in batch experiments, solvents like acetone, ethanol, and diethyl ether (DEE) are commonly utilized and their prolonged use can escalate the HTL process cost. Gravimetric separation technique emerges as a more advantageous and cost-effective choice for both pilot and commercial facilities.

5.4. HTL with Hydrotreatment (Taking as a Whole-Process Chain)

Broadening the research scope beyond biomass liquefaction to encompass bio-crude upgrading processes, specifically focusing on deoxygenation and denitrogenation, is pivotal for comprehensive objectives. Special emphasis must be placed on the examination of inorganic components in bio-crude, particularly metals, given their catalytic role, as they significantly influence the design and feasibility of the upgrading stage. Quantitative assessment of H₂ consumption during the upgrading process, particularly in cases involving external hydrogen sources, is indispensable. To ensure sustainability and cost-effectiveness, it is imperative to explore methods for hydrogen production from HTL and renewable energy sources like solar or wind. Paramount considerations include various strategies for bio-crude upgrading, such as co-processing with fossil crude fractions in existing hydro treaters, co-processing in fluid catalytic crackers, and the fractional distillation of bio-crude, followed by the co-processing of individual fractional cuts.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/fuels5010005/s1>, Table S1: GCMS of bio-crude.

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