

Valorization of hydrothermal liquefaction aqueous phase: pathways towards commercial viability



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ABSTRACT

Hydrothermal liquefaction (HTL) is a thermochemical conversion technology that shows promising commercial potential for the production of biocrude oil from wet biomass. However, the inevitable production of the hydrothermal liquefaction aqueous phase (HTL-AP) acts as a double-edged sword: it is considered a waste stream that without additional treatment clouds the future scale-up prospects of HTL technology; on the other hand, it also offers potential as an untapped nutrient and energy resource that could be valorized. As more researchers turn to liquefaction as a means of producing renewable fuel, there is a growing need to better understand HTL-AP from a variety of vantage points. Specifically, the HTL-AP chemical composition, conversion pathways, energy valorization potential, and the interconnection of HTL-AP conversion with biofuel production technology are particularly worthy of investigation. This paper extensively reviews the impact of HTL conditions and the feedstock composition on the energy and elemental distribution of process outputs with specific emphasis on the HTL-AP. Moreover, this paper also compares and contrasts the current state of value-added products separation along with biological (biomass cultivation, anaerobic fermentation, and bioelectrochemical systems) and thermochemical (gasification and HTL) pathways to valorize HTL-AP. Furthermore, life cycle analysis (LCA) and techno-economic assessments (TEA) are performed to appraise the environmental sustainability and economic implications of these different valorization techniques. Finally, perspectives and challenges are presented and the integration approaches of HTL-AP valorization pathways with HTL and biorefining are explored.

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1. Introduction

Global climate change caused by the accumulation of greenhouse gas (GHG) emissions has caused concerns regarding the world's continued reliance on fossil fuels. Thus, the shifting of society's dependence away from petroleum to renewable biomass resources is generally viewed as an important contributor to the development of a sustainable industrial society and effective way to manage the reduction of GHG emissions [1,2]. In recent years, the production of transportation fuels from wet biomass has received increasing attention due to its promising potential. For example, there are 77 million dry tons of wet biomass generated per year in the United States, including sludge, animal manure, and food waste [3]. Hydrothermal liquefaction (HTL) is a thermochemical conversion technology that converts wet biomass into biocrude oil at elevated temperatures (250–400°C) and pressures (4–22 MPa) [4,5]. Unlike other thermochemical technologies, such as combustion and pyrolysis, HTL can sidestep the energetically costly drying step by directly utilizing wet biomass (food waste, microalgae, lignocellulose, sewage sludge, etc.) as a feedstock to produce biocrude oil [6–9]. HTL can produce biocrude oil with a modest yield (40–83%) and appreciable heating value (28–40 MJ/kg) similar to that of petroleum crude oil [10]. Chen et al. verified that HTL-derived biocrude oil could be further upgraded via distillation combined with esterification, and the results demonstrated that the viscosity, acidity, and energy content of the upgraded oil were commensurate with existing transportation infrastructures based on engine tests [11]. Now, research has shifted towards mild upgrading techniques, including emulsification, esterification, and hydrotreating to further improve the quality of biocrude oil for large-scale production [11,12].

Despite the potential of HTL technology, a distinct bottleneck of the HTL process that limits its economic and technical scalability is the production of a by-product known as the hydrothermal

liquefaction aqueous phase (HTL-AP). It's well known that a given feedstock with a high water content can be directly treated via HTL due to the incorporation of water as the reaction medium. The feedstock water content can be classified as either free water (water that can be separated mechanically) or bound water (water that is difficult or unable to be isolated due to entrapment or attraction to materials). The conversion of the bound water within the feedstock into free water is the main water loss pathway during HTL [13]. In the subcritical hydrothermal region, the weakening of hydrogen bonds in water coupled with a decrease in the dielectric constant leads to the dominance of in situ hydroxyl radicals which further promotes the thermochemical conversion of organic matter in the raw materials [14,15]. Thus, the water molecules within HTL-AP are derived from not only the moisture present within the feedstock but also from the dehydration of feedstock components enhanced via HTL. A large amount of organic matter will also be converted into the liquid phase during HTL, and the direct dissolution of inorganic materials in the feedstock will inevitably lead to the transformation of metal ions into the HTL-AP [16]. These are the main pathways that explain the evolution of the aqueous phase production and composition during thermochemical conversion.

Since biocrude oil is the primary product of interest when conducting HTL, little attention has been placed on the HTL-AP, in spite of the fact that a substantial amount of C and N are transferred to HTL-AP through various reaction pathways [17–19]. The characteristics of the HTL-AP are highly dependent on the initial feedstock and reaction conditions used during the HTL process. Additionally, the conversion pathway and migration trends of the chemical components in the feedstock to the aqueous products are still unclear.

The valorization of HTL-AP plays a critical role in determining the pathways towards commercial viability of HTL of wet biomass (Fig. 1). The U.S. Department of Energy (DOE) has even recognized

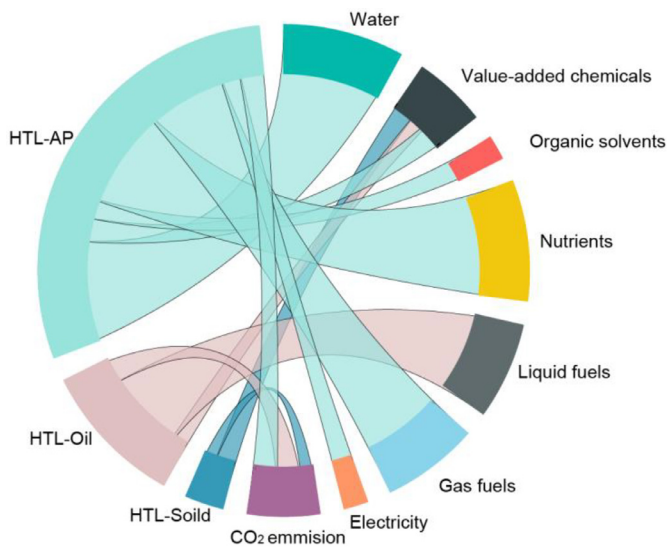


Fig. 1. Chord diagram based on the HTL conversion of biomass.

valorizing HTL-AP as a critical enhancement that needs to be met before HTL-derived oil can achieve an overall fuel selling price of \$3.00/gallon gasoline equivalent (GGE) [20]. To date, HTL-AP has only been viewed as a waste by-product and not viewed as a potential avenue of energy and economic output. Due to the chemical complexity and general toxicity of HTL-AP, anaerobic fermentation, hydrothermal gasification, biomass cultivation, thermochemical recycling and/or integrated pathways have shown potential as advantageous routes towards treating and re-utilizing HTL-AP compared with conventional wastewater treatment. Previous studies have confirmed that gas fuels (hydrogen, methane) and electricity could be produced via biological [21,22], bioelectrochemical [23,24], and thermochemical processing of HTL-AP [25,26]. Further the remaining nutrients and water could support the cultivation of microalgae [27]. In addition, valued added chemicals and organic solvents can be separated and concentrated [28]. However, there are still some unsolved challenges that face the valorization of HTL-AP. For example, inhibition

has been observed for biological conversion. In addition, limited information is provided in the literature comparing technical, economic, and environmental challenges of these approaches. In order to determine how the valorization of the aqueous phase would impact the HTL process from energetic, economic, and environmental vantage points, the intricacies of these processes need to be further elucidated. To maximize the economic and energetic upscale viability of the HTL process, it is essential to determine the methodology needed to unleash the energy present within HTL-AP.

Herein, a current review of the state of the art technology utilized to valorize HTL-AP is elucidated. First, a description of the current state of HTL research is expounded, emphasizing the impact of the feedstock and reaction conditions on the product balance, elemental balance, and energy balance. Second, the predominant conversion pathways for the valorization of HTL-AP are illustrated, including value-added products separation, biological conversion, thermochemical conversion, and a combination of the aforementioned processes. Third, life cycle assessments (LCA) and techno-economic assessments (TEA) are presented in order to quantify the benefits of the different processes and assess the feasibility of upscaling and commercializing HTL technology. Finally, the challenges and future prospects for the valorization of HTL-AP are explained and described.

2. Hydrothermal liquefaction

2.1. Process description and scale-up challenges

HTL produces four primary products: biocrude oil, solid residue, aqueous phase, and gaseous phase. Previous studies have primarily focused on analyzing the impact of the reaction temperature (250–375°C), retention time (5–90 min), solid fraction (5–20%), and reaction pressure (10–20 MPa) on bench scale HTL process outputs. However, there are notable differences between HTL conducted at the bench scale and pilot scale. Fig. 2 illustrates representative examples of the HTL experimental procedure and setup conducted at the bench scale and the pilot scale.

Although standardization of operating procedures and reaction methodology has been achieved at the bench scale, one notable difference between these two scales of HTL is the incorporation of an extraction solvent in bench studies. The extraction agent is

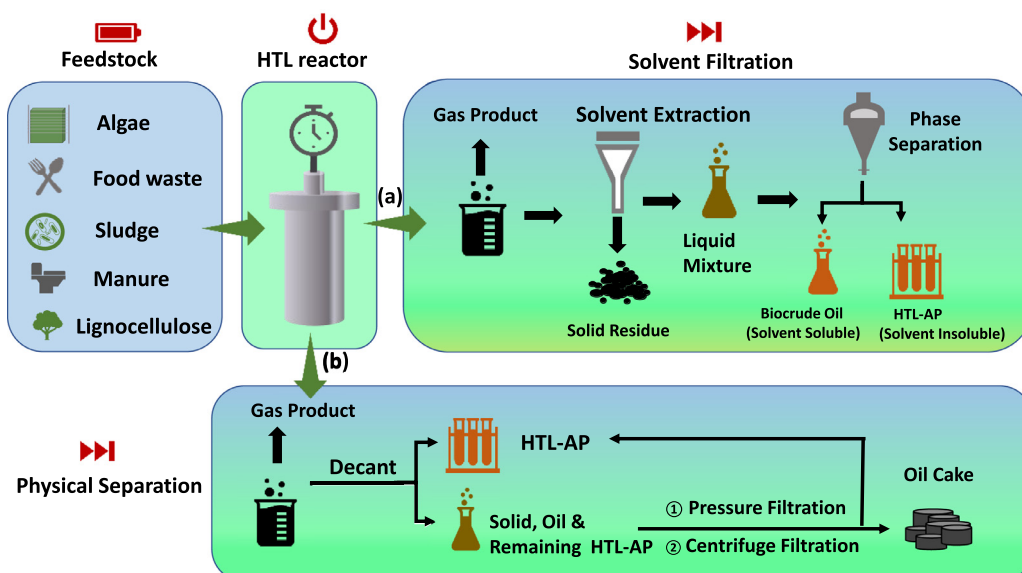


Fig. 2. Representative depiction of the HTL process at the bench scale (a) and the pilot scale (b).

Table 1
Recent HTL studies conducted at both the bench continuous scale and the pilot scale.

Feedstock	Temperature (°C)	Pressure (Bar)	Time (min)	Solid content (wt.%)	Yield (wt.%)	Reference
Bench Scale Continuous						
Wastewater algae	300–340	165	7–17	5	12–22	[33]
Microalgae	350	185	1, 6	10	40	[37]
Microalgae	350	200	15	18	43–55	[34]
Macroalgae	350	200	40	22	59	[38]
Dried distillers grain	350	250	15	20	39	[35]
Grapes pomace	350	200	29	17	50–56	[39]
Pilot Scale						
Fungi	300–400	270	12–30	4	48–61	[43]
Aspen wood	400	300	50	17	20–33	[40]
Wood	390–420	350	NA	17–20	45	[41]
Energy grass, microalgae, sewage sludge	350	220	20	16	25–33	[44]
Macroalgae	300–350	120–200	3–5	5	25	[45]
Food waste, swine Manure	260–280	100	30–120	10–15	NA	[11]

NA: not available.

incorporated to selectively isolate biocrude oil from the solid residue and aqueous fraction [29,30]. Currently, three extraction solvents are commonplace in the literature: acetone, dichloromethane, and toluene [6,29,31,32]. However, pilot scale HTL does not necessitate the incorporation of an extraction solvent; reaction products are instead separated by density. Therefore, whether or not bench scale data can be utilized to predict the potential of pilot scale technology remains a point of contention among researchers.

In recent years, bench continuous HTL reactors (as opposed to batch HTL reactors) have become the focal point of process development for biocrude oil production technologies. Although there is no specific boundary to delimit batch and pilot scale processes, a reactor volume of 1 L is used to demarcate the difference between bench and pilot scale HTL processes in the subsequent analysis. Table 1 depicts recent studies conducted at both the bench continuous and pilot scale for HTL conversion. Different bench scale continuous reactors have also been reported in recent years. These reactors are one step closer to the pilot scale implementation of HTL technology since this operation leads to similar mass and energy transfer outputs in comparison to pilot scale reactors. Wagner et al. designed a vertical double tube reactor to liquefy microalgae and achieved higher biocrude oil yields than conventional batch reactors [33]. A 190 mL continuous stirred tank reactor (CSTR) was also used to conduct continuous bench-scale HTL, which presented lower yields and a higher distribution of heavy chemical compounds in comparison to oil produced from a batch reactor [34]. Plug flow reactors (PFR) are the most common continuous HTL reactor implemented at the bench scale. Dried distillers grain from the bioethanol industry was successfully converted into bio crude oil with a PFR in a preceding study, leading to a mass yield of $38.9\% \pm 3.2\%$ [35]. Microalgae were also studied with two different PFRs that had different reactor sizes (0.098 L and 1 L) using the same reaction temperature. Both reactors resulted in promising biocrude yields, 37–40% and 38–64%, respectively, which indicated the feasibility of using microalgae as a bench scale continuous HTL feedstock [36,37]. Microalgae in this preceding study was able to be reliably used up to a solid content of 35 wt.%. Pacific Northwest National Laboratory also conducted HTL on macroalgae and grape pomace with a 1 L PFR, and the yield amounted up to 58.8% and 50–56% under identical reaction conditions (350°C and 200 bar), respectively [38,39]. Most of the above bench scale continuous HTL reactors faced similar engineering challenges. For example, high-pressure slurry pumping, heat exchange integration, and continuous product separation all remained critical obstacles impeding ideal HTL processing.

Studies concerning bench scale continuous reactors have provided a solid foundation for the development of pilot scale reactor

design. However, there are still only a limited number of studies conducted at the pilot scale (reactor volume greater than 1 L). Aalborg University conducted co-liquefaction of aspen wood and glycerol with a total reactor volume of 10 L [40]. The biocrude oil yield in this study ranged from 20–33%. However, in another study where the oil and aqueous phase were recycled from the previous run and mixed with the wood in the feed slurry, the biocrude oil yield was able to reach up to 45% [41]. Recirculation of the oil and aqueous product promoted additional conversion of oil products because water soluble organics and phenolic oil compounds demonstrated the ability to improve homogeneity and rheological properties of the feed [42]. Suesse et al. reported that filamentous fungi also generated a similar biocrude oil yield (48–61%) to microalgae utilizing a 1.5 L PFR [43]. A 20 L HTL PFR was developed by Aarhus University, and this pilot scale reactor was utilized to conduct HTL with a variety of feedstocks, including energy grass, microalgae, and sewage sludge [44]. The average reported biocrude oil production yield was 26%, 33%, and 25% for these three feedstocks, respectively. Another PFR with a reactor volume of approximately 5 L was developed by the University of Sydney which used organic co-solvents and short residence times (3–5 minutes) to reach a yield up to 25% with macroalgae [45]. Finally, the University of Illinois developed a pilot scale HTL PFR using food waste and swine manure as the feedstock. The biocrude yield was not documented in this study; however, the biocrude quality was studied and the resulting product could be upgraded and was successfully implemented as a drop-in fuel for a diesel engine [11]. According to the data present in the literature, the scale of the HTL system is inversely correlated with the biocrude oil yield. In other words, bench scale PFR systems led to greater yields than pilot scale PFR systems. This might be caused by reactant interaction, heat transfer, and mass transfer limitations at the pilot scale compared to the bench scale. However, the specific reasons need to be further investigated and elucidated.

Although HTL shows promise as a means of producing biocrude oil and other products via a myriad of feedstocks at the bench and pilot scale, the Environmental Protection Agency still has yet to certify any HTL pathways under the Renewable Fuel Standard [46]. According to the literature, the primary pitfalls and challenges facing the scale-up of HTL technology from the bench-scale are listed below:

- Due to the incorporation of subcritical water as the reaction medium, upscale HTL technology faces large issues with reactor corrosion [47]. However, this problem can be sidestepped by adjusting the reaction medium pH through the addition of homogeneous catalysts (Na_2CO_3 , KOH, K_2CO_3 , etc.) [40,48].

- Research suggests that increasing the feedstock solid content augments the biocrude oil yield and process efficiency while maintaining a near constant energy ratio [49]. However, maintaining a pumpable, homogeneous slurry with a high solid content (>30 wt.%) remains a critical process development challenge necessitating the further development of high pressure pumps [48].
- The feedstock type (lignocellulosic biomass, algae, etc.) leads to economic, energy, and operation complexity tradeoffs that must be considered when transitioning from batch to continuous biocrude oil production. Establishing a pumpable slurry is a crucial process development hurdle that can be handled via mechanical (grinding, milling, etc.), technical (high-pressure feeding system), or chemical (acid/base pre-treatment) methodologies [50,51].
- The formation of char derivatives (phenolic char, polyaromatic char, etc.) via polymerization and re-polymerization reactions is a large issue which reduces the biocrude oil yield and can lead to clogging of large-scale systems [52,53].
- Catalysts incorporated to decrease reaction severity, improve the yield, and enhance the quality of biocrude oil are susceptible to poisoning, coking, and sintering by nitrogen-containing and sulfur-containing species. Current catalyst usage, recovery, and reactivation techniques are cumbersome, inefficient, and costly [54]. New techniques need to be developed in order to efficiently improve the reusability of catalysts.
- Biocrude oil from biomass feedstock contains a relatively high content of oxygen-containing and nitrogen-containing derivatives. Thus, further upgrading and subsequent economic expenditure is necessary for HTL-derived biocrude oil to be a viable commodity on the market.
- Novel strategies need to be investigated that explore the possibility of integrating or retrofitting conventional crude oil refining techniques within the biocrude oil production paradigm.

Strategies might include concurrent upgrading of a biocrude oil and petroleum oil blend via conventional hydrotreating reactors, co-processing using fluid catalytic crackers, or fractional distillation with subsequent co-processing [49,55].

- Pilot scale data is needed in order to assess the real economic, environmental, and societal implications of HTL technology.
- Large-scale biocrude oil production leads to the continual discharge of HTL-AP, which cannot be directly discharged into the environment due to the presence of concentrated organic contaminants. Methods need to be explored to efficiently and effectively valorize (gasification, anaerobic digestion) or re-use (recirculation to reactor) this aqueous product [49] in order to further improve the economic, energetic, and process viability of HTL technology.

2.2. Mass balance during HTL

HTL has been extensively studied for a myriad of feedstocks. Many studies extensively focus on algae biomass, since algae have a high biomass productivity, its growth sidesteps the food-versus-fuel debate, it can be grown on wastewater, and it can recycle carbon from CO₂-rich flue gas emissions from stationary sources [56]. Furthermore, oleaginous microalgae have demonstrated the ability to outproduce oilseed crops in terms of biocrude oil yield [56]. In addition to algal biomass, other feedstocks have also garnered attention in recent years, including animal waste, agricultural waste, human waste, and processing waste [6,57–59]. Research has shown that the composition of the feedstock in tandem with the reaction conditions (temperature, retention time, etc.) impact the HTL product and by-product mass balance, elemental balance, and energy recovery. Table 2 summarizes the recent modeling studies conducted utilizing the contents of biochemical components in the HTL feedstock to predict the biocrude

Table 2
Correlation between HTL feedstock biochemical components and the prediction of the biocrude oil and HTL-AP yield.

Feedstock	Conditions ^a	Biocrude Oil Predicted Yield (wt.%) ^b	HTL-AP Predicted Yield (wt.%)	Ref.
<i>Nannochloropsis oculata</i>	300°C, 30 min, 20%	$0.97 \times L + 0.42 \times P + 0.17 \times C$	(defat AQ yield) × (100%-FAs)	[65]
Microalgae	300°C, 30 min	$0.85 \times L + 0.45 \times P + 0.22 \times C$	$0.24 \times P + 0.86 \times A$	[64]
Cornstarch, soy, sunflower oil	300°C, 20 min, 15%	$0.95 \times L + 0.33 \times P + 0.06 \times C - 0.016 \times L \times C + 0.27 \times L \times P - 0.016 \times C \times P$	NA	[61]
Cornstarch, soy, sunflower oil	350°C, 60 min, 15%	$0.94 \times L + 0.35 \times P + 0.12 \times C - 0.003 \times L \times C - 0.21 \times L \times P + 0.4 \times C \times P$	NA	[61]
Cellulose, albumin, castor oil	300°C, 20 min, 15%	$0.95 \times L + 0.32 \times P + 0.06 \times C - 0.21 \times L \times C + 0.36 \times L \times P + 0.04 \times C \times P$	NA	[61]
Cellulose, albumin, castor oil	350°C, 60 min, 15%	$0.85 \times L + 0.34 \times P + 0.12 \times C + 0.10 \times L \times C + 0.02 \times L \times P + 0.34 \times C \times P$	NA	[61]
Sunflower oil, soy protein, starch	350°C, 60 min, 10%	$0.8 \times L + 0.18 \times P + 0.06 \times C$	NA	[66]
Soybean oil, cellulose, xylan, alkalkine lignin, soy protein isolate	270–320°C, 5–20 min, 8–17%	$0.97 \times L + 0.20 \times P + 0.10 \times SA + 0.02 \times LIG - 0.33 \times P \times L + 0.26 \times SA \times LIG + 0.60 \times SA \times L - 0.66 \times LIG \times L - 0.25 \times LIG \times L \times T - 0.19 \times L \times P \times TI - 0.39 \times P \times L \times SC$	NA	[67]
Glucose, guaiacol, alkaline lignin, glutamic acid, linoleic acid	300°C, 30 min, 15%	$0.95 \times L + 0.05 \times C + 0.18 \times C \times P + 0.79 \times C \times LIG + 0.45 \times C \times L + 0.23 \times P \times LIG + 0.44 \times P \times L - 0.3 \times LIG \times L$	$0.95 \times L + 0.48 \times C + 0.05 \times P + 0.68 \times LIG + 0.50 \times C \times P + 0.94 \times C \times LIG + 0.42 \times C \times L + 0.39 \times P \times LIG + 0.42 \times P \times L - 0.28 \times LIG \times L$	[63]
<i>Chlorella</i> , <i>Nannochloropsis</i> , <i>Pavlova</i> , <i>Scenedesmus</i>	280°C	$0.90 \times L + 0.32 \times P + 0.22 \times C$	NA	[68]
<i>Chlorella</i> , <i>Nannochloropsis</i> , <i>Pavlova</i> , <i>Scenedesmus</i>	320°C	$0.96 \times L + 0.43 \times P + 0.30 \times C$	NA	[68]
<i>Nannochloropsis</i>	280°C, 60 min, 10%	$0.9 \times L + 0.39 \times P + 0.025 \times C + (0.052 \times L \times P)/(L-P) + (0.093 \times L \times C)/(L-C) + (0.003 \times P \times C)/(P-C)$	NA	[69]
Food Waste	280–380°C, 10–60 min, 20%	$1.61 \times L - 0.558 \times P - 0.00625 \times Ti^2 + 0.00565 \times P^2 + 0.00324 \times T \times Ti + 0.0108 \times L \times C - 0.00273 \times L \times T - 0.00465 \times L \times Ti - 0.00772 \times C \times Ti$	NA	[70]

^a Reaction conditions are the temperature, retention time, and solid content (wt.%) utilized for determination of the regression model;

^b L: lipid, P: protein, C: carbohydrate, A: ash-to-aqueous conversion ratio; SA: saccharide, LIG: lignin, T: temperature, Ti: time, SC: solid content; FAs: percent dry weight of fatty acid methyl esters; ^c Retention time and solid content utilized for determination of the regression model were not reported; NA: not available

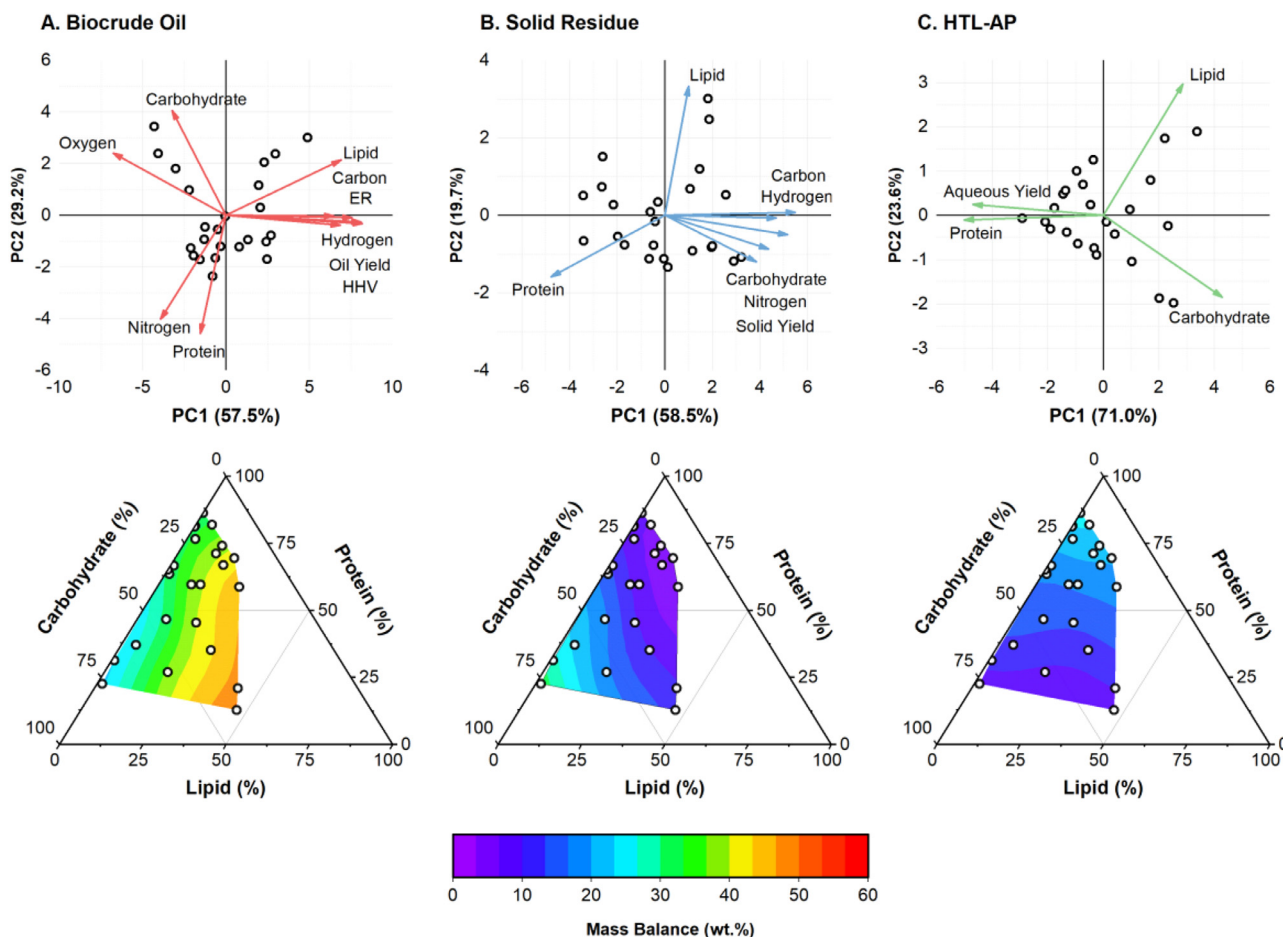


Fig. 3. Principal component analysis (PCA) and ternary chart depicting correlations between the composition of the feedstock and the quantity and quality of the biocrude oil (A), solid residue (B), and the HTL-AP (C). Data collected from [64].

oil and HTL-AP yield. ANOVA analysis conducted by researchers has led to the consensus that the content of lipids (0.85–0.97) and proteins (0.2–0.42) in the HTL feedstock significantly contribute to the biocrude oil yield while the content of carbohydrates (0.05–0.22) only plays a minor role in modeling the predicted yield of biocrude oil (Table 2). Binary and ternary studies have indicated that carbohydrates could play a greater role in influencing the biocrude oil yield when interacting with protein components in the feedstock, which is known as the Maillard reaction [60]. However, previous studies have concluded that binary mixtures of proteins and carbohydrates can both contribute negatively (-0.016) and positively (0.4) to biocrude oil predictions models [60,61]. This may be attributed to the Maillard reaction resulting in the accumulation of the solid residue at low temperatures (300°C) while forming biocrude oil components at high temperatures (350°C) [62].

With regard to the HTL-AP, researchers have not reached a consensus on the extent to which the biochemical components contribute to the HTL-AP yield. Li et al. previously reported that the protein content (0.24) dictates the yield of HTL-AP, whereas Fages et al. conversely came to the conclusion that the lipid (0.95) and carbohydrate content (0.48) are better indicators of the HTL-AP yield [63,64]. Therefore, further modeling studies need to be conducted in order to better understand the impact of the biochemical components on the HTL-AP yield. However, correlation analysis has begun to shed light on the impacts of the biochemical components on the product mass balance and the characteristics of the different HTL products.

Fig. 3 presents the principal component analysis (PCA) and ternary chart indicating the correlation between the HTL feedstock components and the quantitative and qualitative characteristics of the biocrude oil, solid residue, and HTL-AP [64]. With regard to the biocrude oil, the lipid content of the feedstock is positively correlated with the C content, H content, energy recovery, oil yield, and higher heating value (HHV). Both the protein content and carbohydrate content are correlated with negative characteristics, including a high O content and N content in the biocrude oil, respectively. With regard to the solid residue, the content of carbohydrates demonstrates positive correlations between the C content, H content, N content, and yield. The lipid content and protein content do not correlate with any of the solid residue output parameters. With regard to the HTL-AP, correlation analysis indicates that the protein content is instrumental in determining the yield. However, it should be noted that these correlations may differ when utilizing a different feedstock and when different reaction conditions are utilized. This is due to the fact that temperature and retention time of HTL have been shown to heavily influence the quantity and quality of the HTL output parameters.

Temperature and retention time are the two reaction conditions which influence the HTL process to the greatest extent [4]. In order to combine the collective effects of both temperature and retention time into a single parameter, the severity factor is often employed [26,71,72]. Fig. 4 illustrates the influence of the severity factor on the mass balance of the HTL process [8,32,58,59,73–80]. Fig. 4 demonstrates that the biocrude oil yield is positively correlated with an increase in the reaction severity up to a certain

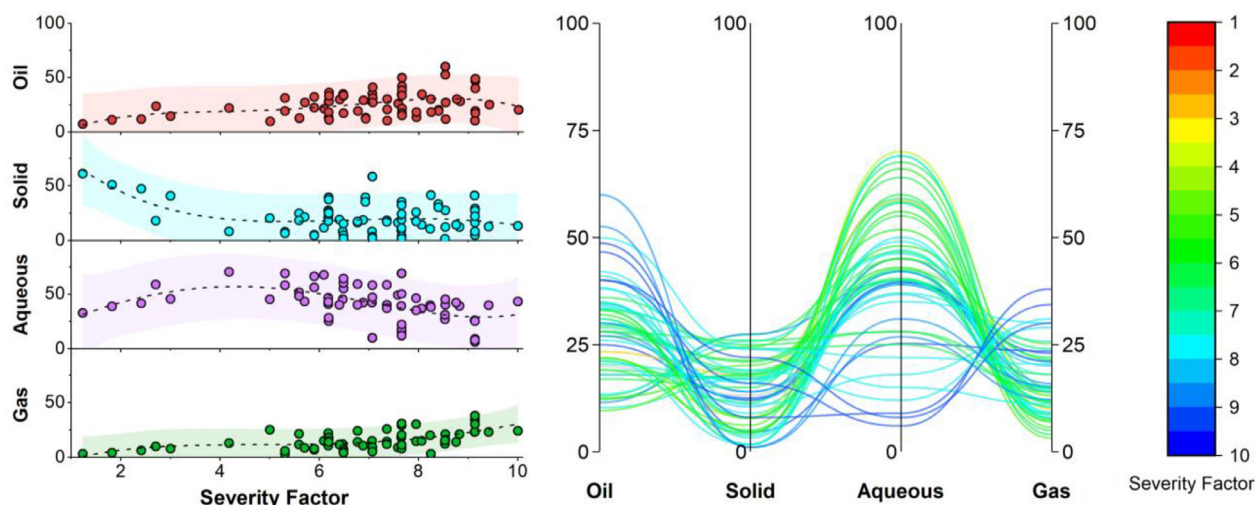


Fig. 4. Influence of the reaction conditions on the product mass balance of the HTL process. Data collected from [32,58,59,73–80].

extent. After a certain severity factor is reached, the biocrude oil yield then decreases. The specific temperature and retention time at which this decrease occurs is dependent on the feedstock chemical composition. The reason for this trend is due to the fact that at lower reaction severities char and organics in the water-soluble fraction can be converted into biocrude oil. This is caused by char accumulating at a low severity factor. A previous study noted that at higher temperatures the activation energy required for bond cessation for hydrolysis and decomposition/depolymerization reactions is easily overcome, resulting in the formation of a greater amount of biocrude oil by conversion of the HTL by-products [81]. Another study noted that at lower temperatures the peptide bonds present in protein molecules are more stable than the glycosidic bonds in carbohydrates and lignin. Thus, at lower temperatures protein derivatives are unlikely to be converted, whereas at higher temperatures these protein derivatives can be effectively cleaved and transformed into the biocrude oil phase [80]. Qu et al. found that at high temperatures (340–360°C), increasing the retention time resulted in a decrease in the biocrude oil yield, which could be explained by the re-polymerization and/or re-condensation of the newly formed oil products [82]. This was also confirmed by another study which discovered that increasing the retention time from 15 minutes to 30 minutes decreased the biocrude oil yield from approximately 20% to 15% [83]. In contrast to raising the retention time, extreme temperature conditions favor biocrude oil cracking reactions which convert the biocrude oil into gaseous compounds [75].

Reactor heating rate is also another factor that can influence the HTL process. Recent studies have shown that high heating rates can enhance fragmentation of biomass and inhibit the formation of char [84]. Biller et al. demonstrated that continuous HTL employed with high heating rates (915 and 230°C/min) and low residence times (1–6 min) led to the highest biocrude oil yields and energy recoveries [37]. Lower heating rates have been hypothesized to decrease the biocrude oil yield through the enhancement of side reactions (re-polymerization, condensation, oligomerization, etc.) that could enhance the production of the solid product yield and lower the biocrude oil yield [84,85]. Tran et al. also noted a clear correlation between heating rate and biocrude oil yield. This study found that when the heating rate increased from 66°C/min to 179°C/min, the biocrude oil yield increased by 16.9%, resulting in a decrease in the solid yield by 16% under the same heating rate [86]. One study demonstrated that HTL conducted at identical severity factors could have different yields and heating values that varied based on the heating rate [87]. Thus, severity factor may not

be able to provide a complete picture, and heating rate may need to be incorporated to better understand a holistic view of how the temperature and time impact the HTL products. However, it should be noted that researchers have found conflicting results. One study found that biomass conversion of 86% could be achieved at a heating rate of 2°C/min and only a 63% conversion could be achieved at a higher heating rate of 20°C/min [88]. This is contrary to previous studies that determined that a high heating rate was correlated with a high biocrude oil yield. These contradictory results were also confirmed by Kamio et al. [89]. Thus, the influence of the heating rate on the biocrude oil yield and properties may work in tandem with other factors to influence the biomass conversion and biocrude oil yield, including the feedstock type, the onset temperature, and the residence time.

With regard to the solid residue yield, studies have confirmed that it decreases as the temperature and reaction time increase. Shakya et al. found that when the HTL temperature for algae increased from 250°C to 300°C the solid residue yield significantly decreased. However, at temperatures exceeding 300°C no significant reduction of the solid yield was observed [80]. This could be explained by the organic components in the solid residue being converted to other HTL products. However, inorganic matter is subjugated to the solid fraction and is not affected by the increased reaction severity. A previous study indicated that the reaction time had an insignificant impact on the solid residue yield and that temperature led to the greatest influence in determining the solid yield [90]. Thus, the general trend is that solid residue accumulates at low reaction severities due to the recalcitrance of lignocellulosic compounds and protein-containing compounds; however, at higher severities these compounds are converted into the biocrude oil or cracked into the gaseous phase.

With regard to the aqueous phase, reports have not yet reached a consensus on the impact of the reaction severity on the HTL-AP yield (Fig. 4). Previous studies have indicated that protein and carbohydrate derivatives tend to preferentially dissolve in the aqueous phase, leading to a greater concentration of the aqueous phase for a high protein and carbohydrate feedstock. Therefore, the aqueous phase is often rich in organic acids, cyclic amine derivatives, and N/O heterocyclic compounds [73,91]. It has also been hypothesized that HTL tends to predominately yield aqueous products at low temperatures and short retention times; however, at high reaction severities oxygen-containing (e.g. phenols, furfurals, etc.) and nitrogen-containing derivatives (fatty acid amides, furans, etc.) can be converted into the biocrude oil phase [92]. At low temperatures, carbohydrate derivatives can degrade into compounds including

cellohexaose, cellopentaose, glyceraldehydes, and furfurals which generally dissolve into the aqueous fraction. Thus, some studies have indicated that for a high carbohydrate feedstock, a higher accumulation of the aqueous phase is expected [63]. However, at higher reaction temperatures these compounds may undergo radical reactions contributing to the formation of large molecular weight components (e.g. asphaltenes, asphaltene derivatives, etc.) in the biocrude oil [93]. Additionally, it has been reported that the water soluble components produced at lower reaction severities could be re-polymerized at higher reaction severities, thereby increasing the yield of biocrude oil [94]. Thus, additional research needs to be conducted to determine the mechanism by which biochemical components and HTL reaction products are converted into the aqueous phase as a function of the reaction conditions.

2.3. Elemental migration during HTL

The feedstock and reaction conditions also work in tandem to influence the elemental migration and distribution of the HTL products. Fig. 5 presents a representative depiction of how the feedstock macromolecules are transferred to the reaction products via HTL as a function of temperature [73]. Generally speaking, the range of chemical constituents that can enter the biocrude oil and HTL-AP phases is quite broad, including N-, O-, and S-containing heterocycles, cyclic and acyclic hydrocarbons (e.g. olefins, alkynes), etc. Conversely, the range of compounds that are distributed to the solid phase is fairly limited (ash, cyclic oxygenates). However, this model has been met with contention. Previous studies have indicated that the HTL process may not be unidirectional and in fact may involve secondary reaction pathways. Valdez et al. used a kinetic model to demonstrate that the formation of HTL-AP and biocrude oil compounds is only dominant within the first few minutes. As the retention time increases, there exists an interconversion between the oil, solid, and HTL-AP phases, thereby allowing for the interlacing of chemical compounds in each fraction [95]. This was further confirmed in a previous study which indicated the

contribution of the Maillard reaction to the solid residue, which is generally associated with the formation of biocrude oil at higher temperatures and lower retention times [62]. Thus, due to the severe reaction conditions employed when using HTL, the specific chemical transformations of biochemical macromolecules are constantly in flux, leading to a lack of transparency on the specific reaction pathways present for HTL.

Fig. 6 illustrates the reported elemental composition and HHV of HTL-derived biocrude oil from numerous studies irrespective of the reaction conditions [6,10,29,37,58,59,66,74,77–80,90,96–102]. According to the results presented in Fig. 6, the average C, H, N, O, S and HHV values of biocrude oil reported in previous studies is 70%, 4%, 15%, 10%, 1%, and 33 MJ/kg, respectively. The C content exhibits the largest content range of all other elements, due to the fact that previous studies have indicated that the C content is more susceptible to changes in the reaction conditions than the other elements. Christensen et al. observed that increasing the temperature from 275°C to 350°C increased the C content in the HTL-derived biocrude oil of algae from 63% to 77% [103]. Yu et al. also corroborated this trend, noting that the C recovery of the biocrude oil produced from low-lipid microalgae increased from 0.4 to 35.4% as the reaction temperature increased from 100°C to 300°C [104]. However, previous studies have noted that the C recovery tends to diminish when the temperature reaches the critical point of water (~374°C), because reactions favoring the cracking of biocrude oil, due to the change in the thermodynamic properties of water, occur when exceeding the supercritical state of water [57].

It should also be noted that at the critical point of water, the density of water and the ionic product drastically changes from 800 to 150 kg/m³ and from a pK range of 11–14 to a pK value of up to 21 [105]. This is under the assumption that both the reaction temperature and pressure are at the supercritical point of water. Even when the supercritical temperature is exceeded, ionic properties of water may be recovered when the pressure is further increased. In previous studies, the impact of supercritical conditions

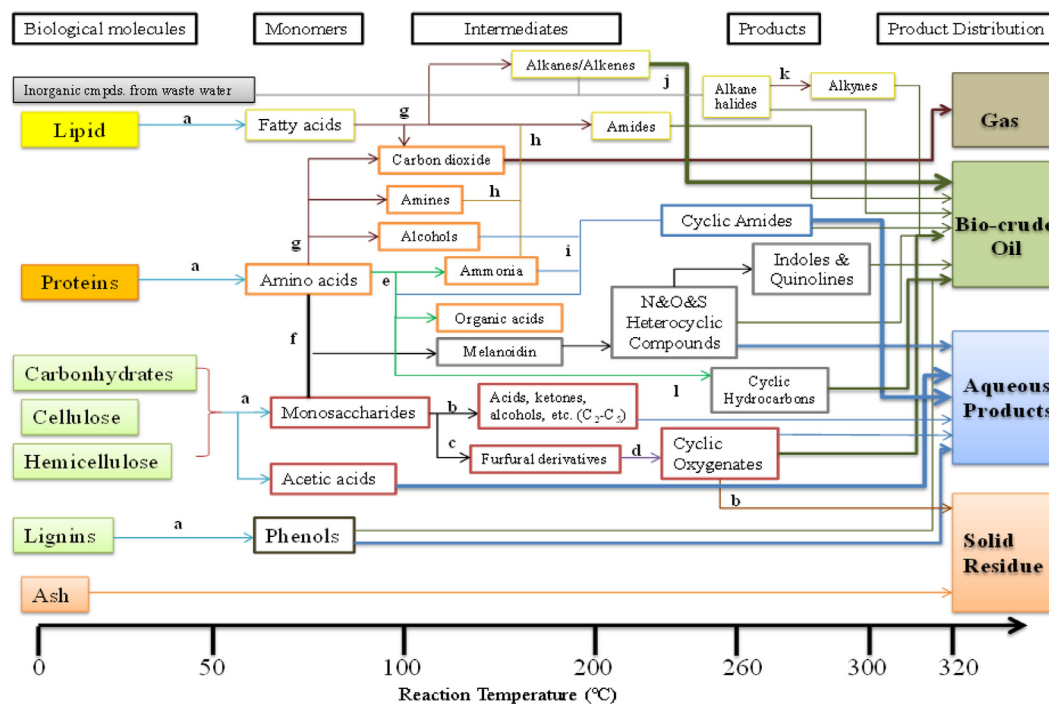


Fig. 5. Reaction pathway of the feedstock macromolecules to the final HTL products. (a) hydrolysis; (b) decomposition; (c) dehydration; (d) polymerization; (e) deamination; (f) Maillard reaction; (g) decarboxylation; (h) aminolysis; (i) cyclization; (j) halogenations; (k) dehydrohalogenation; (l) condensation+pyrolysis. Reprinted from [73] with permission from Elsevier.

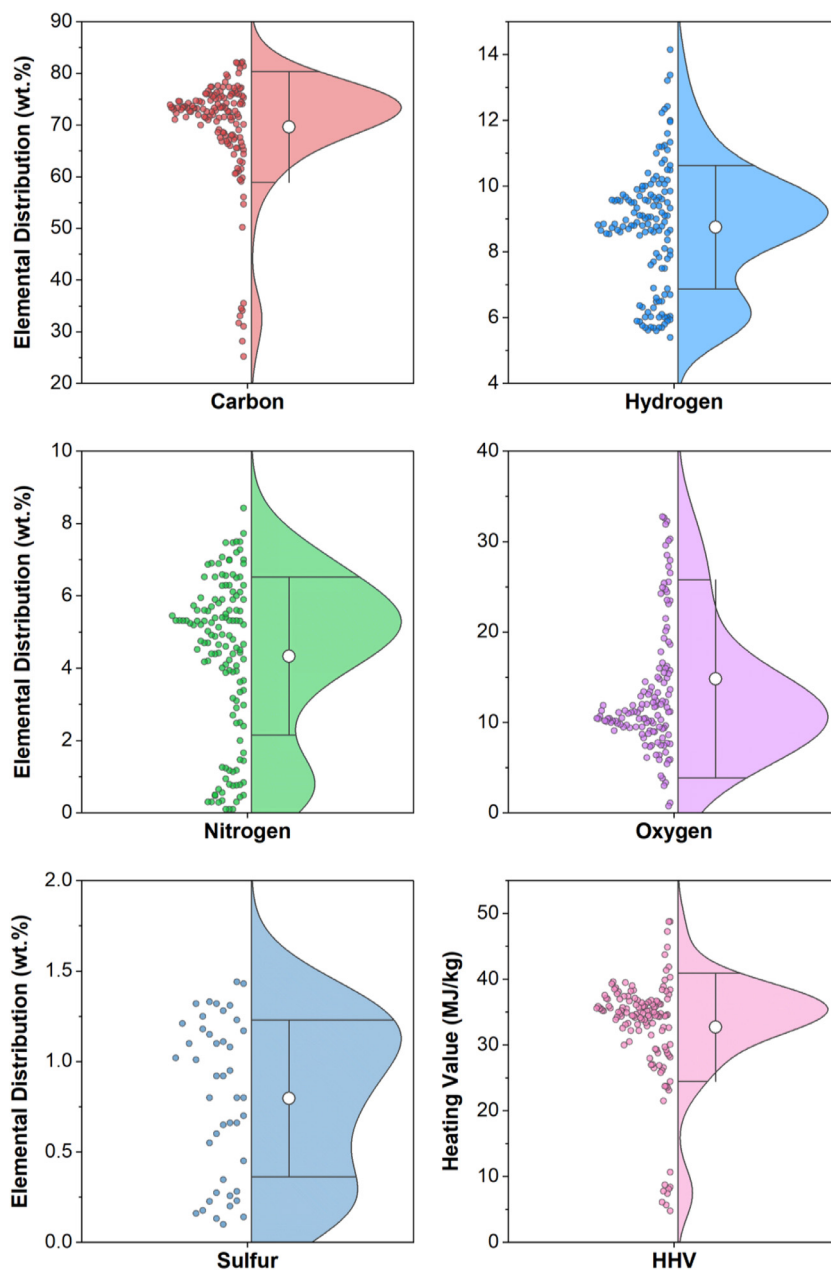


Fig. 6. Violin plot of the reported elemental and energy distribution of HTL-derived biocrude oil. Data collected from [6,10,29,37,58,59,66,74,77–80,90,96–102].

on the kinetics of HTL reactions was investigated. One study noted that exceeding the supercritical conditions diminished the kinetics of glucose and fructose degradation due to the shift from ionic reactions to free-radical reactions [106]. Thus, reactions without a dependence on ions (retro-aldol condensation reactions, etc.) are favored under supercritical conditions; however, reactions with a dependence on ions (dehydration reactions, isomerization reactions, etc.) are diminished [107]. Another hypothesis is that the reaction pathway may shift towards char formation for the thermochemical conversion of lignocellulosic materials when high reaction temperatures are incorporated. Compared with supercritical water, subcritical water has relatively limited interaction with the resulting solid residue product due to the lower diffusivity of water under these conditions [108]. Preceding studies have also demonstrated that the decomposition rate constants associated with some chemical species was facilitated by pressure when HTL reactions occurred near the critical pressure and temperature of

water [109,110]. Thus, the conversion efficiency is highly enhanced when water reaches its supercritical point [111,112]. In essence, the effect of pressure is different on subcritical and supercritical water. Under subcritical water, temperature is the predominant factor that influences the ionic properties of water and the reaction efficiency, whereas above the supercritical temperature of water, pressure also plays an important role and needs to be considered.

Retention time also has an influence on the C recovery, but the impact of retention time is severely diminished at high temperatures. With respect to the other biocrude oil elements, most preceding studies have found that regardless of the reaction temperature and retention time, biocrude oil from myriad feedstocks still contains an unfavorable amount of O ($13.7 \pm 8.3\%$), N ($4.3 \pm 2.2\%$), and S (0.8 ± 0.4), all of which are significantly higher than conventional oil products. In particular, one previous study noted the recalcitrance of oxygen-containing and nitrogen-containing

derivatives in the biocrude oil [78]. Thus, standard HTL reaction temperatures and retention times are not sufficient to produce a high-quality oil; upgrading with the incorporation of catalysts needs to be employed in order to effectively reduce the O and N content in HTL-derived biocrude oil and thereby allow HTL the opportunity to become a mature and commercialized technology for mass fuel production [11,32,65,101,113]. In fact, recent studies have shown that both deoxygenation and denitrogenation are achievable through the incorporation of a NiMo/Al₂O₃ sulfided catalyst. In this study, the oxygen content from the biocrude oil produced from three different HTL feedstocks could be effectively reduced to low levels (from an initial oxygen content ranging from 6.9–19.6 wt.% to 0–0.8 wt.%) and nitrogen could also be reduced (from an initial nitrogen content of 1.7–7.7 wt.% to 0.8 – 4.0 wt.%) [114]. Thus, despite the presence of heteroatoms after HTL, the presence of these O- and N-containing derivatives are by no means prohibitive; it is possible to significantly reduce their content through subsequent processing.

With regard to the solid residue, an abundance of inorganic compounds which take the form of ash tend to accumulate in this fraction [115,116]. However, reaction conditions involving a low pH and a low heating rate can also lead to the production of char derivatives which can accumulate in the solid fraction thereby increasing its C content. Previous studies are in agreement that increasing the reaction temperature and retention time is beneficial towards converting organic matter from the solid residue into the biocrude oil and/or aqueous phase. One previous study employing cornstarch as an HTL feedstock found that increasing the temperature from 210°C to 310°C decreased the C content of the solid residue by nearly 60% [58]. However, as previously mentioned, at temperatures above the critical point of water (~374°C), this trend is not substantiated, and C in the aqueous phase, solid residue, and biocrude oil is converted to the gas phase. However, the presence of carbonification reactions at supercritical conditions may also lead to the conversion of carbon compounds into recalcitrant char or lignite in the solid residue, thereby indicating that at high temperatures the chemical content of the feedstock may play a larger role in determining the elemental migration into the solid residue [117].

With regard to the HTL-AP, previous studies have noted that nearly one third of the organic carbon in the feedstock is transferred to the aqueous phase during the HTL process [104,118]. Moreover, a majority of nitrogen-containing compounds have been found to accumulate in the aqueous phase. This is due to the deamination of amino acids which produces aqueous-soluble ammonia (Fig. 5). Thus, as the HTL temperature increases, nitrogen derivatives preferentially dissolve into the HTL-AP. Yu et al. demonstrated that increasing the reaction temperature decreased the N recovery in the biocrude oil while increasing the N recovery in the aqueous phase from 1.1% to 73.5% [104]. Previous studies have also noted the abundance of organic acids (acetic acid, lactic acid, etc.) and alcohol derivatives in the HTL-AP, which could lead to a high C content in the aqueous phase at low temperatures [59]. The N and O content can also be attributed to the presence of oxygen-containing and nitrogen-containing heterocycles (pyrrolidine, pyrrole-derivatives, etc.) [18]. Previous studies noted that both higher temperatures and higher reaction times resulted in an aqueous phase with a high content of N [118]. In particular, one study found that as the reaction temperature increased from 260°C to 340°C, the total organic carbon (TOC) of the HTL-AP only increased slightly from 50.92 mg/L to 57.14 mg/L while the total nitrogen (TN) increased dramatically from 1,973 mg/L to 3,836 mg/L [119]. However it should be noted that the feedstock chemical composition will heavily impact the content of N that inevitably ends up in the aqueous phase. Despite the high content of nitrogen-containing and oxygen-containing derivatives, the HTL-AP

has the potential to be recycled and reused due to its high nutrient content [120].

2.4. Energy and nutrient balance during HTL

Based on the above analysis of the pathways and elemental distribution from the feedstock to the HTL products, the C, N, and energy recovery of recent HTL studies was quantified irrespective of reaction conditions and feedstock composition to discern the current state of energy and nutrient balances within the HTL paradigm. Fig. 7 illustrates the C, N, and energy balance of the oil, solid, and aqueous via a 2D kernel density diagram [29,58,59,75,116,121]. The ability to recover a large portion of the feedstock energy through HTL has been previously reported. Yu et al. demonstrated that a maximum energy recovery of 65.4% was achieved at 280°C with a 120 min retention time for biocrude oil derived from low-lipid microalgae [104]. Reddy, et al. similarly found that a large fraction of the initial energy in the *Nannochloropsis* sp. (78.0%) and *Chlorella* sp. (61.3%) could be converted into biocrude oil [94]. Similarly to the preceding studies, analyzing the impact of extraction solvents on the HTL process found that the energy consumption ratio (ECR) from high-carbohydrate, high-protein, and high-ash algae ranged from 0.29–0.73 [29]. Similar to the biocrude oil yield trends, the energy recovery of the HTL process initially reaches an apex and thereafter decreases with increasing reaction severities. Tang et al. verified this trend by noting that the energy recovery resulting from the HTL of two algae species, *Nannochloropsis* sp. and *Chlorella* sp., increased from 52.6% (220°C) and 31.3% (220°C) and reached a maximum energy recovery of 69.9% (280°C) and 58.1% (260°C) but then decreased thereafter to 66.6% (300°C) and 37.0% (300°C), respectively [78]. This trend has also been corroborated by another preceding study [79]. The decrease in the energy recovery at high reaction temperatures could be attributed to the cracking of biocrude oil [78]. However, this could also be attributed to charring/condensation reactions which shift the product distribution to produce more solid residue as opposed to biocrude oil.

Energy return on investment (EROI) analysis indicated that a low-lipid HTL feedstock is not attractive from an energetic perspective, and that this type of feedstock is only feasible when the biocrude oil is utilized as a low-grade burning fuel [101]. Further, it has been shown that low temperature HTL (200°C) for microalgae with a high lipid content is ideal, because it produces oil that can be easily catalytically converted due to its low concentration of heteroatoms and asphaltenes [101]. This was confirmed by a previous study which found that mild reaction conditions also produced the highest energy content (40.1 MJ/kg) for a low lipid content algae in comparison to harsh reaction conditions. However, this trend was not substantiated for a low-lipid feedstock [122]. Anastasakis et al. also demonstrated that the HTL process is energy intensive when the water loading is high. This can be attributed to the high heat capacity of water, which caused the ECR in this study to increase from 0.9 to 3.8 as the biomass/water ratio increased from 2:10 to 2:40 [83]. This study came to the conclusion that high reaction temperatures and a high water content can lead to unfavorable energy recovery values and high (>1) ECR values. However, it should be noted that these conclusions assume the use of sub-critical water. When water exceeds the supercritical point (374°C, 22 MPa), energy conclusions will be impacted accordingly due to changes in the water characteristics, including the specific heat and specific enthalpy of water [123].

Fig. 7 also demonstrates that a large portion of energy (37.9 ± 18.0%), C (36.1 ± 14.0%), N (75.4 ± 18.9%) remains trapped within the HTL-AP. Therefore, inefficiency plagues the HTL process, indicating the need for further processing and valorizing of the HTL-AP to ensure the commercial viability of HTL technology. One previous

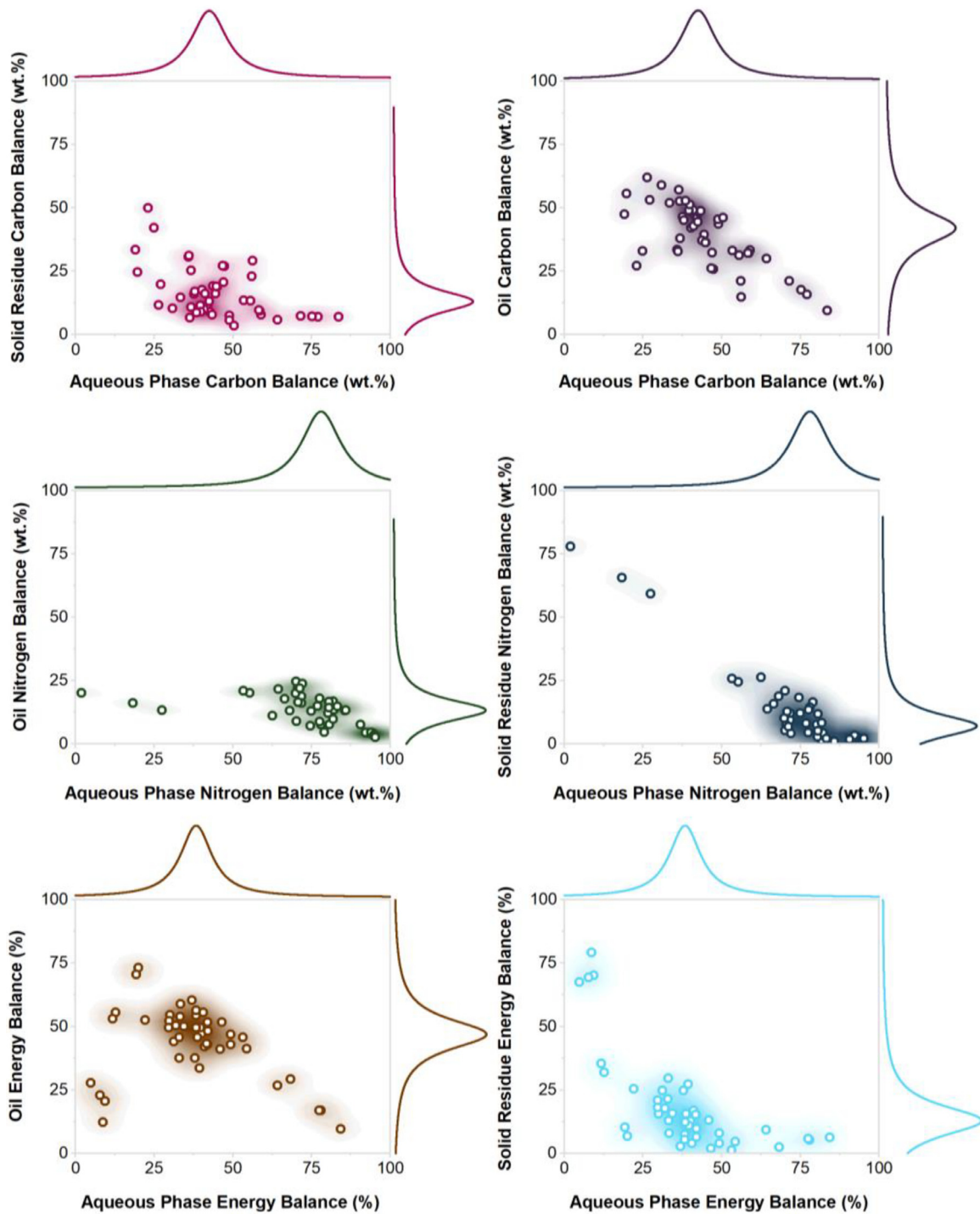


Fig. 7. 2D kernel density diagram depicting the C, N, and energy balance of the HTL process. Data collected from [29,58,59,75,116,121].

study analyzing the EROI for treatment of HTL-AP noted that treatment technology for the aqueous phase reduced the HTL EROI by upwards of 30%. However, this could be mitigated by recovering the nitrogen and phosphorus within the HTL-AP [124]. Thus, the energy ramifications of HTL-AP treatment techniques needs to be carefully considered before implementation. It should be noted that HTL also produces a gaseous product that constitutes a relatively miniscule fraction of the mass balance (<10%) [27,29,58,59]. Previous studies have indicated that the composition of the gaseous product primarily consists of carbon dioxide (>90%) [59]. Therefore, the gaseous fraction was assumed to be purely composed of carbon dioxide. Thus, according to the mass

balance and elemental composition of the HTL gaseous fraction, the gaseous fraction only accounted for $8.6 \pm 5.3\%$ of the C balance. Specific trends regarding the C and N balance are influenced both by the feedstock composition and the reaction conditions (Figs. 3, 4, and 6). However, the energy utilized in the HTL reaction process and in the resulting products can be looked at from a couple of different vantage points.

2.5. The characteristics of HTL-AP

The feedstock and reaction conditions (temperature, total solid content, and reaction time) have proven to complicate the

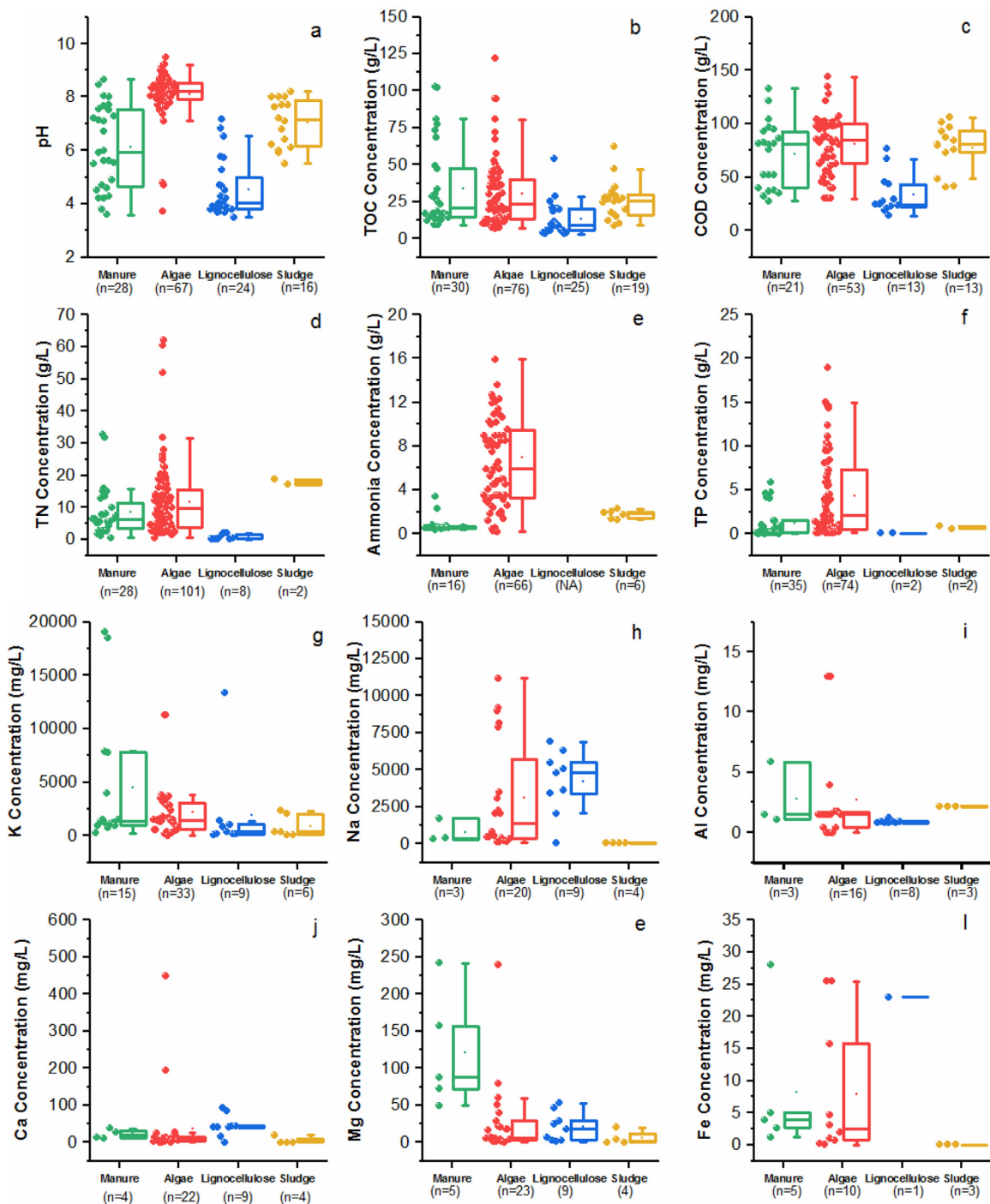


Fig. 8. pH (a), total organic carbon (TOC) concentration (b), chemical oxygen demand (COD) concentration (c), total nitrogen (TN) concentration (d), ammonia concentration (e), total phosphorus (TP) concentration (f), potassium (K) concentration (g), sodium (Na) concentration (h), and aluminum (Al) concentration (i), calcium (Ca) concentration (j), magnesium (Mg) concentration (k), and ferrum (Fe) (l) concentration in HTL-AP generated from manure [23,26,27,59,116,125–133], algae [17–19,25,27,77,97,119,120,127,134–156], lignocellulose [22,24,40,118,141,157–162] and sludge [128,146,163–165], respectively. The HTL temperature ranged from 200–350°C and the total solid content ranged from 5–20%. NA: not available. n: number of data points.

composition of HTL-AP. Fig. 8 summarizes the reported characteristics of typical HTL-AP from various feedstocks in previous studies, including manure [23,26,27,59,116,125–133], algae [17–19,25,27,77,97,119,120,127,134–156], lignocellulose [22,24,40,118,141,157–162], and sludge [128,146,163–165]. The pH of the HTL-AP derived from lignocellulose biomass showed a significant difference compared to the HTL-AP derived from other types of feedstock, which normally tend to be acidic with a pH ranging from 3.5–5. As a means of comparison, HTL-AP from algae typically had an

alkaline pH that ranged from 7.8–8.5. HTL-AP derived from manure and sludge showed a wider pH range, but the average pH amongst preceding studies was predominantly neutral. Thus, the pH of HTL-AP has been shown to be tightly related to the feedstock composition. Table 3 summarizes the main composition of typical feedstock utilized for HTL. Algae with a high protein content tends to result in a HTL-AP with a high content of ammonia derived from protein hydrolysis and deamination, which in turn leads to an alkaline pH [168]. This is also confirmed by the TN and ammonia

Table 3

Proximate analysis, biochemical, and organic elemental composition of the swine manure [166], algae [10], lignocellulose [167], and sludge [146] utilized as a feedstock for HTL.

	Manure	Algae	Lignocellulose ^a	Sludge
Lipid (%)	10.6 ± 0.1	14.1 ± 0.3	NA	NA
Protein (%)	26.4 ± 0.7	52.4 ± 1.2	NA	NA
Hemicellulose (%)	34.0 ± 0.9	NA	29.68 ± 0.31	NA
Cellulose (%)	12.2 ± 0.1	NA	45.06 ± 0.70	NA
Lignin (%)	5.4 ± 0.2	NA	5.65 ± 0.27	NA
Ash (%)	17.09 ± 0.95	6.3 ± 0.04	3.98 ± 0.05	17.2 ± 10.3
C (%)	49.67 ± 0.02	43.7	41.62 ± 0.10	43.4 ± 4.6
H (%)	6.84 ± 0.39	7.7	5.47 ± 0.03	6.3 ± 0.5
N (%)	4.66 ± 0.06	7.5	1.10 ± 0.02	5.3 ± 2.3

^a Cornstalk; NA: not available.

concentration in HTL-AP (Fig. 8). As for utilizing lignocellulose as an HTL feedstock, the acidic nature of the aqueous stream is likely the result of the presence of organic acids which formed from the degradation of either monomeric sugars or carbohydrates present in lignocellulose. The resulting pH of HTL-AP has broader implications on its valorization potential, because a neutral pH is recommended for methane production via anaerobic digestion, and low pH values are favored for the use of HTL-AP as an acidic catalyst to improve the heat pretreatment efficiency of lignocellulose biomass [169].

HTL-AP has a high concentration of organics, which has been confirmed by the chemical oxygen demand (COD) concentration (Fig. 8). Similar COD values for HTL-AP derived from manure, algae, and sludge have been reported, which led to average COD values of 80.5, 84.4, and 80.8 g/L, respectively. HTL-AP derived from lignocellulose biomass tended to lead to a lower COD (24.3 g/L) than the other types of HTL-AP. Similar distribution trends were also observed with respect to the TOC concentration. Both the COD and TOC values indicated that a substantial amount of energy remained in the HTL-AP, which suggests that further valorization of HTL-AP would benefit the energy recovery of the HTL system. However, HTL-AP valorization techniques have stringent requirements, as most biological conversion techniques may not accommodate high organic loadings. For example, the organic loading of anaerobic fermentation is typically around 10 g COD/L [170], and this value is typically 1–6 g COD/L for bioelectrochemical systems [23], which suggests that heavy dilution is necessary before biological conversion methods can be incorporated.

The TN concentration mostly varied from 3–12 g/L and from 4–15 g/L for HTL-AP derived from manure and algae, respectively. HTL-AP derived from sludge tends to have a high TN content, although the available data for this type of feedstock is limited. The HTL-AP derived from lignocellulose biomass had the lowest N distribution with an average value of 0.8 g/L. TN in HTL-AP mainly consisted of ammonia and organic nitrogen. Only a limited content of nitrate nitrogen was observed (constituting only 9.0–0.1% of the total TN) [120,135,147]. HTL-AP derived from manure and sludge had similar ammonia contents with an average value of 0.8 and 1.7 g/L, respectively. In comparison, the HTL-AP derived from algae had a much higher ammonia content which varied from 0.2–16.0 g/L, leading to an average value of 6.9 g/L. The total phosphorus (TP) content in HTL-AP derived from algae was found to be much higher than the other three types of feedstocks. This was attributed to the higher content of phospholipids, DNA, and phosphate monoesters present within algae. In addition, the TP content in HTL-AP was related to the metal contents in the feedstock and the extraction method utilized to separate HTL-AP from the biocrude oil [168]. Moreover, high contents of potassium (K), sodium (Na), and magnesium (Mg) were found in the HTL-AP derived from both manure and algae. In particular, the average concentration of K in the HTL-AP derived from these two types of

feedstock reached up to 4,258 and 2,251 mg/L, respectively. Other metals including aluminum (Al), calcium (Ca) and iron (Fe) were also observed in HTL-AP; however, the concentration of these metals remained low, only accounting for a concentration of less than 100 mg/L.

Fig. 8 suggests that HTL-AP derived from lignocellulose biomass had a lower TN concentration than HTL-AP derived from algae, manure, and sludge. This is because the composition of HTL-AP is correlated with the feedstock composition [64]. HTL-AP derived from lignocellulose biomass was reported to have the lowest N content compared with manure, algae, and sludge (Table 3). PCA further confirmed the positive correlation between TN, ammonia, and the protein content of the feedstock. Conversely, a negative correlation existed between the TN, ammonia content, and the carbohydrate/lipid content. The TOC concentration in HTL-AP also showed a strong positive relationship with the protein content, whereas a negative relationship between the TOC concentration and the lipid and carbohydrate content was observed. This further validates the fact that HTL-AP generated from algae, manure, and sludge had a higher TOC concentration than that of HTL-AP derived from lignocellulose biomass (Fig. 9), since the latter consists of carbohydrates and only a limited amount of protein compared to the other types of feedstock (Table 3). HTL-AP tends to be a high-strength TOC and TN stream, since in most cases wet biomass with a high protein content (algae, manure, etc.) is applied to the HTL process. In addition, the C and N contents in HTL-AP are also influenced by the HTL conditions. For example, Liu et al. reported that the Fe/HZSM-5 catalyst affected elemental migration during the HTL process, and an increase in the N content and decrease in the organic carbon content present within the HTL-AP was observed [19].

2.5.1. Distribution of organic compounds in HTL-AP

The HTL-AP contains a high concentration of organics, which pose a significant challenge for subsequent valorization. The general quantification of organics reported in previous studies for HTL-AP is described in Fig. 8. A further look into the composition of the organic components in HTL-AP is required in order to better understand the HTL-AP and develop optimal valorization approaches. Table 4 summarizes the quantification of major organic constituents (wt.%) identified in the HTL-AP derived from sludge [146], food industry wastes (FIW) [146], algae [145], and lignocellulosic feedstock [159], respectively. The HTL-AP was obtained using the same continuous processing bench scale system (Pacific Northwest National Laboratory) with similar operational conditions for all types of feedstock (339–353°C, 10.3–17.6 wt.%, 1.3–2.1 L/h). The quantified results illustrate the complicated composition and significant difference between HTL-AP resulting from different types of feedstock. A higher organic acids concentration (over 2 wt.%) was found in HTL-AP resulting from lignocellulosic biomass (corn stover and loblolly pine) when compared with other feedstock. The organic acids mainly included acetic acid, glycolic acid, formic acid, glycolic acid, and propanoic acid. In particular, the concentration of acetic acid and glycolic acid in HTL-AP derived from corn stover reached up to 0.878 wt.% and 1.678 wt.%, respectively. It is well-known that hemicellulose and cellulose are hydrolyzed into monosaccharides during HTL. These monosaccharides are unstable and could be converted into furfural, 5-HMF, glycolaldehyde, and methylglyoxal. At harsh reaction conditions, these products could be further converted into organic acids such as acetic acid [167]. In addition, phenol, 2-methoxyphenol, and 4-ethylphenol are also observed in the HTL-AP of lignocellulosic biomass. Barbier et al. confirmed these compounds were converted from lignin [171]. For HTL-AP derived from food waste, an abundant content of acetic acid (0.590 wt.%) and ethanol (1.021 wt.%) was observed. The high concentration of ethanol present in HTL-AP of food waste may have resulted from the feedstock. For

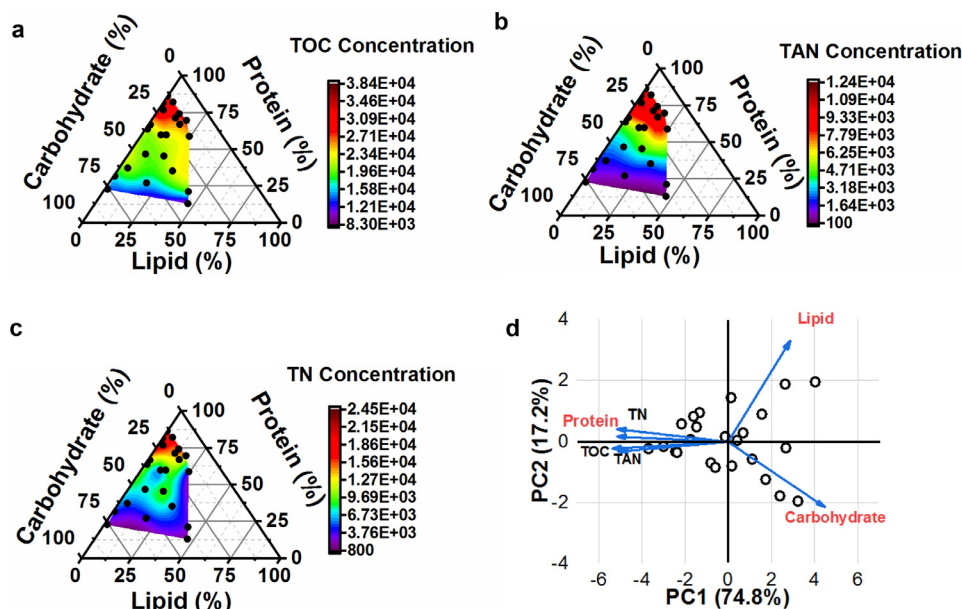


Fig. 9. Characterization of HTL-AP generated from feedstock with different compositions: (a) TOC concentration (b), total ammonia nitrogen (TAN) concentration (c), total nitrogen (TN) concentration (c), and principal component analysis (PCA) (d). Data points (24) collected from [64].

instance, a significant amount of ethanol is retained by wet grape pomace following wine fermentation [146]. The HTL-AP derived from sludge was also reported to have a similar distribution of organics in comparison to the HTL-AP derived from food waste. However, compared with HTL-AP from food waste, HTL-AP from sludge has a lower acetic acid and ethanol concentration, and it has a much higher concentration of nitrogen-containing organics, including amides (N-methyl succinimide) and N-heterocyclic compounds (pyrazine, methyl pyrazine, 2-pyrrolidinone, 1-methyl 2-pyrrolidinone, and 2-piperidinone). It has been reported that organic nitrogen constituted 7–40% of the TN when HTL was operated at 350°C [127]. Although organic nitrogen only accounts for a small percentage fraction of organic nitrogen in TN, organic nitrogen is still one of the most important entities present within HTL-AP when considering its high concentration (Fig. 8). The HTL-AP derived from algae resulted in the highest concentration of nitrogen-containing organics (reaching up to 1.153 wt.%), consisting of a wide variety of nitrogen-containing derivatives, including N-heterocycles, amines, and amides (Table 4).

To date, a substantial amount of organics in HTL-AP have been quantified (Table 4), but there are some organics in HTL-AP that remain unknown. Approximately 64–82% of the TOC for HTL-AP derived from lignocellulosic feedstock is able to be successfully quantified [159]. This range was reportedly much higher than HTL-AP generated from algae (45–72% of the TOC) [145]. The percentage of quantifiable TOC of HTL-AP generated from FIW and sludge has a similar range of 40–70% [145]. As for the nitrogen organics, 5–59% of the components within HTL-AP are unable to be determined [145,146]. One reason to explain this could be the presence of many low concentration compounds that are below the detection limit. Additionally, these organics may be high molecular weight molecules that are unidentifiable by conventional chromatography apparatuses. Maddi et al. discovered two kinds of protein oligomers in HTL-AP which have molecular weights of 210 and 250, respectively [145]. Chen et al. verified the presence of high-molecular-weight organics (MW>1000) in HTL-AP from rice straw via gel filtration chromatography, and these organics proved to be difficult to biologically convert [157]. Si et al. confirmed that these high molecular weight organics were associated with nitrogen-containing moieties [21]. These high molecular weight

molecules in HTL-AP may originate from monosaccharides and amino acids reacting together via the Maillard reaction [172]. This assumption also could be supported by the fact that more compounds are unidentifiable for the HTL of feedstocks rich in protein and carbohydrates (algae and sludge) rather than feedstocks with a composition solely dominated by carbohydrates (lignocellulosic biomass). This is due to the fact that a feedstock with a high protein and high carbohydrate content tend to promote the Maillard reaction whereas feedstock only containing lignocellulosic material does not. However, the characteristics of high molecular weight organics have still not been fully understood, including their specific structure, quantification, and potential application outside the HTL paradigm. Therefore, this area of work needs to be further investigated.

2.5.2. Distribution of inorganic compounds in HTL-AP

Inorganic compounds are abundantly distributed in HTL-AP, such as ammonia, PO_4^{3-} , K, Na, Mg, Al, Ca, and Fe. The distribution of these inorganic elements are tightly related to the composition of the biomass utilized for HTL. For example, HTL-AP derived from algae and manure exhibit a high ammonia concentration because of the large content of N in the feedstock compared with lignocellulosic biomass. A previous study noted that the aqueous stream generated from HTL of saline-water algae contained a higher content of Na, Mg, K, and Ca than that of freshwater algae cultures which can be attributed to the growth substrate [145]. Table 5 shows the heavy metals distribution in HTL-AP for various types of feedstock. The highest concentration of Zn was observed in HTL-AP derived from manure. This is because Zn is typically added to animal feed to promote healthy conditions for animal growth, but it is eventually excreted into urine and manure. In addition, Cu, Pb, Cd, Cr were also detected in livestock manure [173]. Lignocellulosic biomass may also concentrate heavy metals from the cultivation medium. For example, the HTL-AP derived from lignocellulose irrigated with untreated household wastewater and sewage was reported to have a Zn concentration of 3 mg/L [118].

Generally, ammonia-nitrogen accounts for the largest fraction of nitrogen in HTL-AP due to the deamination of protein in the feedstock and the cracking of N-containing derivatives [174]. As for P, only a limited number of studies have investigated the distribution

Table 4

Concentration (wt.%) of major organic constituents identified in the HTL-AP generated from sludge [146], food waste [146], algae [145], corn stover [159], and loblolly pine [159].

Feedstock	Food waste ^a (n = 4)	Sludge ^b (n = 3)	Algae (saline) (n = 4)	Algae (fresh) (n = 4)	Corn stover (n = 4)	Loblolly pine (n = 4)
HTL conditions^c						
Temperature (°C)	339 (331–349)	340 (332–350)	347(343–350)	346 (340–350)	350 (349–352)	353 (347–359)
Total solid (%)	13.1 (10.6–14.9)	10.3 (8.5–11.5)	17.6(17.0–18.1)	16.7(13.4–19.4)	10.6 (8.6–12.4)	11.7 (10.6–13.5)
Feed rate (L/h)	2.1(1.5–4)	1.5 (1.5–1.5)	1.9(1.5–3)	1.8 (1.5–2.0)	1.5(1.5–1.5)	1.3 (1.0–1.5)
Chemical compounds						
Acetic acid	0.59 (0.022–1.083)	0.321 (0.308 –0.331)	0.565(0.455–0.721)	0.0303(0.027–0.393)	0.878 (0.730–1.080)	0.443 (0.360–0.500)
Formic acid	NA	NA	NA	NA	0.069 (0.058–0.080)	0.056 (0.043–0.086)
Glycolic acid	NA	NA	NA	NA	1.678 (1.430–1.780)	1.098 (0.650–1.50)
Propanoic acid	0.055 (0.015–0.073)	0.056 (0.042–0.097)	0.100(0.093–0.107)	0.077(0.050–0.123)	0.109 (0.076–0.130)	0.119 (0.094–0.130)
Methanol	NA	NA	NA	NA	0.203 (0.073–0.300)	0.355 (0.240–0.460)
Ethanol	1.021 (0.058–2.085)	0.041 (0.031–0.051)	0.124(0.0634–0.247)	0.138(0.055–0.201)	0.068 (0.019–0.100)	0.052 (0.025–0.068)
1-Propanol	NA	NA	NA	NA	0.012 (0–0.017)	0.013 (0.006–0.016)
Propylene glycol	NA	NA	NA	NA	0.016 (0.006–0.025)	0.011 (0.006–0.017)
Ethylene glycol	NA	NA	NA	NA	0.076 (0.044–0.120)	0.065 (0.011–0.140)
Isosorbide	0.067 (0.000–0.269)	NA	NA	NA	NA	NA
Acetone	0.084 (0.117 –0.015)	0.095 (0.050–0.132)	0.088(0.065–0.123)	0.079 (0.056–0.093)	0.061 (0.021–0.100)	0.059 (0.034–0.081)
2-Butanone	0.024 (0.045–0.007)	0.033 (0.023–0.038)	0.030(0.022–0.039)	0.034 (0.024–0.058)	0.027 (0.018–0.039)	0.020 (0.012–0.026)
2-Pentanone	NA	NA	0.003 (0.002–0.004)	0.002 (0–0.004)	NA	NA
3-Pentanone	NA	NA	0.002 (0.001–0.002)	0.002 (0–0.004)	NA	NA
2-Butanone, hydroxy	0.020 (0.000–0.079)	0.015 (0.000–0.045)	NA	NA	NA	NA
Cyclopentanone	0.007 (0.003–0.014)	0.006 (0.005–0.013)	0.008 (0.004–0.011)	0.012 (0.005–0.027)	0.017 (0.006–0.023)	0.018 (0.013–0.021)
2-Cyclopenten-1-one	0.002 (0.000–0.008)	0.011 (0.002–0.0186)	NA	NA	0.014 (0.006–0.021)	0.013 (0.006–0.020)
2-Methyl-cyclopentanone	NA	NA	NA	NA	0.004 (0–0.006)	0.004 (0–0.006)
2-Methyl-2-cyclopenten-1-one	NA	NA	NA	NA	0.033 (0.018–0.041)	0.029 (0.021–0.034)
3-Methyl-2-cyclopenten-1-one	NA	NA	NA	NA	0.023 (0.010–0.030)	0.017 (0.013–0.020)
2,3-Dimethyl-2-cyclopenten-1-one	NA	NA	NA	NA	0.014 (0.007–0.020)	0.007 (0.007–0.008)
g-Butyrolactone	NA	NA	NA	NA	0.023 (0.006–0.041)	0.029 (0.017–0.041)
g-Valerolactone	NA	NA	NA	NA	0.010 (0–0.019)	0.017 (0.012–0.022)
2(3H)-furanone, dihydro-5-methyl	0.010 (0.007–0.015)	0.006 (0.000–0.010)	NA	NA	NA	NA
Phenol	0.014 (0.013–0.017)	0.014 (0.013–0.015)	NA	NA	0.030 (0.015–0.037)	0.012 (0.010–0.014)
2-Methoxyphenol	NA	NA	NA	NA	0.015 (0.009–0.019)	0.033 (0.030–0.037)
4-Ethylphenol	NA	NA	NA	NA	0.014 (0.012–0.017)	BDL
Pyridine	NA	NA	0.080 (0.061–0.098)	0.010 (0–0.023)	NA	NA
Pyrazine	0.011 (0.016–0.008)	0.020 (0.012–0.028)	NA	NA	NA	NA
Pyrazine, methyl	0.003 (0.000–0.012)	0.026 (0.040–0.012)	0.043 (0.026–0.072)	0.078 (0.017–0.129)	NA	NA
Dimethyl/ethyl pyrazine	NA	NA	0.018 (0.009–0.036)	0.012 (0–0.022)	NA	NA
2-pyrrolidinone, 1- methyl	0.025 (0.011–0.044)	0.035 (0.027–0.043)	0.040 (0.025–0.051)	0.046 (0–0.078)	NA	NA
2-pyrrolidinone, ethy	NA	NA	0.043 (0.039–0.053)	0.063 (0–0.104)	NA	NA
2-pyrrolidinone	0.022 (0.000–0.041)	0.066 (0.053–0.080)	0.082 (0.048–0.115)	0.220 (0–0.378)	NA	NA
1-butyl-2-pyrrolidinone	NA	NA	BDL	0.003 (0–0.012)	NA	NA
2-piperidinone	0.012 (0.015–0.021)	0.029 (0.026–0.033)	0.084 (0.061–0.111)	0.053 (0–0.079)	NA	NA
3-pyrindol, 6-methyl	NA	NA	0.004 (0–0.018)	0.040 (0.032–0.047)	NA	NA
3-pyrindol, 2,6-dimethyl	NA	NA	BDL	0.020 (0.019–0.021)	NA	NA
Acetamide	NA	0.112 (0.100–0.131)	0.106 (0.071–0.166)	0.129 (0–0.204)	NA	NA
N-methyl-acetamide	NA	0.095 (0.091–0.098)	0.129 (0.098–0.178)	0.090 (0–0.172)	NA	NA
N-butyl-acetamide	NA	NA	0.066 (0.043–0.103)	0.093 (0–0.172)	NA	NA
N-methyl succinimide	0.023 (0.017–0.029)	0.043 (0.031–0.054)	0.164 (0.128–0.189)	0.090 (0.042–0.225)	NA	NA
N-ethyl succinimide	NA	NA	0.034 (0.014–0.056)	0.038 (0–0.081)	NA	NA
N-(hydroxyethyl) succinimide	NA	NA	0.014 (0–0.032)	0.018 (0–0.028)	NA	NA
a-methyl-a-propyl succinimide	NA	NA	0.018 (0.012–0.022)	0.017 (0–0.023)	NA	NA
N,N-dimethyl acetamide	NA	NA	0.039 (0–0.078)	0.064 (0–0.257)	NA	NA
N-ethylacetamide	NA	NA	0.087 (0–0.146)	0.070 (0–0.149)	NA	NA

^a food waste from four sources;^b primary sludge, secondary sludge and digested sludge;^c HTL conducted in a continuous processing bench scale system; NA: not available; BDL: below detection limit.

Table 5

Heavy metals distributed in HTL-AP derived from manure [5,59,116,131,132], algae [142,144,156], lignocellulose [118], and sludge.

Metals (mg/L)	Manure	Algae	Lignocellulose ^a	Sludge
Cu	0.022 ± 0.016	0.25 ± 0.35	BDL	0.2
Zn	1.39 ± 1.36	0.46 ± 0.53	3	0.5
As	0.18 ± 0.15	NA	NA	0.6
Pb	0.004 ± 0.004	<2.5	NA	NA
Cd	0.0003 ± 0.0004	<0.5	NA	NA

^a Wastewater irrigated willow; BDL: below detection limit; NA: not available.

of P in the aqueous phase, and the P content in HTL-AP is typically very low. The phosphorus speciation in HTL-AP consists of reactive P (inorganic phosphorus and loosely-bound organic forms of phosphorus released by hydrolysis during HTL) and unreactive P (organic and condensed forms of phosphorus) [175]. Shi et al. demonstrated that more than 80% of the feedstock P was transferred to HTL-AP, and approximately 98% of the P could be recovered by struvite precipitation by varying the pH of the hydrothermal conversion process with HCl [176]. Huang et al. reported that the predominant speciation of P derived from sludge via hydrothermal treatment was orthophosphate due to the hydrolysis of pyrophosphates and polyphosphates in the aqueous medium [177]. A similar finding was also observed by Wang et al. [178]. The limited content of P in the HTL-AP is due in part to a large fraction of the feedstock P preferentially being distributed into the solid residue during hydrothermal conversion. This results from the presence of metals (e.g. Mg, Al, and Ca) which can impact the phase migration of P-containing derivatives, thereby leading to P retention in the solid residue. For instance, previous studies have reported that manure and sludge, feedstocks that contain a high content of metals (e.g. Ca, Mg, Cu, Cd and Zn), caused the formation of insoluble phosphate precipitates enhanced by the presence of P-binding metals [179–181].

In addition, the metals soluble within HTL-AP are related to the chemical properties of each distinctive metal. HTL-AP has been reported to recover between 30–50% of Mg in the HTL feedstock [150]. Heavy metals were found to almost exclusively migrate into the solid residue phase. It has been reported that most of the K (>89%) and Na (>73%) in the manure were released into the aqueous phase while a majority of the Ca (>89%), Mg (>81%), Al (>88%), Fe (>72%), and Zn (>94%) migrated into the solid residue [59]. Xu et al. found that only a limited (0.5–1.0%) amount of heavy metals (Cu, Cr, and Zn) were distributed into the HTL-AP derived from sewage sludge, while the vast majority (93.2–98.9%) of metals were distributed into the solid residue [165]. Another study investigating six types of animal manure also confirmed that the majority of heavy metals (70%–98% of Zn and Cu, 71%–99% of Pb, and 87%–98% of Cd) were concentrated into the solid residue. Thereby,

a migration and transformation pathway of heavy metals during HTL was proposed, in which most heavy metals in the feedstock were transferred into the solid residue through various mechanisms, including cation exchange, physical adsorption, precipitation, complexation, and crystallization [5].

The inorganics in HTL-AP would affect downstream processing. For example, the dominant inorganics (ammonia, TP, K, Na, and Mg) within HTL-AP were derived from macronutrients, and these inorganics could potentially be used as a fertilizer or as culture media for algae growth. However, nickel (Ni) in HTL-AP was found to be the main inhibitory factor for algal growth [120]. Moreover, the alkali and alkaline earth metals, such as Na, Mg, K, and Ca, may interfere with other catalytic materials used during hydrothermal gasification [145].

2.5.3. Toxic compounds

Due to its high concentration of toxic compounds, HTL-AP poses a potential safety and health hazard if it is directly discharged into the environment. Pham et al. investigated the mammalian cell cytotoxicity of specific nitrogen organics used as a surrogate to represent HTL-AP, a mixture of multiple nitrogen organics extracted from HTL-AP and the complete HTL-AP matrix [182]. The results showed that the mixture of nitrogen organics extracted from HTL-AP was highly cytotoxic to mammalian cells, and a 7.5% raw HTL aqueous phase concentration led to a 50% reduction in cell density during a chronic cytotoxicity assay. Elliott et al. summarized a list of hazardous constituents in the HTL-AP, which mostly consisted of aromatic compounds and nitrogen-containing organics. In particular, some of the compounds were considered hazardous even at very low concentrations, such as 2-propenol, 2-propenal, aziridine, and 2-methylaziridine [183].

The heavy metals in HTL-AP also pose a significant environmental and safety concern, especially for HTL-AP derived from sludge and manure. Various heavy metals, including Pb, Zn, Cu, Cd, Cr, and Ni have been detected in HTL-AP. The specific distribution of metals among the output products during the HTL process has been reported to be directly related to the reaction conditions (temperature, catalyst, and addition of other feedstock). One point to clarify is that HTL has been proven to reduce the risk associated with heavy metals compared with the raw feedstock. Li et al. reported that HTL significantly reduced the contamination level of speciation fractions for multi-metals and single metals (Cu, Zn, Pb, and Cd) in livestock manure using individual contamination factor (ICF) and global contamination factor (GCF) risk assessments [5]. Similar results were also found by Leng et al., which confirmed the reduction of risk associated with Pb, Zn, Cu, and Ni in sewage sludge after HTL [184].

As shown in Fig. 10, previous research has verified that the majority of heavy metals in the HTL feedstock are concentrated

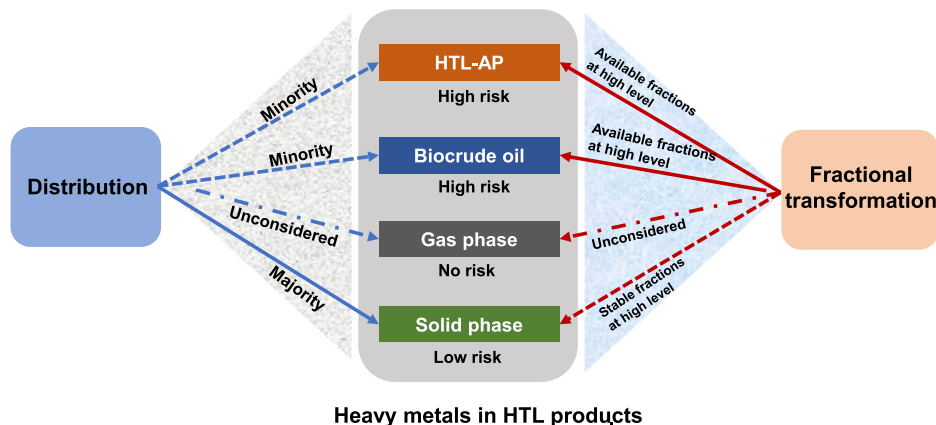


Fig. 10. The migration and transformation of heavy metals during HTL. Adapted from [7].

into the solid residue, which constitutes a low to medium environmental risk [184]. The low concentration of heavy metals in HTL biocrude oil is beneficial for enhanced combustion, thereby improving oil stability during storage and further upgrading processes [136]. Although HTL lessens the risk associated with heavy metals by migrating a majority of the metals to the solid residue, safety hazards still exist for the subsequent usage of HTL-AP due to the presence of heavy metals [7]. For example, the mercury (Hg) in rice grains was found to be much higher than the maximum allowable amount when using HTL-AP from swine manure as a fertilizer for cultivation [185]. Hence, further investigation is needed to better understand the valorization techniques necessary to promote toxicity remediation. One way to approach this problem is to develop methodology to ensure that the heavy metals remain concentrated and immobilized in the solid residue. In addition, demetalization of the feedstock before HTL or demetalization of HTL-AP before valorization could also be effective techniques.

3. Separation of value-added chemicals from HTL-AP

3.1. Separation of organics in HTL-AP

Organic compounds in HTL-AP have a wide variety of applications ranging from the production of liquid fuels to the extraction of high-value chemicals. For example, ethanol is a substitute transportation fuel for gasoline, and the application of ethanol could reduce crude oil consumption, conserve nonrenewable energy, and reduce GHG emissions [186]. The acetic acid present within HTL-AP could be used as an input for the manufacturing of vinyl acetate monomers and terephthalic acid, which could be further used for the production of polyethylene terephthalate [187]. Glycolic acid which accumulates in high concentrations in the HTL-AP derived from lignocellulosic biomass has been proven to be an effective cosmetic ingredient, and in recent years is in increasing demand [188]. Phenol could be easily and directly used by conventional petrochemical processes which is used for pigments, dyes, resin resins, antioxidants, urea resins, formaldehyde resins, and alkyl phosphite production [189]. Various nitrogen organics that accumulate in HTL-AP derived from manure, sludge, and algae can be utilized as intermediate chemicals for the production of value-added products. Higashio and Shoji reported the application of these nitrogen organics as commodities (e.g. pharmaceuticals and agrochemicals) due to their high biological activities [190]. Pyridine is an excellent solvent for dehydrochlorination reactions and the extraction of antibiotics. Methylpyridines are used as starting materials for pharmaceuticals (anti-tuberculosis agents), agrochemicals, and serve a critical role in the production of feed additives and anion exchangers. Pyrazines play an important role as intermediates for perfumes, pharmaceuticals, and agricultural chemicals [190]. In addition, nitrogen organics, such as 1-methyl-2-pyrrolidinone, are used as solvents during synthesized homogeneous catalysis [191]. Additionally, acetamide has shown reasonably good thermal stability as a latent heat storage material in a solar system [192]. Amides have been used as fuel detergent-dispersant additives to improve engine performance, inhibiting the formation of gum and sludge in the combustion process and decreasing fuels consumption and pollution emissions [193,194].

However, HTL-AP is a complicated aqueous mixture consisting of dozens of chemicals. The separation and concentration of these chemicals from HTL-AP is a critical barrier to value-added chemical extraction. The separation of high-value organics from HTL-AP has been conducted in several preceding studies. Chen et al. reported the extraction of phenolic compounds from rice straw HTL-AP using a modified resin, and the total content of phenolic compounds in the aqueous solution increased from 18% to 78% after separation [28]. Lyu et al. conducted a separation of rice straw HTL-AP using

two-stage nanofiltration, and the HTL-AP was fractionated into three parts: glucose concentrate, monophenol and cyclopentenone concentrate, and acetic acid permeate [195]. Zhang et al. also recovered carboxylic acids from a model HTL-AP solution [196]. Previous studies have also conducted separation of high-value chemicals using HTL-AP from lignocellulosic biomass or model HTL-AP solutions which have a simple distribution of organics. The separation of chemicals from complicated HTL-AP, such as HTL-AP derived from algae, has not yet been reported.

It has been reported that separation technology currently accounts for 60–80% of the process costs of most mature chemical processes [197]. Hence, the economics and sustainability of HTL-AP separation technology needs to be evaluated in the context of a whole chemical process. The needed separation and concentration technology could be expensive and needs more R&D work before it can become a mainstream valorization option.

3.2. Separation of inorganics in HTL-AP

The inorganics within HTL-AP, such as N, P, and K, could be further separated for commercial fertilizer application. The nutrients, which are plagued by fluctuating energy costs, are also critical elements of food production. For example, the production of 1 ton of N requires the energy equivalent of seven barrels of oil [198]. In addition, P from geological deposits is being continually depleted [199]. Hence, separation of nutrients from HTL-AP is an attractive avenue to solve this quandary. The high concentration of these nutrients in HTL-AP indicates its potential as a source for nutrients separation. The concentration of N, P, and K in HTL-AP generated from manure and algae have been reported to range from 5–20 g/L, 1–10 g/L, and 1–8 g/L, respectively (Fig. 8). Shanmugam et al. proposed to collect the N and P in HTL-AP as struvite, and the results showed that 99% of P and 40–100% of ammonium nitrogen in HTL-AP could be collected [200]. A high phosphate recovery amounting up to 75% was also achieved from HTL-AP microalgae using struvite [201]. The extracted struvite displayed excellent fertilizer qualities under specific conditions when compared with standard fertilizers [202]. Stripping is another approach to recover ammonia in HTL-AP which has been commonly employed in industrial applications. The stripped ammonia could be adsorbed by an acidic solution and form a mineral fertilizer. It has been reported that up to 90% of the ammonia in HTL-AP was recovered using air stripping [201]. Membrane distillation is another technology which has been verified to generate liquid fertilizer with high concentrations of N and P from HTL-AP [133].

Although the separation of N and P has been proven to be feasible, further optimization of the separation methods needs to be conducted. For example, both ammonia stripping and struvite formation highly depend on the pH and operating temperature, and the separation of K still remains an unsolved challenge. In addition, high concentrations of organics left in the remaining aqueous stream would need further valorization.

4. Biological conversion of HTL-AP

HTL-AP is a monetary and environmental burden to HTL biorefineries. Biological conversion strategies may enable the valorization of HTL-AP, which could lead to the production of hydrogen, methane, electricity, and chemicals through different pathways. These processes would subsequently make HTL technology more energy productive and cost-effective.

4.1. Pretreatment before biological conversion

The primary challenge hindering biological conversion of HTL-AP is the potential inhibitors, which may lead to a low conversion

Table 6
Comparison of pretreatment methods for biological conversion.

Pretreatment	Main process	Benefits	Ref.
Partial oxidation	Incorporation of ozone, UV, and H ₂ O ₂ in order to oxidize the aromatic ring structures and N-heterocyclic compounds	Recalcitrant compounds are converted into more biodegradable products	[149,204]
Adsorption	Adsorb organics and inorganics using activated carbon and zeolite	The potential inhibitors for biological conversion are adsorbed, including N-heterocyclic compounds, aromatic compounds, and ammonia.	[143,151]
Extraction	Extraction of organics and inorganics through organic solvents, resins, nanofiltration, and struvite formation	The potential inhibitors for biological treatment are extracted from HTL-AP, including aromatic, nitrogen-containing organics, and ammonia	[157,200]

efficiency and even a failure of biological conversion. The biochemical oxygen demand (BOD)/COD ratio of HTL-AP was reported to be within the range of 0.16–0.31 [24,129,203]. BOD/COD values in this range tend to make HTL-AP recalcitrant to biological conversion. Thus, proper pretreatment is required to enhance the efficiency of downstream units. The main methods of pretreatment are partial oxidation, adsorption, and extraction (Table 6). The purpose of pretreatment is to remove or convert the inhibitors into easily biodegradable compounds.

4.1.1. Partial oxidation

Partial oxidation combined with biological conversion has been proposed to be an economically favorable alternative for treatment of recalcitrant waste streams [205]. For example, Somensi et al. reported a significant improvement of biodegradability and a reduction of toxicity when comparing raw textile wastewater with wastewater treated via partial oxidation [206]. Oxidation methods primarily include ozonation, H₂O₂ treatment, UV irradiation, and the chlorine and photo-Fenton process. Ozone treatment is one of the most attractive methods due to its high oxidation potential. The primary product of ozonation is oxygen gas, and no secondary pollutant compounds are produced. It has been proven that the inhibitors for biological conversion in HTL-AP, including aromatic ring structures [207], N-heterocyclic compounds [208], and furfural [209], can be converted using ozone, and the produced carboxylic acids can then be easily converted utilizing biological methodology [205]. A preliminary study of ozone treatment was conducted by Yang et al., and the results showed that all phenols and over 20% of the N-heterocyclic compounds in swine manure HTL-AP were transformed. Further, the biodegradability of HTL-AP was improved by 33% [129]. H₂O₂ oxidation can also reduce the HTL-AP recalcitrance and lead to a higher production of methane during subsequent anaerobic fermentation [210]. However, the mechanism of partial oxidation for the complicated assortment of compounds present within HTL-AP still needs to be further investigated. In addition, the oxidation process needs to be well controlled in order to selectively convert the toxic compounds rather than all of the organics. In this manner, selective treatment of the recalcitrant compounds can decrease the economic input and concomitantly circumvent the formation of other recalcitrant precursors. Jayakody et al. reported that when an excessive amount of H₂O₂ was applied, anaerobic fermentation was negatively impacted. Specifically, the methane yield decreased and the lag-phase increased [210]. A similar result was also observed for ozone-treated HTL-AP. In this study, an increased lag-phase was observed; however, a higher methane production rate and yield were achieved and the formation of recalcitrant compounds during ozonation was also confirmed [21].

4.1.2. Adsorption

Adsorption selectively isolates the inhibitors from HTL-AP utilizing a variety of different materials. Zeolite could effectively adsorb ammonia from HTL-AP to avoid inhibition caused by a high concentration of ammonia [211]. However, ammonia may not be

the main problem for biological treatment compared with other toxic organics in HTL-AP. Further research conducted by Li et al. verified that not only ammonia but also a portion of the nitrogen organics in HTL-AP could be adsorbed by zeolite, which led to an improved methane yield and shortened the lag-phase [143]. Activated carbon has also been extensively investigated as an adsorbent material for various waste streams [212]. Zhou et al. reported that activated carbon was shown to effectively mitigate the impact of recalcitrant compounds, thereby enhancing methane production and allowing digestion to proceed at higher HTL-AP concentrations (up to 33.3%), likely due to the ability of activated carbon to sequester toxic organic compounds [130]. Zheng et al. compared the effect of zeolite, granular activated carbon (GAC), and polyurethane matrices addition on the aerobic digestion of HTL-AP. The results showed that GAC achieved the highest methane improvement and also demonstrated a good recovery of adsorption capacity in the second batch [156]. This suggested the superiority of activated carbon as an adsorbent. Pham et al. found the GAC could significantly reduce the cytotoxicity of HTL-AP [182]. Erkelens et al. reported that the growth of *Tetraselmis* sp. could be significantly improved with the application of activated carbon due to the adsorption of organic inhibitors [138]. Park et al. detoxified hydrothermal-treated *Gelidium amansii* with activated carbon powder to diminish the inhibitory impact of 5-hydroxymethylfurfural (5-HMF) and other potential inhibitory compounds [213]. A similar result was also reported in a methane production process using 30% GAC pretreated HTL-AP, resulting in an increase of the methane yield by 162% [151].

However, one primary issue with adsorption is that this method just transfers the inhibitory compounds to another medium. Thus, once the inhibitors have been isolated, further treatment still remains an issue. Hence, the regeneration of the adsorbent is very important. The used activated carbon has been previously reported to be effectively regenerated through thermal methods [214], but the economic and practical consequences still need to be evaluated. Bioregeneration is another possible treatment method; however, bioregeneration depends on the types of adsorbed organic compounds and the long-term feasibility of this method has yet to be elucidated.

4.1.3. Extraction

Extraction is another pretreatment method that can selectively isolate and enrich chemicals from HTL-AP. Petroleum ether, cyclohexane, dichloromethane, and ethyl acetate were previously used to extract compounds from rice straw HTL-AP. Results showed that petroleum ether extraction resulted in increased methane yields which was attributed to the separation of furans, ketones, and phenols from HTL-AP [157]. A similar result was also reported during algae cultivation using HTL-AP after using ethyl ether to extract nitrogen-containing and oxygen-containing derivatives [155]. Nitrogenous organic compounds were also extracted from *Spirulina* HTL-AP using dichloromethane; however, the resulting HTL-AP still showed cytotoxicity to mammalian cells [182]. Phenolic compounds, known inhibitors for biological conversion, have been

Table 7
Summary of algae cultivation in HTL-AP.

Algae	Cultivation conditions ^a	HTL process conditions ^b	Biomass concentration (HTL-AP) g/L	Biomass concentration (Control) g/L	Ammonia removal	P removal	Ref.
<i>Chlorella minutissima</i>	500×, flask	350°C, 60 min, <i>Spirulina</i>	0.52	1.03	NA	NA	[142]
<i>Chlorogloopsis</i>	400×, flask	300°C, 60 min, <i>Chlorogloopsis</i>	0.50	0.39	83–98	50–100	[120]
<i>Spirulina platensis</i>	400×, flask	300°C, 60 min, <i>Spirulina</i>	0.66	0.71	NA	NA	[120]
<i>Chlorella vulgaris</i>	100×, flask	300°C, 60 min, <i>Chlorella</i>	0.88	1.20	91–100	15–19	[120]
<i>Scenedemus dimorphous</i>	400×, flask	350°C, 60 min, <i>Scenedemus</i>	0.05	0.12	35–100	9–47	[120]
Algal-bacterial	100×, flask	300°C, 30 min, <i>Spirulina</i>	2.50	NA	100	95	[27]
<i>Chlorella protothecoides</i>	50–100×, NA	300°C, 30 min, <i>Spirulina</i>	NA	NA	NA	NA	[182]
<i>Tetraselmis</i> sp.	1000×, flask ^c	350°C, 10 min, NA	0.41	0.49	NA	NA	[138]
<i>Phaeodactylum tricoratum</i>	25×, FPA-PBR ^d	350–400°C, 50 min, <i>Phaeodactylum</i>	13.4	NA	100	100	[222]
<i>Scenedesmus</i>	392×, flask with medium	350°C, 15 min, <i>Scenedesmus</i>	0.10	0.30	68	NA	[144]
<i>Chlorella</i>	392×, flask with medium	350°C, 15 min, <i>Scenedesmus</i>	0.25	0.23	>86	NA	[144]
<i>Phaeodactylum</i>	571×, flask with medium	350°C, 15 min, <i>Nannochloropsis</i>	0.17	0.52	>84	NA	[144]
<i>Nannochloropsis</i>	571×, flask with medium	350°C, 15 min, <i>Nannochloropsis</i>	0.35	0.41 b	>89	NA	[144]
<i>Chlorella vulgaris</i>	15×, flask	300°C, 60 min, <i>Nannochloropsis</i> sp.	0.67	NA	20–50 ^f	20–100 ^g	[154]
<i>Chlorella sorokiniana</i>	200×, flask	NA, <i>Tetraselmis</i> sp.	2.9–3.8	4.9	NA	NA	[217]
<i>Scenedesmus obliquus</i>	150×, flask	NA, <i>Tetraselmis</i> sp.	7.3	4.3	NA	NA	[217]
<i>Chlamydomonas reinhardtii</i>	140×, flask	310/220°C, <i>Chlamydomonas</i> , NA	0.9/1.7	1c	NA	NA	[218]
<i>Picochlorum SE3</i>	1000×, Pond	NA	0.25	NA	NA	NA	[153]
<i>Desmodesmus</i>	160×, glass vessel	300°C, 5 min, <i>Desmodesmus</i>	0.18	0.81	67	NA	[140]
<i>Scenedesmus</i>	500–125×, flask ^h	350°C, 27 min, <i>Chlorella</i>	0.6–0.9	0.8	54–78 ^e	46–57 ^f	[201]
Algal-bacterial	20–100×, MPBR ^h	300°C, 60 min, <i>Spirulina</i>	0.5–1.5	NA	84–100	NA	[152]
<i>Chlorella vulgaris</i>	20×, flask ⁱ	270°C, 60 min, swine manure	1.2–2.4	NA	20–66	83–100	[204]

^a Dilution times/reactor;

^b Temperature/reaction time/feedstock;

^c Pretreated with activated carbon;

^d Flat panel airlift photobioreactor;

^e Based on total nitrogen;

^f Based on total phosphorus;

^g Struvite was added;

^h Membrane photobioreactor;

ⁱ Treated via anaerobic digestion; NA: not available.

reported to be successfully extracted by modified resins [28] and two-stage nanofiltration [195]. The ammonia in HTL-AP derived from algae could also be collected as struvite, and this method could enhance subsequent biological treatment as it can prevent related inhibition [200]. One of the most advantageous aspects of extraction as a pretreatment method is that the extracted organics and inorganics from HTL-AP could serve as value-added chemicals as previously discussed in Chapter 3. Moreover, extraction also augments the potential for further biological treatment via inhibitor isolation.

4.2. Nutrients for biomass production

4.2.1. Algae cultivation

Biofuels production from algae is a promising avenue for renewable fuel production, because growth of algae does not compete with food resources and involves no significant changes to land use. However, media that can support rich algal growth still requires the input of expensive nutrients including N, P, and K [215]. HTL-AP contains a high concentration of N, P, K, and micronutrients, which can be used as a growth media for algae production. Jena et al. first evaluated the feasibility of algae cultivation using HTL-AP. The results reported that a 50.5% algae yield could be achieved compared with a synthetic medium [142]. In recent years, extensive studies have been conducted to reveal the feasibility of algae cultivation using HTL-AP (Table 7). An “Environment-Enhancing Energy” (E2-Energy) paradigm was proposed by Zhou et al. (Fig. 11), involving the production of algae biofuels while simultaneously recycling the inputs by internally capturing and recycling C and nutrients for the cultivation of algae biomass [27]. Based on the simulated mass balances for long-term

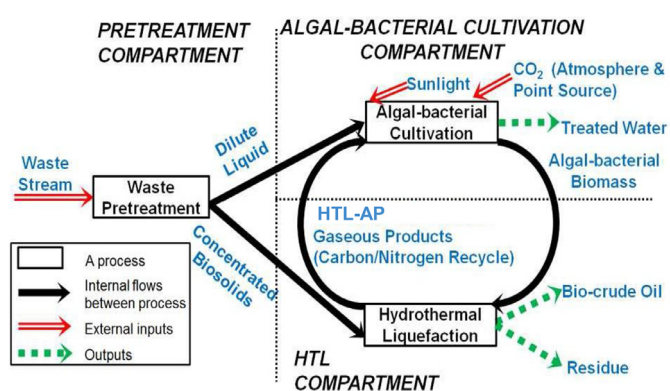


Fig. 11. Schematic of the Environment-Enhancing Energy paradigm for integrated HTL and algae-bacteria cultivation. Adapted from [27].

E2-Energy operations with internal recycling of nutrients and C, the proposed system could amplify biomass and biofuel production from wastewater by up to 10 times, thereby demonstrating the potential of this paradigm to replace fossil fuels using a wastewater-grown feedstock and carbon dioxide from the atmosphere as a point source [216].

Table 7 summarizes recent studies conducting algae cultivation using HTL-AP as a growth medium. Various factors will affect the efficacy of biomass production including the HTL conditions and algae cultivation process. Algae have been used as the predominant HTL feedstock in a majority of preceding studies, and most studies demonstrated that the nutrients present within HTL-AP could support algae growth. In particular, even higher biomass concentrations (0.05–13.4 g/L) were achieved in HTL-AP than was obtained

by using conventional synthetic media (0.12–4.9 g/L) (Table 7). Previous studies have demonstrated that N and P in HTL-AP could be converted through algae uptake and assimilation. Table 7 shows that most of the inorganic nitrogen (mainly consisting of ammonia) was removed during algae growth (over 80%). This could be attributed to the fact that microalgae cells preferentially utilize ammonia nitrogen, most likely because it is easier to convert ammonia nitrogen into amino acids [140]. The residual nitrogen was assumed to consist of many recalcitrant or slow-degrading compounds containing ring structures and nitrogen heteroatoms [27]. P has also been reported to be efficiently converted and utilized by algae (Table 7). Notably, *Desmodesmus* sp. cultivation using HTL-AP from the same microalgae demonstrated that the lack of (macro-/micro-) nutrients was considered to be the main cause of growth inhibition rather than toxicity due to insufficient dilution [140]. However, Edmundson et al. validated that all macronutrient components could be derived from HTL-AP, and there was no reported statistical difference between the group containing trace metals and the control with respect to algae cultivation [217]. This conflicting result indicated that the macronutrients in HTL-AP for algae cultivation are related to the feedstock of HTL and the specific requirements of different algae species for effective growth.

The effectiveness of algae cultivation using HTL-AP also highly depends on the HTL process conditions. Hognon et al. found that the HTL temperature had an impact on the efficacy of using HTL-AP as an algae cultivation medium [218]. This study showed that a much higher biomass yield was achieved using HTL-AP produced at 220°C rather than that at 310°C. More specifically, an algal-growth assay and response surface methodology was used to study how HTL operating conditions (260–300°C, 30–90 min, 15–35% total solids ratio) affect the inhibition of algae by HTL-AP. In this study, it was found that the algae biomass yield generally decreased as the total solids ratio, temperature, and retention time increased [216]. This was attributed to the distribution of inhibitors at various HTL conditions, which especially impacted the distribution of the heterocyclic compounds and straight chain oxygenates [216].

Chlorella has been the most commonly used algae strain when utilizing HTL-AP as a cultivation medium (Table 7). This could be explained by the fact that some species of *Chlorella* are obligate heterotrophic microalgae [219], which can assimilate organic compounds in HTL-AP, including glycerol and acetate [26]. Godwin et al. previously tested the growth of *Ankistrodesmus falcatus*, *Chlorella sorokiniana*, *Pediastrum duplex*, *Scenedesmus acuminatus*, *Scenedesmus ecornis*, and *Selenastrum capricornutum* using HTL-AP as a culture medium, and results showed that *Chlorella* could only tolerate up to 2% HTL-AP, and polycultures of 2–6 species of algae were viable at up to 10% [220]. Furthermore, this strategy of utilizing polycultures was better at balancing N and P efficiency in comparison to monocultures [221]. *Phaeodactylum tricornerutum* was cultivated with 25-fold dilution of HTL-AP, which suggested that this strain was less sensitive than others to possible inhibitors in the HTL-AP [222]. Zhou et al. set up an algal-bacteria co-culture system to enhance biomass production, and biomass cultivation with 100-times diluted HTL-AP was achieved after long-term adaptation [27]. A similar system was also reported by Wang et al., in which a symbiotic relationship evolved between the algae and bacteria [152]. Microalgae generate oxygen gas and extracellular compounds that allow aerobic bacteria to degrade organic pollutants, and the bacteria thereby benefit algae metabolism by converting organic inhibitors, producing growth-promoting factors, and consuming oxygen gas from the medium to relieve the oxygen damage to the microalgae.

In addition, the efficiency of algae cultivation is also affected by the bioreactors. A biomass yield of 0.25 g/L was achieved in an algal pond using seawater and 0.1% (vol.%) HTL-AP [153],

whereas a 13.4 g/L biomass yield was achieved in a flat panel airlift-photobioreactor [222]. Heimann et al. outlined a novel biofilm cultivation strategy that is water-smart and also offers the opportunity for direct energy conversion via HTL [223]. A synergistic growth of microalgae and bacteria with a biomass yield of 1.6 g/L using HTL-AP was achieved in a membrane photobioreactor (MPBR), in which a membrane module was used for retaining the biomass and further purifying the wastewater [152]. Another interesting research approach for incorporating HTL-AP as a medium was for the growth of algae and a rice co-culture, which showed promising results for co-production of both food and energy [185]. However, the accumulation of heavy metals in rice grains was still a concern.

There are some challenges for algae cultivation using HTL-AP. First, HTL-AP contains a large number of inhibitors, including organics and heavy metals (discussed in detail by a recent review paper [168]). Hence, heavy dilutions of HTL-AP, commonly around 100-times dilution (Table 7), are required to avoid growth inhibition caused by recalcitrant compounds. However, the concern with dilution is that this method would consume a lot of clean water and make algae cultivation using HTL-AP economically unviable. One potential solution is to incorporate low-strength wastewater [27], such as the primary effluent of a local municipal wastewater treatment plant [152] and mill cove wastewater [201]. However, the chemical constituents present within each type of low-strength wastewater will not be uniform, and properties will vary based on local conditions. Application of activated carbon has been proven as a way to significantly improve algae cultivation using HTL-AP due to the adsorption of organic nitrogen and carbon [138]. Zhang et al. reported that proper biocrude-aqueous separation (ethyl ether extraction) could relieve the potential toxicity of nitrogen-containing organic compounds to microalgae. A biomass yield of 0.67 g/L was achieved at 15-times diluted HTL-AP, which was the highest HTL-AP concentration reported for algae cultivation [154]. Using zeolites to adsorb inhibitors also promoted the tolerance of microorganisms to the high HTL-AP concentrations and increased biomass production by 67.2% [152]. However, the potential for commercial application of these methods still needs to be further evaluated. In addition, although algae cultivation demonstrates a high N recovery, most of the N is inorganic, and no evidence can be found for the consumption of any organic nitrogen [144]. The recalcitrant and/or slow-degrading compounds in the effluent from algae cultivation contain nitrogen heteroatoms [216]. This was further confirmed by Pham et al., and only 30% of the toxicity, which mainly resulted from the nitrogenous organic compounds, was removed biologically by recycling *Spirulina* HTL-AP back into algal cultivation [182]. Hence, the integration of algae cultivation with other approaches to remedy the inhibitors and enhance the nutrients recovery is required.

4.2.2. Pure microbes cultivation

HTL-AP has also been reported as a microbial growth medium, and the produced biomass could be the feedstock for biofuels and value-added chemicals production. Compared with algae cultivation, microbes can more actively convert organic constituents via heterotrophic pathways. Different pure cultures have been investigated to convert the organics in HTL-AP. For example, Shende et al. cultivated a *Enterobacter* species in 15 vol.% HTL-AP derived from lignocellulosic biomass, and a maximum 9.4-fold increase in the dry cell weight was observed [224]. The *Rhodococci* species was also reportedly able to convert 93.4% COD of HTL-AP within 11 days [141]. Nelson et al., found that *Escherichia coli* and *Pseudomonas putida* could grow using 10–40 vol.% aqueous phase from the liquefaction of the algae *Nannochloropsis*, and the best growth occurred at 20 vol.% [148]. Jayakody et al. demonstrated that

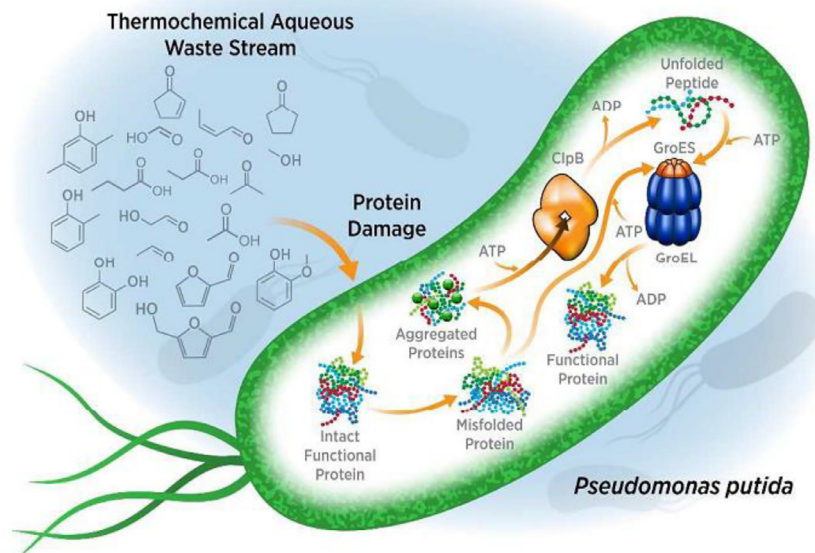


Fig. 12. Chaperone-dependent tolerance mechanism of engineered *Pseudomonas putida* to thermochemical wastewater streams. Reprinted from [210] with permission.

aldehydes were the most inhibitory compounds in representative HTL-AP, and the inhibitors damaged the proteins which caused the protein derivatives to be misfolded and aggregated [210]. Although the challenges of toxicity hinder microbial conversion, efforts have been made to use engineered aerobic monocultures or designer consortia. The genome-modified *Pseudomonas putida* improved the tolerance towards thermochemical aqueous phase samples by up to 200-fold (Fig. 12) [210]. The cultivation of pure microbes using HTL-AP suggested the promising potential for biomass production and conversion of organics. However, the complicated and multivariate composition of HTL-AP needs further investigation to realize the application of this technology.

4.3. Anaerobic fermentation

Anaerobic fermentation is one of most cost-effective conversion technologies, and it has been implemented worldwide for commercial production of electricity, heat, and compressed natural gas [225]. The diversified and synergistic characteristics of microbial communities in anaerobic fermentation make this methodology able to effectively convert HTL-AP. Fermentation primarily includes two main approaches: anaerobic digestion for methane production and two-stage fermentation for simultaneous hydrogen and methane production.

4.3.1. Anaerobic digestion for methane production

Although HTL-AP is a new feedstock for methane production by anaerobic digestion, wastewater streams such as coal gasification wastewater [226,227], cosmetic wastewater [228], and olive mill wastewater [229], which have a similar distribution of inhibitors (phenols and long chain acids), have been extensively studied. This indicates the promising potential of anaerobic digestion to effectively and efficiently valorize HTL-AP. However, the composition of HTL-AP is more complicated than the aforementioned wastewater. For example, abundant nitrogen organics, furfurals, and inorganics are present in HTL-AP but not present in other wastewater streams. Therefore, detailed investigation to understand the energy production pathways using HTL-AP for anaerobic digestion is necessary.

Table 8 summarizes the anaerobic digestion of HTL-AP using different types of feedstock. Previous studies indicated that

a methane yield range of 14–314 mL/g COD (average value of 194 mL/g COD) was observed, and most studies reported a yield of around 200 mL/g COD which corresponded to an energy recovery of 57%. This suggested that most of the organics in HTL-AP could be converted to methane for energy production, which was also confirmed by the COD removal performance (Table 8). However, there is a tradeoff between biocrude oil and methane production using model biomass as the HTL feedstock [230]. Obviously, HTL conditions should be screened and optimized based on biocrude oil production results, since this is the main contributing factor for determining the energy recovery of the HTL process (Fig. 13). Fig. 13 illustrates that 300–350°C is the best temperature range to recover the greatest amount of energy from the HTL feedstock when combined with anaerobic digestion. However, in some cases (e.g. carbohydrates-proteins and carbohydrates-proteins-lipids), 200°C seems to offer the highest (or second highest) energy recovery from the biomass. Considering the energy needed to heat the reactor, it is estimated that 200°C actually may have a lower ECR.

Inhibition of anaerobic digestion activity has been extensively reported when increased fermentation concentrations of HTL-AP were utilized [17,130,139]. The toxicity threshold of anaerobic digestion of HTL-AP derived from *Spirulina* has been previously conducted using an anaerobic toxicity assay (Fig. 14). Significant inhibition could be observed when the volumetric inclusion ratios of HTL-AP were higher than 5 vol.%, and a nearly complete inhibition occurred at an inclusion ratio higher than 24 vol.% [156]. Similar results were reported by Zhou et al., which showed that successful anaerobic digestion occurred at relatively low concentrations of HTL-AP (6.7 vol.%), producing a biogas yield of 0.5 ml/mg COD_{removed} and an energy recovery efficiency of 53%. However, higher concentrations (13.3 vol.%) of HTL-AP had an inhibitory effect, as indicated by delayed, slowed, or even complete inhibition of biogas production [130].

Inhibition during anaerobic digestion of HTL-AP can be attributed to various classes of organics in HTL-AP (Table 8), including furans, ketones, phenols, and N-heterocyclic compounds. These compounds are known to be inhibitors to microbes of anaerobic digestion. Si et al. revealed the transformations of fermentation inhibitors and microbial response (Fig. 15) [170]. The complete degradation of furfural and 5-HMF, and the partial

Table 8
Summary of methane production via anaerobic digestion using HTL-AP.

Feedstock	HTL conditions ^a	Anaerobic digestion ^b	Treatment	COD removal %	Methane yield (mL/g COD)	Energy recovery ^c	Rate-limiting/Inhibitors	Main conclusion	Ref.
Wastewater algae	260–320°C, 1 h	1000×, NA, 0.04 g/L	NA	44–61	NA	NA	Acetogenesis/Phenols and cyclic hydrocarbons	HTL-AP produced at 300°C lead to the highest lag phase and the smallest production rate	[17]
Spirulina	300°C, 0.5 h	15×, 37°C, 5.9 g/L	GAC 2 g/L	52	245	70	Acetogenesis/Ammonia, phenol and benzene	Methane yield increased by 13%, increased maximal methane production rate	[156]
Spirulina	300°C, 0.5 h	15×, 37°C, 5.9 g/L	Zeolite 2 g/L	37	227	65	Acetogenesis/Ammonia, phenol and benzene	Methane yields improved by 5%	[156]
Spirulina	300°C, 0.5 h	15×, 37°C, 5.9 g/L	PM 20 g/L	43	278	79	Acetogenesis/Ammonia, phenol and benzene	Methane yields improved by 29%, increased maximal methane production rate	[156]
Nannochloropsis	320°C, 0.5 h	97×, 37°C, 1 g/L	Struvite recovery	59	182	52	NA/Ammonia	Methane yield in struvite-recovered group improved by 250%	[200]
Nannochloropsis	320°C, 0.5 h	97×, 37°C, 1 g/L	GAC pretreatment 30%	67	84	24	NA/Nitrogen organics	Methane yield in 30% GAC pretreated group improved by 163%	[151]
Swine manure	NA	7.5–30.3×, 37°C, 3.4–13.8 g/L	PAC add 2 g/L	45–55	150–175	43–50	NA/Low pH, cyclic compounds and nitrogen-containing compounds	PAC addition shortened the lag phase and allowed anaerobic digestion to occur at high concentration (up to 33.3 vol.%)	[130]
Rice straw	170–320°C, 0.5–4 h	15–39×, 37°C, 0.75 g/L	NA	NA	217–314	62–89	NA/Phenols, furan and 5-hydroxym-ethylfurfural	More non-biodegradable organics were produced with the increase of HTL temperature	[22]
Rice straw	280°C, 0.5 h	28×, 37°C, 0.75 g/L	PE extraction	NA	235	67	NA/Furans, ketones, and phenols	PE extraction improved methane yield by 28%	[157]
Corn straw	260°C, 0 h	5×, 37°C, 8 g/L	NA	67	156	45	Acetogenesis/Phenol and nitrogen-containing organics	Complete degradation of furans and 54.0–74.6% of nitrogen-containing and phenolic compounds	[170]
Activated sludge and sawdust	200–350 °C, 0.17–1h	NA, 37°C, NA	NA	46	NA	NA	NA/NA	No lag-phase was observed	[163]
Swine manure	270°C, 1 h	2×, 37°C, 20 g/L	Ozone pretreatment 2.1 g/L	44	111	32	Acetogenesis/Phenol and nitrogen-containing organics	Methane yield improved by 109%, increased lag-phase and methane production rate	[21]
Swine manure	270°C, 1 h	2×, 37°C, 20g/L	GAC 20 g/L	93	212	61	Acetogenesis/Phenol and nitrogen-containing organics	Methane yield improved by 298%, shortened lag-phase and increased methane production rate	[21]
Spirulina	300°C, 0.5h	24–31 ×, 37°C, 4–5g/L	H ₂ O ₂ oxidation	50–59	NA	NA	NA/N-heterocyclic compounds	Improved the anaerobic biodegradability of HTL-AP	[149]
Chlorella	300°C, 0.5h	11–38 ×, 37°C, 2–7g/L	Zeolite pretreatment 0.3–0.36 g/mL	14–61	NA	NA	NA/Ammonia, N-heterocyclic compounds	Methane yield improved by 32–117%, shortened the lag phase	[143]
Sewage sludge	170–320 °C–0.5–6h	NA, 37°C, 0.75 g/L	NA	NA	136–286	39–81	NA/ nitrogen-containing organics, phenols, and furfural	Methane yield decreased with the increase of hydrothermal retention time and temperature	[164]
Mixture	NA	40 × ^d , 37°C, NA	Co-digestion	NA	267	NA	NA/NA	HTL-AP in combination with sewage sludge is feasible	[231]
Testraselmis	NA	1.67–5 × ^e , 37°C, NA	Co-digestion	NA	31–313	NA	NA/Chloride salts and nitrogen-containing organics	HTL-AP 30 vol.% can be co-digested with manure	[139]
Chlorella	NA	1.25–5 × ^e , 37°C, NA	Co-digestion	NA	14–244	NA	NA/Chloride salts and nitrogen-containing organics	HTL-AP 30 vol.% can be co-digested with manure	[139]

^a Temperature/reaction time;

^b Dilution times/reactor operation temperature/HTL-AP concentration;

^c Calculated based on the ratio to theoretical value (350 350 mL methane /g COD);

^d Diluted with mixed sewage sludge;

^e Diluted with swine manure; NA: not available.

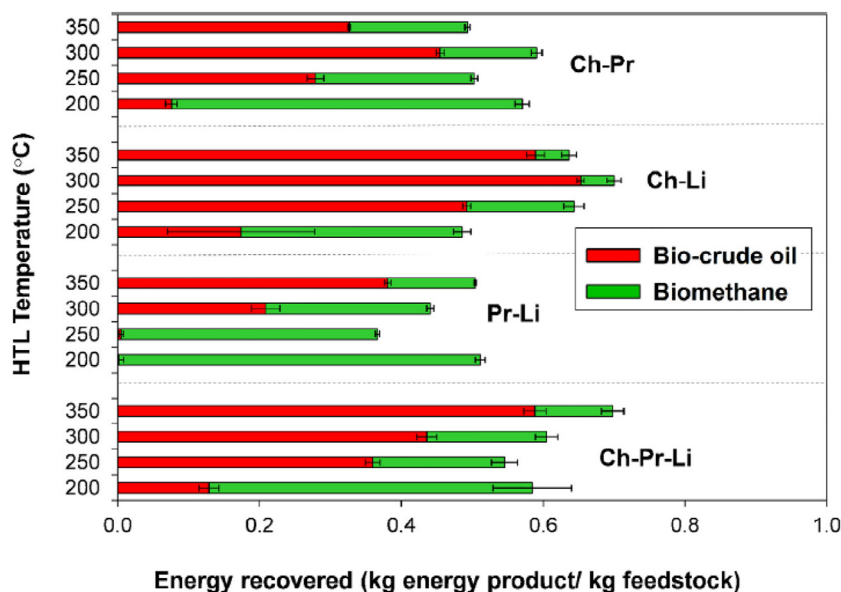


Fig. 13. Energy integration between oil and methane recoveries from different mixtures and different temperatures. Ch: carbohydrates, Pr: proteins, and Li: lipids. Reprinted from [230] with permission from Elsevier.

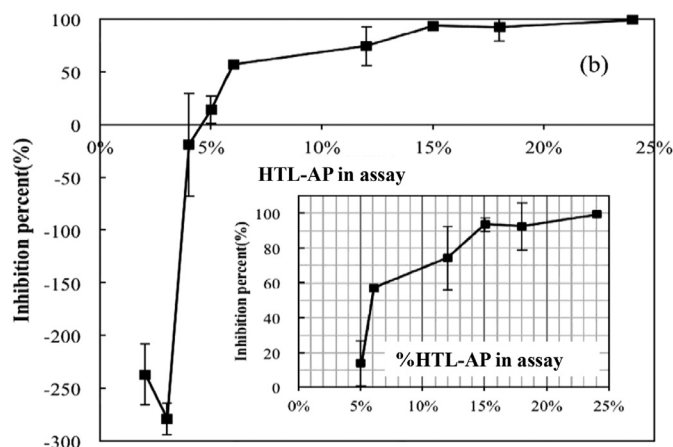


Fig. 14. Percent inhibition for HTL-AP at each inclusion ratio in anaerobic toxicity assays. The negative values indicated that the HTL-AP was considered non-toxic at such low inclusion ratios. Adapted from [156].

degradation (54.0–74.6%) of organic nitrogen and phenolic compounds was observed. The aromatic compounds and nitrogen organics were considered to be the primary inhibitors. The great stability caused by the resonance energy of the aromatic ring and the inertness of C-C and C-H bonds in these hydrocarbons make aromatic compounds recalcitrant to biodegradation. The incorporation of protein-rich feedstocks like algae and municipal wastes lead to the production of a HTL-AP with a high content of N-heterocyclic compounds [145,146]. The conversion of efficiency of N-heterocyclic compounds during anaerobic fermentation is relatively slow and thus less attractive for full-scale application [232]. This was further confirmed by Shanmugam et al., in which high levels of nitrogen organics in HTL-AP significantly decreased the methane yield [200]. Although pyrazine, pyridine, and pyrrolidinone can be anaerobically fermented, a heavy dilution and a long treating time need to be incorporated [139,156]. These inhibitors may also suppress acetogenesis [17,156,170,204], which is a rate limiting step during anaerobic digestion. As a result, a significant accumulation of propionate, butyrate, and valerate was observed. The inorganics (ammonia and chloride salts) in HTL-AP

were also reported as inhibitors to anaerobic digestion (Table 8). Ammonia concentrations in HTL-AP of algae have been reported to reach up to 16 g/L (Fig. 8), which is much higher than the reported ammonia inhibition concentration (2.8–11.0 g/L) [233]. Fernandez et al. reported a significant inhibition towards methane production from algae HTL-AP due to the accumulation of chloride in the reactor [139]. Cd, Cr, Cu, Ni, Zn, and Pb found in HTL-AP can also inhibit methane production [234]. Notably, synergistic effects of multi inhibitors in HTL-AP, in other words, the enhanced toxicity effect of one inhibitor in the presence of small amounts of another inhibitor, were reported. For example, Ni has been proven to be synergistic in Ni-Cu, Ni-Mo-Co, and Ni-Hg systems [234]. Similar synergistic relationships were also reported between phenol and nitrogen organics (pyridine) in which pyridine degradation would be inhibited when the phenol concentration was higher than 400 mg/L [235]. Pham et al. reported that although all 9 nitrogen organic compounds in the *Spirulina* HTL-AP were not cytotoxic to mammalian cells at their detected concentration, a mixture of them expressed a synergistic cytotoxicity effect [182]. Hence, a proper strategy that removes inhibitors one-by-one should be proposed to avoid such synergistic effects. For example, Yang et al. reported that the complete conversion of phenols significantly improved biodegradability of HTL-AP by 33%; however, only a limited conversion (21.7%) of N-heterocyclic compounds was observed [129].

The formation of inhibitors during the HTL process is also highly dependent on the feedstock. The highest reported methane yield (314 mL/g COD) resulted from HTL-AP generated from lignocellulose biomass [22,161]. HTL-AP from lignocellulose biomass mainly consisted of organic acids and sugars converted from cellulose and hemicellulose which can be easily converted by anaerobic microbes. In contrast, the HTL-AP from sludge, algae, and livestock manure showed a lower methane yield (14–313 mL/g COD) (Table 8). Posmanik et al. further confirmed the relationship between the HTL feedstock selection and methane production by using model compounds. This study concluded that the HTL of protein-rich biomass produced heavy nitrogenous polymers and non-polar nitrogenous compounds, such as pyridine and pyrazine, resulting in a reduced biodegradability of HTL-AP [230]. The operational conditions of HTL were also reported to contribute to the methane production potential for the anaerobic digestion of

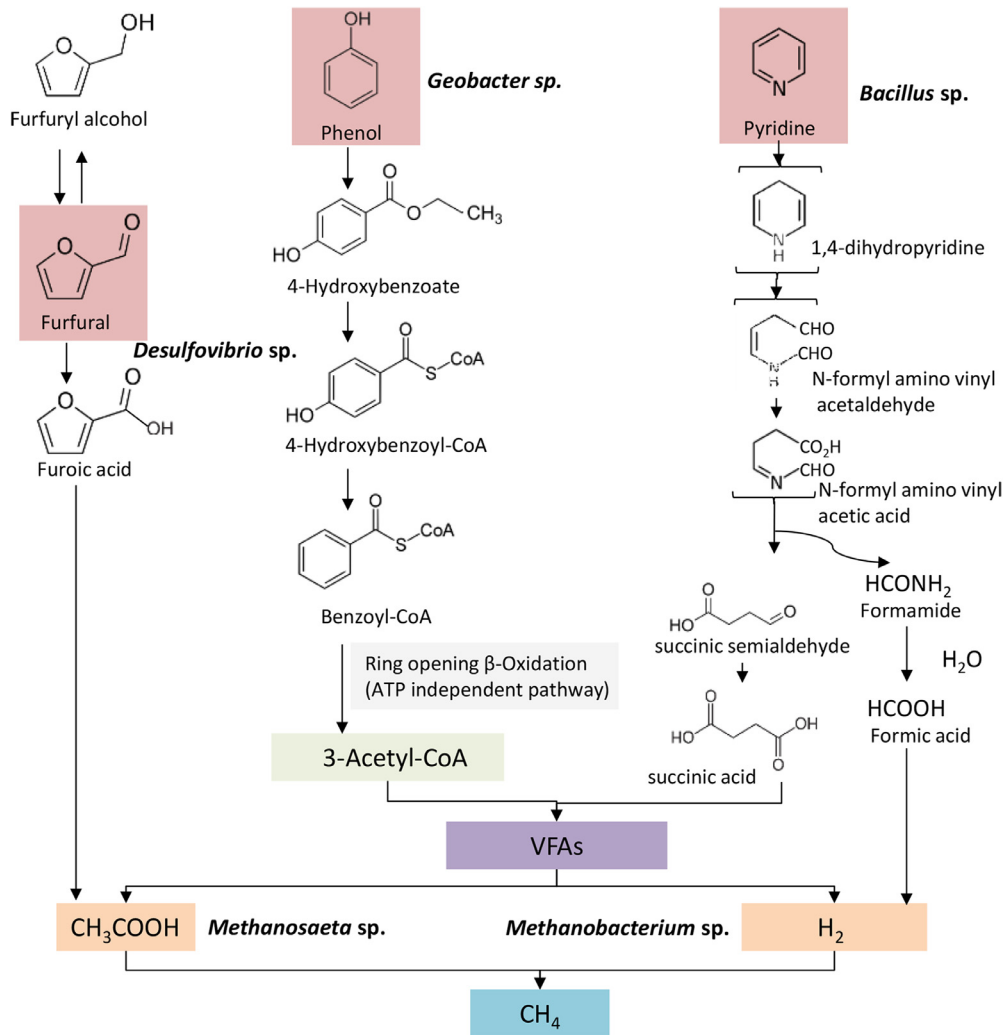


Fig. 15. Metabolism pathway and involved microorganisms for the anaerobic metabolism of dominant fermentation inhibitors (furfural, phenol, and pyridine) during anaerobic digestion of HTL-AP. Reprinted from [170] with permission from Elsevier.

HTL-AP. Tommaso et al. reported that increasing the HTL temperature from 260 to 320°C significantly benefited the production of methane [17]. Further, Chen et al. confirmed that both temperature and retention time of HTL affected the anaerobic biodegradability of rice straw HTL-AP. These two factors were reported to change the distribution of inhibitors (furans, phenols, etc.) and easily biodegradable organics (sugars and volatile fatty acids) [22]. However, contradictory findings have also been reported which stated that an increased hydrothermal temperature and residence time negatively impacted methane yields of HTL-AP, stemming from the production of recalcitrant compounds production, including humic acid, melanoidins, nitrogen heterocyclics, and phenols [164].

To enhance anaerobic digestion of HTL-AP, various treatment methods have been investigated (Table 8). Pretreatment and addition of activated carbon have been used to adsorb the organic inhibitors, including phenol derivatives, furans, and nitrogen containing compounds. Activated carbon addition was reported to improve the methane yield (13–298%), shorten the lag-phase, and allow anaerobic digestion to occur at a high concentration. Zeolite addition and struvite recovery were also applied to remove ammonia to circumvent inhibition during anaerobic digestion of the HTL-AP derived from algae. An increased methane yield (5–117%) and shortened lag-phase was observed in these studies. Partial oxidation including ozone treatment and H_2O_2 oxidation has also been

proven to effectively increase the methane yield and organics conversion, but an increase of the lag-phase was also observed which suggested that potential recalcitrant compounds may be produced as secondary by-products. Co-digestion with an easily biodegradable feedstock to dilute the inhibitors has been utilized as another strategy. Si et al. previously added glucose during the anaerobic digestion of HTL-AP [161]. Fernandez et al. found that a methane yield of 244–313 mL/g COD was achieved using 20–40% (vol.%) of HTL-AP mixed with manure [139]. Microbes have been shown to play a critical role in methane production when using HTL-AP as a feedstock. Currently, there is limited information regarding the function of microbes during the anaerobic digestion of HTL-AP. Only a few studies have investigated the microbe structures during anaerobic digestion of HTL-AP generated from lignocellulosic biomass [21,22,157,170]. Bio-augmentation is a method which involves the addition of microbe cultures to accelerate the rate of degradation of recalcitrant compounds. Using bio-augmentation to engineer the microbial communities could be another method to improve the methane production. For example, acetogenesis was considered as the rate-limiting step during anaerobic digestion of HTL-AP (Table 8), and bio-augmentation of acetogens could be a meaningful manner to address this kinetic issue. Directed evolution with long-term operation is another promising approach. Attributed to the enrichment of detoxification bacteria *Anaerolineaceae*, *Burkholderiaceae*, *Peptococcaceae* and also syntrophic

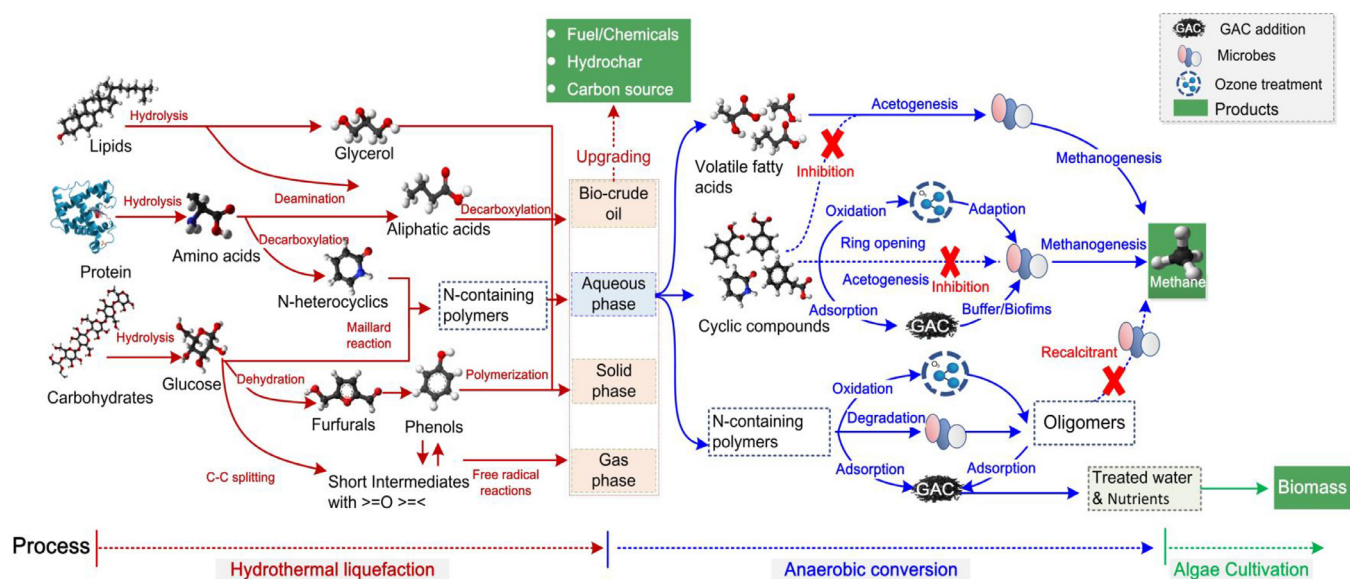


Fig. 16. Biorefinery roadmap of waste biomass through combined HTL and enhanced anaerobic fermentation. Reprinted with permission from Si et al., 2019 [21].

acetogens after two batches of experiments, a shortened lag-phase and an enhancement of the conversion of acids during anaerobic digestion of HTL-AP was achieved [21]. Application of high-rate anaerobic reactors could improve treatment efficiency due to the increased concentration of microbes and an increase in the solid retention time. Si et al. investigated the anaerobic digestion of cornstalk HTL-AP in high rate reactors, and the detoxification bacteria families such as *Geobacter* sp., *Desulfovibriosp.*, *Pseudomonas* sp., and *Bacillus* sp. were reported to increase in concentration in response to the feed shift from synthetic wastewater to HTL-AP [170].

It has been reported that over 40% of the organics remain in the HTL-AP after anaerobic digestion (Table 8). Thus, better understanding of the fate of organics within HTL-AP during anaerobic digestion would be helpful to evaluate the influence of anaerobic digestion on the environment. Chen et al. discovered that high molecular weight organics (MW >1000) in HTL-AP were difficult to convert via anaerobic digestion [157]. Si et al. elucidated the reaction pathways of the recalcitrant organics during anaerobic digestion by analyzing macro- and micro-molecules (Fig. 16) [21]. Although organic acids are easily converted to methane, acetogenesis would be inhibited with the increase of cyclic compounds. Anaerobic digestion has been previously reported to reduce the molecular size of nitrogen-containing macro-molecules in HTL-AP; however, subsequent minimization of these compounds was found to be cumbersome [21]. These high molecular weight organics were believed to be the polymers (or oligomers) of HTL intermediates and the toxicity of these nitrogen-containing compounds need to be further characterized. Luckily, the produced recalcitrant compounds can be adsorbed by GAC and a 93.3–96.8% organics removal has been reported [21]. However, it is difficult to biologically regenerate the GAC after being used as an adsorption agent. Thus, the development of biochar from cheap sources (e.g. biowaste) to replace costly commercial GAC is recommended. Combining this method with other treatment approaches (aerobic) would also be an effective treatment approach. This strategy has been proven during the conversion of dyes, which demonstrated that the nitrogen organics were effectively transformed using a sequential anaerobic and aerobic system [236]. However, this technique needs further evaluation since aerobic systems are expensive and energetically costly. In general, recent studies have indicated that anaerobic digestion is a promising and mature

technology to convert most organics in the HTL-AP, and the produced methane could be recycled back into the HTL paradigm for heating the HTL reactor. Although dilution of HTL-AP is required for anaerobic conversion, it is much less than the dilution required for algae cultivation. In particular, anaerobic digestion (with GAC addition) could be conducted while only utilizing 2-times diluted HTL-AP.

4.3.2. Two-stage fermentation for hydrogen and methane production

HTL-AP containing sugars [167] and glycerol [26,144,148] could be the ideal feedstock for hydrogen production [237]. In addition, HTL could be considered as a sterilization process due to the high reaction temperature employed during thermochemical conversion. This feature set offers the benefit of controlling biohydrogen production, since high reaction temperatures prevents the growth of hydrogen-consuming microbes in the feedstock. The products after biohydrogen production, mainly consisting of organic acids and alcohols, could then be the feedstock for subsequent methane production. Establishing a two-stage fermentation system for both hydrogen and methane production could realize this goal. This is important because the produced gas, a mixture of hydrogen and methane (hythane), is respected as a clean and efficient vehicle fuel [238].

Compared with conventional anaerobic digestion (one-stage fermentation), two-stage fermentation leads to an increased theoretical energy recovery (by 10–12%) [237]. More importantly, two-stage fermentation has demonstrated a strengthened biochemical process when handling complicated substrates. During two-stage fermentation, first, hydrogen production (first stage) plays a role as a buffer and detoxification agent for the methane production process. Liu et al. reported that furfural and 5-HMF in thermally treated cornstalk (below 1 g/L) were almost completely degraded during biohydrogen production, which suggested that hydrogen fermentation could be a detoxification step [239]. The toxic compounds principally obstructed the activities of the sensitive obligate hydrogen-producing acetogens and methanogenic portions of the digester population [234]. The acidogens (for hydrogen production) are also believed to be more resistant to heavy metal toxicity than methanogens [234]. However, one study pointed out that furanic (5-HMF and furfural) and phenolic compounds were found to be stronger inhibitors of microbial activity for hydrogen fermentation than the full anaerobic digestion process [240]. Second,

hydrogen fermentation was reported to have a positive effect on subsequent biomethane production. Methane production in the two-stage system led to enhanced acetogenesis and an enriched acetate-utilizing microbial community [241]. The detoxification of hydrogen fermentation and the strengthened methane production in two-stage fermentation was also verified when compared to conventional anaerobic digestion using HTL-AP derived from cornstalk as a substrate [161]. However, hydrogen production was fully stopped with an increase in the concentration of HTL-AP. This could be attributed to the metabolic shift from hydrogen-producing pathways (e.g. acetate and butyrate) to non-hydrogen-producing pathways (e.g. lactate, ethanol and propionate) caused by toxic compounds in HTL-AP [240]. A recent study proved that a hydrogen yield of 29.3 mL/g COD and a methane yield of 254.3 mL/g COD could be achieved from HTL-AP using two-stage fermentation, and further techno-economic and sensitivity analysis supported the feasibility of this approach [242]. However, most current studies incorporating two-stage fermentation still only operate at the bench scale. This is due to the fact that there are still some unsolved challenges for upscaling the hydrogen system, including maintaining the stability of the biohydrogen reactor and further controlling and integrating the two-stage fermentation system [243].

4.4 Bioelectrochemical systems
Compared with conventional biological conversion technologies, bioelectrochemical processes including electrochemical oxidation and electrochemical reduction are also effective strategies for the conversion of recalcitrant compounds to electricity or gas [244]. Bioelectrochemical systems, including microbial fuel cells (MFC) and microbial electrolysis cells (MEC), depend on the positive (MFC) or negative (MEC) difference of electricity generated and the Gibbs free energy change of the corresponding reaction.

4.4.1. Microbial fuel cell (MFC)

Phenols, furan derivatives, and N-heterocyclic compounds, which were proven to be the predominant toxic and recalcitrant compounds in HTL-AP, have been extensively investigated in bioelectrochemical systems [245–247]. In particular, N-heterocyclic compounds were efficiently converted in bioelectrochemical systems, whereas only a limited conversion of these compounds was observed during anaerobic digestion and algae cultivation. Zhang et al. reported a 95% removal of pyridine in a graphite-packed MFC within 24 h of operation, and the efficiency reported in this study was much higher than reported using anaerobic and aerobic conditions (Fig. 17) [246]. Further research confirmed the possibility of electricity production with pyridine, quinolone, and indole using two-compartment MFC reactors, and the maximum degradation efficiency of these substrates and COD removal amounted up to

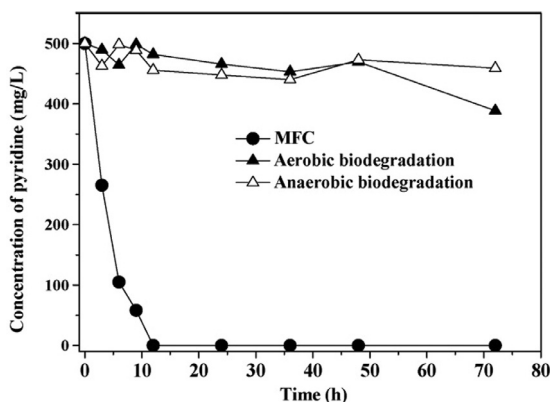


Fig. 17. Biodegradation of pyridine in three systems: MFC, anaerobic biodegradation, and aerobic biodegradation systems. Reprinted from [246] with permission from Elsevier.

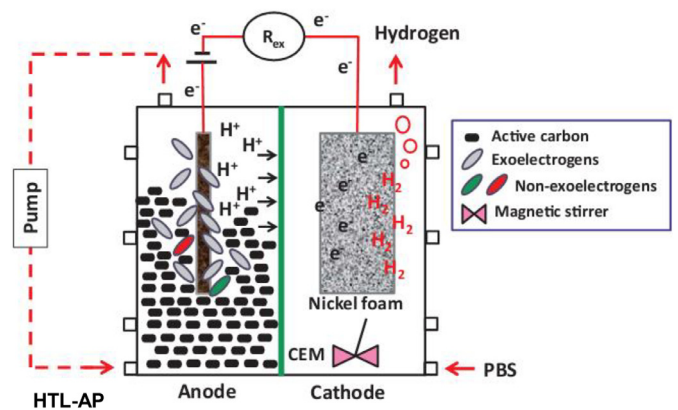


Fig. 18. Schematic diagram of the MEC system used for conversion of swine manure HTL-AP. Adapted from [23].

90% and 88%, respectively [248]. For HTL-AP, Liu et al. reported a carbon nanotubes-constructed fixed-bed MFC for continuous electricity generation using HTL-AP derived from cornstalk, and a maximum power density of 680 mW/m³ and a COD removal of over 80% was achieved [24].

4.4.2. Microbial electrolysis cell (MEC)

MEC is another bioelectrochemical system which could efficiently convert recalcitrant compounds in HTL-AP and produce hydrogen without the limitation of thermodynamics. Shen et al. found that MEC could convert furfural, HMF, dimethyl phthalate, and diethyl phthalate in the HTL-AP generated from cornstalk, and a hydrogen production rate of 3.92 mL/L/d could be achieved [203]. A two-chamber fixed-bed MEC was also used for converting swine manure HTL-AP (Fig. 18), and excellent performance in organics removal (>90%) and hydrogen production rate (168.01 ± 7.01 mL/L/d) was achieved [23].

Although bioelectrochemical systems demonstrated feasibility for converting HTL-AP to electricity or hydrogen, bioelectrochemical systems presently need intensive efforts devoted to realizing full-scale commercial application in terms of cost-effectiveness and sustainability. In particular the following areas of study within this field need to be emphasized: 1) Decrease the startup time, which usually takes a couple of weeks to months, 2) develop new, durable, and low-cost electrode materials with a high activity, conductivity, and stability, 3) improve the efficiency at process scale-up, and 4) develop a low-cost proton exchange membrane [249–251].

5. Hydrothermal conversion of HTL-AP

5.1. Hydrothermal gasification

One of the thermochemical methods of valorizing HTL-AP by transformation organic matter into a usable product is through hydrothermal gasification. Generally speaking, hydrothermal gasification utilizes high reaction temperatures (>400°C) and a variety of homogenous and heterogeneous catalysts to chemically reform the bonds in organic compounds into basic chemical constituents: hydrogen, methane, carbon dioxide, and carbon monoxide [26]. Gasification is of particular interest because it has the potential to convert over 99% of the organic compounds in the HTL-AP into gaseous products [252]. There are three primary factors that influence the efficacy of gasification as a treatment methodology for HTL-AP valorization: reaction temperature, retention time, and selection of catalyst.

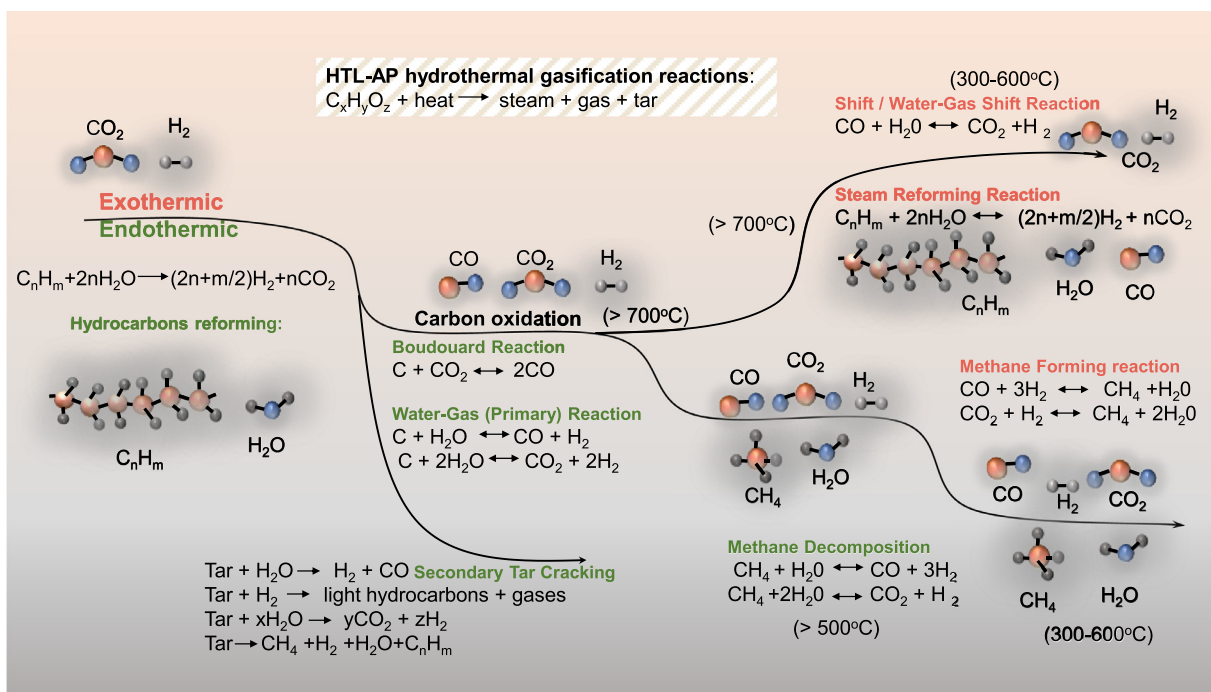


Fig. 19. Reaction diagram of the reactions present within the gasification of HTL-AP.

5.1.1. Primary factors influencing gasification

The desired reaction products conducted through the gasification of HTL-AP can be heavily influenced by the selection of the temperature, retention time, and the catalyst. Therefore, the reaction conditions should be selected and catered to the desired reaction products.

Temperature is generally the main influencing parameter that has a direct influence on the production of the reaction product. One study found that increasing the reaction temperature of gasification from 250°C to 520°C increased the hydrogen gas fraction from approximately 21% to 38%, but then the hydrogen fraction decreased to 32% as the temperature increased to 700°C [253]. This trend was also corroborated by a previous study gasifying HTL-AP from human feces which found that as the severity of the reaction increased from 2.6 to 3.1, the mass of hydrogen increased from 1.8 mg to 9.5 mg but then decreased thereafter to 7.0 mg as the reaction severity further increased to 10.8 [26]. This trend has also been corroborated by multiple previous studies utilizing cellulose and polyvinyl alcohol wastewater as a gasification feedstock [254–256]. This trend is attributed to not only the methanation reaction, which produces methane at the expense of hydrogen and carbon monoxide at higher reaction temperatures, but also the water-gas shift reaction, since both reactions are enhanced at higher reaction temperatures and pressures. Therefore, the competitive nature of these two reactions between 300–600°C can influence the selectivity of gaseous products in this temperature range. Temperature is also an influencing factor because it alters the molecular and chemical structure of water. This in turn leads to poor intra- and inter-molecular hydrogen bonding characteristics of water which results in the decomposition of biomass [257]. Previous studies have demonstrated that above the critical point of water, reactions are shifted from covalent/ionic to radical, therefore the free radical mechanism is heavily favored which augments the production of gaseous products. This in turn also favors the water-gas shift reaction, leading to higher accumulations of hydrogen and carbon dioxide through the consumption of the produced carbon monoxide [258,259]. Steam reforming can also occur at higher temperatures due to its mildly endothermic characteristics, which preferentially

favors the production of hydrogen and carbon dioxide [260]. The general reaction pathway of macromolecules to gasification products is illustrated in Fig. 19.

Retention time also has an evident impact on the gas composition. A previous study noted that a longer retention time favors the production of methane and carbon monoxide by promoting thermal cracking reactions at elevated temperatures. Further, higher methane concentrations can also result from the secondary methanation reactions which only occur at sufficiently long retention times [261–263]. A longer retention time not only influences the gas composition, it also has an evident impact on the overall gas production. Gong et al. demonstrated that as the retention time increased from 30 min to 90 min that the gas yield increased from 1.2 mol/kg to 1.7 mol/kg [258]. Another study confirmed this observation using lactose as a gasification feedstock which represented a model compound of dairy industry effluent and demonstrated that the gas yield increased from 1.19 L/g at 30 s to 1.69 g/L at 60 s and 1.68 L/g at 75 s [262]. Thus, a minimum retention time is needed to ensure the complete conversion of organic material into gaseous products; however, the gas production tends to plateau at longer retention times. If hydrogen is the target objective for gas production, research has shown that residence time will increase the hydrogen yield up to a maximum, but after reaching an apex no significant improvement will be observed [264]. Therefore, there is a tradeoff when it comes to maximizing gas production and maximizing the content of hydrogen. Further, as the retention time increases, the water-gas shift reaction, reforming reactions, and the methanation reactions are all enhanced. Thus, at higher temperatures and retention times, the gaseous reaction products often react amongst themselves to produce methane through hydrogenation and methanation reactions [259]. A previous study also noted that the feed concentration could drastically impact the gas composition. Utilizing glycerol as a gasification feedstock, one study found that as the feed concentration increased from 5 wt.% to 40 wt.% the content of hydrogen decreased from 6.5 mol/g glycerol to 2 mol/g glycerol while the methane content increased from 0.3 mol/g glycerol to 1.0 mol/g glycerol [261]. Since water is a primary factor influencing the

hydrogen content, a greater feed concentration would lead to the production of less hydrogen gas while shifting the product distribution to the production of carbon monoxide, carbon dioxide, and methane.

Incorporation of catalysts in the gasification process can preferentially shift the production of specific gaseous products and aid in the conversion of organic matter. Catalysts can be classified into two broad categories: heterogeneous catalysts and homogeneous catalysts. Homogeneous catalysts are able to dissolve in the reaction medium, whereas heterogeneous catalysts are in a phase different than that of the reaction medium. Typical homogeneous catalysts employed in gasification processes involve alkali derivatives, including NaOH [26,265–268], K_2CO_3 [269–272], $KHCO_3$ [269], and KOH [256,267,269]. Previous studies indicated that homogeneous catalysts tend to substantially increase the concentration of hydrogen and carbon monoxide in the gaseous product by improving the water-gas shift reaction [263] (Fig. 19). However, one drawback of the use of homogeneous catalysts includes the low gasification efficiency associated with these catalysts. This is due to the fact that catalysts such as NaOH and KOH can form formate and carbonate complexes which precipitate out of solution consuming carbon dioxide and carbon monoxide. Thus, carbon is first gasified to carbon dioxide and then captured in the aqueous phase [269,273]. Moreover, besides leading to a poor gasification efficiency, homogeneous catalysts pose large problems for recovery because they are difficult to isolate from the feedstock after the reaction, therefore homogeneous catalysts are not viewed as a catalyst but instead as a reactant additive [273].

Contrary to homogeneous catalysts, heterogeneous catalysts can be separated from the reaction medium. However, due to their incorporation of transition metals, heterogeneous catalysts tend to incur a substantial monetary cost and can be deactivated due to poisoning, coking, and sintering by organic material or heteroatoms during gasification processes. Thus, catalyst recovery and reactivation techniques need to be investigated and employed in order to reduce the additional pecuniary costs associated with the inclusion of heterogeneous catalysts. Among all the transition metal catalysts selected for gasification purposes, Ru and Ni tend to be the most commonly employed. Ni derivatives primarily include NiO [274,275] and Ni_2AlO_3 [258,276,277]. Previous studies have indicated that Ni catalysts promote the tar cracking and steam reforming reactions [276]. Furthermore, a previous study demonstrated that Ni catalysts tend to favor the methanation reactions, leading to reduced hydrogen yields and increased methane yields. This is due to the fact that Ni is an effective hydrogenation catalyst which decomposes organic matter into carbon monoxide and hydrogen which is subsequently transformed into methane via the methanation reactions at higher feed concentrations [258]. Further, Ni catalysts have a strong ability to cleave C-C bonds, which result in a high carbon conversion efficiency (CCE) and aid in the production of methane [269]. Another study also reported that Ni-derivatives have the ability to cleave O-H, C-C, and C-H bonds, thereby decomposing recalcitrant tar derivatives as well as long-chain oxygenates into gases [278]. However, the specific mechanism and trends for the production of gaseous products via Ni catalysts has been met with contention. One previous study conversely found that Ni catalyzed the steam-reforming reaction resulting in the promotion of hydrogen at the expense of methane [279,280]. Thus, the feedstock and reaction conditions need to be considered when employing Ni-derivatives to cater the production of gaseous product to the desired gas. Ni catalysts can produce an appreciable amount of methane when a high feed concentration and mild reaction conditions are employed (300–600°C) for gasification, but hydrogen production is favored when more severe reaction conditions are utilized (>700°C) and when lower feed concentrations are utilized [273]. This is due to the fact that the water-gas

shift reaction and steam reforming reactions are heavily favored at high temperatures whereas methanation reactions are favored at milder temperatures.

Ni catalysts are not only favorable due to their high selectivity of gaseous products, they also enhance the efficiency of the conversion of organic matter into gaseous products. Further, the efficiency of Ni-derivatives is also aided in part by catalyst supports. In particular, one study found that the CCE and the hydrogen conversion efficiency (HCE) all improved for catalytic versus non-catalytic gasification; however, the CCE and HCE amongst the Ni/zeolites exhibited the trend: Ni/HY > Ni/MCM-41 > Ni/H β > Ni/HZSM-5 > Ni/SAPO, where the zeolite supports were HY (Na₂O = 0.5%, 0.8%), MCM-41 (Si = 100%, 50%), H β -type, HZSM-5 (SiO₂/Al₂O₃ = 50:1, 150:1, 170:1), SAPO-11 [260]. Further, all catalyst supports enhanced the hydrogen production between 1.7–2.3 times versus non-catalytic runs. However, a large problem with Ni catalysts regardless of catalyst support inclusion is the susceptibility of Ni-derivatives to deactivation. Previous studies have noted that the main cause of deactivation can come from the adherence of amorphous carbon to the surface of the catalyst which in turn causes insufficient contact between Ni and the biomass [281]. Moreover, supercritical conditions (>374°C, >22 MPa) have also been shown to readily deactivate the catalyst due to harsh sintering. Thus, Ni has not been shown to be a reliable or effective catalyst after recycling [282].

Ruthenium is another commonly employed transition metal which can catalyze the decomposition of organic matter in wastewater. One study found that RuCl₃ and Ru/C showed the highest selectivity of all catalysts for selectively isolating hydrogen, leading to a 44.5% and 38.5 (mol.%) composition of hydrogen for the supercritical water gasification of a kenaf plant [283]. A previous study also noted the ability for Ru to enhance hydrogen production at low temperatures but enhance methane production at high temperatures. In particular, it was found that the hydrogen concentration in the output gas decreased when employing Ru/Al₂O₃ ranging from 5.9–12.0% at 400°C and then ranging from 4.6–11.0% at 600°C [284]. Another study verified this trend by demonstrating that Ni/Al₂O₃ produced a greater amount of hydrogen when compared to RuTiO₂ [285]. Both Ni and Ru catalysts have been shown to promote the water-gas shift reaction, but Ru has been shown to enhance the methanation reaction to a greater extent than Ni [286]. Ru/Al₂O₃ has also been shown to be able to convert recalcitrant compounds currently present in numerous wastewater studies. Specifically, Ru/Al₂O₃ was able to promote the hydrogenation of phenol to cyclohexanol, subsequently leading to a ring-opening to hexanone or hexenol. Thus, ruthenium catalysts have the potential to catalytically convert some of the recalcitrant compounds in wastewater, thereby inhibiting the formation of tar and char from gasification and also leading to a cleaner water which can be discharged or utilized for algae growth [286].

5.1.2. Gasification as a valorization technique

Recently, gasification has been utilized in a few preceding studies to valorize the organic matter trapped within HTL-AP and various wastewater feedstocks while concomitantly treating the wastewater for environmental disposal, algae growth, etc. Table 9 summarizes the recent progress on studies utilizing gasification as a means of producing hydrogen, methane, and reducing the COD and TOC of HTL-AP and various wastewater effluents.

Due to the low content of total solids in wastewater, many studies have set out to produce a rich hydrogen gas by employing non-catalytic gasification as a treatment technique. Duan et al. demonstrated that the composition of the HTL-AP greatly impacted the resulting gas distribution. In particular, under 600°C with a 120 minute retention time the highest hydrogen content was 1.08 mmol hydrogen/g HTL-AP [77]. However, hydrogen yields

Table 9
Summary of hydrothermal gasification utilizing HTL-AP and wastewater as a feedstock.

Feedstock	Reaction Conditions ^a	H ₂ (vol.%)	CH ₄ (vol.%)	CCE (%)	TOC _r /COD _r (%)	Ref.
Oily wastewater	500–700°C, 180–220 s, KOH	35–79	9–36	8–98	20–98	[253]
HTL-AP derived from <i>Chlorella</i> sp.	350°C, 0–60 min, NaOH	38–71	20–23	52–99	56–99	[25]
HTL-AP derived from Human feces	400–600°C, 30 min, Raney Ni/Ru	28–57	4–20	24–58	31–71	[26]
HTL-AP derived from sewage sludge	600–750°C, WHSV ~2.5 h ⁻¹ , Al ₂ O ₃ /AC	45–55	12–16	90–92	NA	[290]
Black Liquor Wastewater	550°C, 0.2 min, No	34–44	15–16	15–77	NA	[291]
Pyrocatechol	300–900°C, 0.25–4 min, KOH	15–47	9–10	NA	NA	[292]
Polyvinyl alcohol-contaminated wastewater	200–600°C, 20–60s, KOH	30–49	20–37	12–96	20–96	[256]
Humic acid (sewage sludge model compound)	325–600°C, 30–90 min, K ₂ CO ₃ , Ni/Al ₂ O ₃ , FeCl ₂ , ZnCl ₂	15–45	8–11	NA	NA	[258]
HTL-AP derived from wastewater-algal biomass	350°C, 4 h, Ru/C	53	24	NA	98	[134]
HTL-AP derived from <i>Auxenochlorella pyrenoidosa</i>	600°C, 2 h	28	37	84	84	[77]
HTL-AP derived from <i>Arthrospira platensis</i>	600°C, 2 h	30	32	69	71	[77]
HTL-AP derived from <i>Schizochytrium limacinum</i>	600°C, 2 h	28	35	94	94	[77]
HTL-AP derived from <i>Nannochloropsis oceanica</i>	600°C, 2 h	34	36	91	93	[77]
HTL-AP derived from <i>Ulva prolifera</i>	600°C, 2 h	28	36	54	57	[77]
HTL-AP derived from <i>Saccharina japonica</i>	600°C, 2 h	31	29	91	92	[77]
HTL-AP derived from <i>Zostera marina</i>	600°C, 2 h	34	27	62	67	[77]
HTL-AP derived from <i>Gracilaria eucheumoides harvey</i>	600°C, 2 h	21	26	64	87	[77]

^a Temperature, retention time, catalyst type; NA: not available

ranged from 21–58% in this study even though the reaction conditions were the same for different types of HTL-AP (Table 9). This could be attributed to the presence of inorganic salts in the HTL-AP, as these compounds may act as a gasification catalyst leading to a higher gasification efficiency and a greater production of hydrogen. Therefore, the TOC and chemical composition of the HTL-AP heavily impact not only the production of gas but also the quality of the gaseous products. Cherad et al. also confirmed that a lower organic loading rate is beneficial for hydrogen production. This study found that when the loading rate decreased from 11,000 mg/L to 2,000 mg/L the hydrogen yield increased significantly from 3.31 to 23.65 mol/kg for the gasification of HTL-AP derived from *Chlorella vulgaris* [25]. Therefore, an appreciable amount of hydrogen gas can be produced with a low concentration of organics in the HTL-AP; however, at higher concentrations of organics the incorporation of catalysts should be considered. Multiple previous studies have noted that a low retention time is beneficial for hydrogen production. One study found that at 500°C and a retention time of 35 s a 33.9% and 21.1% mole fraction of hydrogen from winery wastewater and wine grape slurry could be produced, respectively. This study found that minimizing the retention time is essential to maximizing hydrogen production in order to suppress the methanation reaction which is favored at a high retention time [287]. A previous study also noted that a high temperature and low retention time is beneficial for hydrogen production. Specifically, gasification of olive mill wastewater generated the greatest hydrogen output (10.8 vol.%) at a temperature of 600°C and a retention time of 30 s and decreased (9.7 vol.%) when the retention time was increased to 120 s [288].

Although the incorporation of a catalyst incurs additional costs, it also drastically increases the hydrogen yield. One study found that both homogeneous and heterogeneous catalysts could increase the hydrogen yield substantially. For the HTL-AP derived from human feces, incorporation of a heterogeneous catalyst (Raney Ni) and a homogeneous catalyst (NaOH) increased the hydrogen yield by nearly 30% and 34%, respectively, compared to non-catalytic gasification conducted at 400°C and a 60 min retention time [26]. However, these catalysts only resulted in slight reductions in the COD and ammonia concentration of HTL-AP, leading to tradeoffs between hydrogen production and organic matter conversion. Another study concluded that utilizing 1.5 M NaOH was able to increase the hydrogen yield from the HTL-AP generated from *Chlorella* by 91% compared to non-catalytic runs [25]. It should also be noted that one study found that the incorporation of a KOH catalyst increased the HCE substantially up to 108% [253] (Table 9).

Since water acts as the reactant medium, water is also able to be converted into hydrogen, leading to HCE values greater than 100%. Finally, one study conducting alkaline gasification using NaOH found that up to 30 vol.% of hydrogen could be produced from pharmaceutical wastewater at a temperature as low as 450°C [289].

For non-catalytic gasification, temperatures below 600°C have been shown to produce an appreciable amount of methane. A previous study gasifying olive mill wastewater noted that methane production increased from 1.1 mol.% at 400°C up to 34.8 mol.% at 550°C and then decreased substantially to 23.3% when the temperature increased to 600°C [288]. This could be attributed to the declined strength of methanation reactions at higher temperatures and the shift to H₂/CO production at the expense of methane. A previous study analyzed HTL-AP model compounds (acetic acid, 1-butanol, acetol, and glucose) on the overall methane yield of non-catalytic gasification. In this study, it was concluded that gasification of acetic acid and 1-butanol led to the highest methane content of 44.3 vol.% and 51.0 vol.%, respectively, at a temperature of 700°C and a flow rate of 1.0 L/h [293]. This study also concluded that the feedstock concentration was positively correlated with the methane content. As the feedstock content in this study increased from 2.5 wt.% to 10 wt.% the methane yield increased from 30.1% to 41.7% while the hydrogen concentration decreased from 7.0 to 5.1 vol.%. The feedstock composition may significantly impact non-catalytic gasification results for the production of methane. Duan et al. noted that gasification results varied significantly for the gasification of microalgae and macroalgae HTL-AP feedstocks. In particular, this study noted that under constant reaction conditions HTL-AP derived from macroalgae consistently produced a greater amount of methane than hydrogen whereas for microalgae the trend was not always consistent [77]. This could have been attributed to the greater amount of organic matter in the HTL-AP of microalgae (~23.9 g/L) than macroalgae (9.8 g/L).

Previous studies have shown that incorporating a catalyst can considerably enhance the gas methane content. A previous study confirmed that a relatively pure form of methane could be produced at lower reaction conditions, noting that a 70.4% content of methane could be produced upon gasifying acetone (another model compound of HTL-AP) with a feedstock conversion of 99% at a temperature of 350°C, a retention time of 20 min, and the inclusion of a Ru/Al₂O₃ catalyst [294]. This study also concluded that feedstock concentration and methane concentration were positively correlated. One study demonstrated that catalysts have a much more pronounced impact at lower temperatures and

retention times. Interestingly, this study found that the selectivity of the Ru/Al₂O₃ catalyst to produce methane tended to exhibit an inverse parabolic correlation with retention time, first increasing in methane content from 24.9% to 35.6% from 30 s to 90 s and then decreasing to 22.6% at 150 s [288]. It could be hypothesized that Ru only selectively favors methane formation at lower retention times and at higher retention times the oxidation of methane to carbon monoxide is favored. Another benefit of Ru derivatives is that they have shown much promise as a promoter for methane gas at low temperatures for the gasification of wastewater. A previous study noted that both Ru/AC and Ru/Al₂O₃ produced large amounts of methane (~32 vol.%) at low reaction severities (400°C, 60 min) for the HTL-AP derived from human feces [26]. Catalysts also bolster the CCE in gasification processes. Studies have demonstrated large ranges (8–98%) in the CCE values of non-catalytic and catalytic gasification (Table 9) [253]. One theory has been proposed regarding CCE values. One study found that the higher the content of nitrogen and oxygen-derivatives in the HTL-AP, the lower the CCE. Further, the greater the total acid number and the amide contents were in the HTL-AP, the higher the CCE [77].

In addition to producing valuable gaseous products, gasification is also an effective means of cleaning HTL-AP and other wastewaters, which leads to large reduction in the COD (COD_r) and TOC (TOC_r) values. A previous study found that at a temperature of 450°C a COD_r of only 10–15% was observed for gasification of cutting oil and vinasses, two types of organic wastewaters generated from the alcohol production process by wine distillation [295]. However, the inclusion of oxygen and a 0.02% KOH catalyst was able to substantially increase the COD_r of vinasses by over 30% at 450°C. Further, at an elevated temperature of 550°C with a retention time of only 7.5s, a COD_r of 87.2% was observed with the inclusion of oxygen and a KOH catalyst. Kipcak et al. also documented that higher reaction severities (up to 600°C and 150 s) led to the highest TOC_r of more than 90% for the non-catalytic gasification of olive mill wastewater [288]. However, this same research group demonstrated that the incorporation of a Ru/Al₂O₃ could lead to a modest TOC_r value of 79.3% at low reaction severities (400°C, 30 s) yet a substantial TOC_r of 97.7% at a high reaction severity (600°C, 150 s) for the catalytic gasification of olive mill wastewater [284]. It should be noted that the Ni/Al₂O₃ catalyst in this study did not lead to a high TOC_r (9.34%) at a low reaction severity (400°C, 30s). Thus, to maximize organic matter conversion while maintaining low reaction conditions, an appropriate catalyst must be selected to balance efficiency and costs. The catalyst concentration has also been shown to increase TOC_r, but only to a limited extent. Gasification of oily wastewater demonstrated that at 600°C with a 200 s retention time, TOC_r increased from 64% to 69% when the catalyst was increased from 0 mg/L KOH to 100 mg/L, but the subsequent addition of 50 mg/L of catalyst only raised the TOC_r by about 4%, indicating a trend of diminishing returns [253]. The initial concentration of the input wastewater also has a pronounced impact on the TOC_r. Decreasing the organic loading of HTL-AP from 11,000 mg/L to 2,000 mg/L increased the TOC_r from 60.1% to 99.2% at a constant temperature and retention time. Further, inclusion of a 1.5M NaOH catalyst also impacted the TOC_r. As the organic loading for HTL-AP decreased from 11,000 mg/L to 2,000 mg/L with the inclusion of NaOH, the TOC_r increased from 82.2% to 99.8% [25].

Few studies have analyzed the incorporation of gasification of HTL-AP into the HTL paradigm in order to increase the overall energy recovery of the HTL process. Duan et al. demonstrated that 14.3–25.6% of the algal biomass energy from microalgae was distributed to the HTL-AP while that derived from macroalgae ranged from 6.0–41.1%. This study demonstrated that 54.8–75.1% of the energy derived from the microalgae HTL-AP and 18.3–49.3% of

the energy derived from macroalgae HTL-AP was transferred into the gaseous products after gasification [77]. Thus, the integration of HTL and gasification can thereby improve the energy recovery of the HTL process compared to just HTL alone. Watson et al. also demonstrated that an energy recovery of up to 70% could be achieved for the gasification of HTL-AP derived from human feces incorporating a Ni:Ru catalyst [26]. More studies need to be conducted which analyze the energy input needed in order to determine the effective energy recovery not only of the feedstock versus the output gas but also to analyze the total output energy versus the input energy needed to heat the water, the energy associated with operating gasification reactors, etc.

5.2. Recycling of HTL-AP

Although most studies perceive HTL-AP as an environmentally hazardous by-product that requires additional treatment, others studies depict HTL-AP as a valuable resource for enhancing thermochemical conversion outputs. In particular, previous studies have shown that HTL-AP can be recycled back into the HTL paradigm as a dilution agent which can influence the biocrude oil yield by altering the pH and introducing alkali salts to catalyze the formation of biocrude oil compounds. Furthermore, in comparison to other HTL-AP treatment methodologies, recycling holds promise because it is simple to incorporate, cost-effective, and relatively easy to scale-up. In addition, HTL requires the input of water, a commodity that may well see price hikes in the future; thus, recycling of the HTL-AP has significant economic implications that could curtail the operating costs of the HTL process.

Table 10 presents the recent studies recycling HTL-AP back into the HTL system. Multiple studies have reported that recycling HTL-AP has the potential to improve the biocrude oil yield. Biller et al. demonstrated that the biocrude oil yield increased by a maximum of 15.1% compared to utilizing fresh water after the HTL-AP was recycled six times. However, the biocrude oil yield showed no further increase after subsequent recycles [296]. Thus, recycling the HTL-AP phase continuously leads to diminished returns. In other words, recycling of HTL-AP initially causes sizeable increases in the biocrude yield and then this rate of increase diminishes with subsequent recycling cycles. Ramos-Tercero et al. also found a similar trend, noting that the biocrude oil yield increased from 14% to 42% after the HTL-AP was recycled six consecutive times [297]. One theory is that the acetic acid and alkali salts present within HTL-AP catalyze the production of biocrude oil [298]. Zhu et al. also proposed this theory, noting that one explanation for the increase in biocrude oil yield through HTL-AP recycling could be explained by the HTL-AP accumulating short chain acids (acetic acid and lactic acid) which could enhance the decomposition of carbohydrates. This was also confirmed by a previous study which noted that the decomposition rate of model carbohydrate compounds was enhanced by the addition of organic acids during HTL experiments [75]. Furthermore, Chen et al. observed that HTL-AP recirculation reduced the content of organic acids in comparison to the original HTL-AP. This was attributed to the short chain acids reacting with intermediate HTL products [299].

Another theory is that the pH of the HTL-AP has a significant impact on the biocrude oil productivity. Grigoras et al. noted that the presence of alkali constituents (NaOH, K₂CO₃, etc.) could retard the formation of char and augment the production of biocrude oil via retro-aldol reactions. Subsequent studies have confirmed this point and noted that alkali components may also promote condensation reactions and inhibit re-polymerization reactions [300–302]. Jensen et al. confirmed this result and added that the water-soluble organics stabilized intermediate products during thermochemical treatment thereby impeding the formation of char [41]. In particular, one study showed that at 400°C and a retention time of 1 hour,

Table 10

Recent studies conducted recycling HTL-AP for the improvement of biocrude oil yield and biocrude oil properties.

Feedstock	Conditions ^a	Total Recycles	Biocrude Oil Yield (wt.%)	Oil C Content (wt.%)	HHV (MJ/kg)	Energy Recovery (%)	Oil O Content (wt.%)	Oil N Content (wt.%)	Aqueous & Gas Yield (wt.%)	TOC (g/L)	TN (g/L)	Ref.
<i>C. glomerata</i>	350°C, 15 min	3	17–25	NA	NA	NA	NA	NA	60–68	NA	NA	[306]
<i>G. gracilis</i>	350°C, 15 min	3	16–25	NA	NA	NA	NA	NA	61–70	NA	NA	[306]
<i>C. vulgaris</i>	275°C, 50 min	4	29–39	66–70	31–34	41–54	13–18	8	45–53	NA	NA	[307]
Blackcurrant pomace	310°C, 10 min	6	26–31	68–73	32–35	48–58	14–19	3	NA	12–35	NA	[305]
Dried distillers grains	350°C, 15 min	3	36–45	73–79	NA	NA	4–11	6–9	31–43 ^a	30–75	NA	[308]
Dried distillers grains	350°C, 20 min	10	35–49	68–75	31–36	68–102	9–18	5–8	NA	25–92	6–26	[296]
Barley straw	300°C, 15 min	4	35–38	68–69	28–29	NA	23–24	1	42–57	NA	NA	[75]
<i>C. vulgaris</i>	220°C, 30 min	3	13–21	69–70	33–34	20–33	17–18	3–6	NA	NA	NA	[297]
<i>C. vulgaris</i>	240°C, 30 min	3	13–30	70–72	33–35	24–50	15	5–7	NA	NA	NA	[297]
<i>C. vulgaris</i>	265°C, 30 min	3	17–35	70–72	33–34	31–58	13–14	6–7	NA	NA	NA	[297]
Algal biomass and sawdust	250°C, 60 min	2	9–11	64–70	31–35	NA	15–22	5	52–58	NA	NA	[304]
Aspen wood	400°C, 9 kg/h	4	NA	NA	NA	NA	NA	NA	NA	54–136	NA	[40]
Pine and Spruce (50:50)	390–410°C, 20–22 kg/h	6	NA	81	39	NA	10	1,124 ^b	NA	NA	NA	[41]
Birch	390–410°C, 20–22 kg/h	5	NA	81	38	NA	10	2,365 ^b	NA	NA	NA	[42]
<i>S. platensis</i>	340°C, 50 min	3	30–40	62–65	25–30	NA	NA	NA	54–63	NA	NA	[299]
α -Cellulose	300°C, 30 min	1	7–12	58–62	23–26	10–20	27–36	0–4	NA	NA	NA	[299]

^a Temperature and retention time; NA: not available.^b Value presented in parts per million (ppm).

a mixture of phenol, water, and lignin could inhibit the formation of char [53]. This could be attributed to the presence of phenols in the recycled HTL-AP which could inhibit re-polymerization reactions thereby reducing char accumulation [303].

In addition to impacting the biocrude oil productivity, HTL-AP recycling has been shown to influence the quality of the biocrude oil. Hu et al. discovered that recycling HTL-AP to adjust the feedstock solid content led to a higher C content (70.3%) in the biocrude oil compared to using a water mixture (64.2%) and a drastically lower O content (15.5%) compared to a water mixture (22.1%) [304]. Biller et al. echoed this trend, finding that the content of O in the biocrude oil decreased by 9.6% when recycling HTL-AP nine times compared to utilizing pure water as a dilution agent. However, the N content in the biocrude oil increased from 5.0% to 8.3% as the HTL-AP was recycled up to nine times [296]. Previous studies have also noted that recycling the HTL-AP could result in the N content of the resulting biocrude oil increasing by a range of 0.1–3% [296,297,304,305]. Therefore, recycling of the HTL-AP leads to a tradeoff in quality, as recycling tends to decrease the O content yet increase the N content of the biocrude oil. Despite the tradeoffs in biocrude oil quality, HTL-AP recycling has been shown to increase the energy recovery of the HTL process. Deniel et al. reported that recycling HTL-AP five times increased the energy recovery in the biocrude oil from 48% to 57% compared to utilizing pure water [305]. Previous studies have also noticed energy recovery increases ranging from 13% to 28% when incorporating HTL-AP recycling into the HTL process [296,297,304]. This is primarily explained by small increases in the HHV and biocrude oil yield accompanied with a high content of C present within the biocrude oil when the HTL-AP is recycled.

Recycling also impacts the composition of HTL-AP. Deniel et al. found that recycling of the HTL-AP caused the TOC to increase from 12 g/L to a maximum of 35 g/L [305]. Biller et al. also reported that the TOC in the HTL-AP increased significantly from 25 g/L to 92 g/L after recycling the HTL-AP derived from the HTL of distillers dried grains a total of eight times [296]. Further, Biller et al. noted that the TN content also increased from 6 g/L to 25 g/L after the recycling of HTL-AP was conducted nine times [296]. A previous study stated this trend could be attributed to the accumulation of acidic compounds derived from carbohydrate derivatives (acetic acid) and ammonia which is commonly produced during

the breakdown of proteins [298]. The large concentration of acetic acid and ammonia in the recycled HTL-AP could lead to another avenue of revenue in the HTL process, since these concentrated compounds could be separated and subsequently sold on the market.

Recirculation of HTL-AP has the potential to significantly improve the economics and footprint of continuous biocrude oil production processes. Previous studies involving a proprietary HydrofactionTM technology, a combination of supercritical HTL and subsequent hydrotreating for the production of drop-in biofuel, discovered that recirculation of the HTL-AP and biocrude oil could improve the feed characteristics, energy balance, oil quality, and the oil yield [42]. Specifically, LCA of HydrofactionTM technology demonstrated that this technology could reduce GHG emissions by between 77–108% (based on different LCA scenarios) in comparison to petroleum-derived products [42]. Fig. 20 provides an illustrative depiction of the HydrofactionTM technology process flow diagram.

In addition to a reduced carbon footprint, recycling HTL-AP led to more a pumpable feedstock slurry during continuous processing. Moreover, recirculation of HTL-AP could mitigate or eliminate operating costs associated with water treatment technology frequently plaguing biocrude oil production processes [41]. However, one contingency to being able to recirculate HTL-AP is that recalcitrant compounds need to be isolated and removed to avoid excessive buildup. For example, Jensen et al. demonstrated that 5–15% of the HTL-AP needs to be first extracted before recirculation in order to prevent the accumulation of chloride, which increased by over 100% after six recirculation cycles when woody biomass was utilized as the feedstock [41]. Thus, recirculation of HTL-AP cannot completely eliminate the need for wastewater treatment technology (anaerobic digestion, gasification, etc.), but it can drastically reduce the volume of wastewater that needs to be treated.

In conclusion, recycling of HTL-AP demonstrates great promise as a means of enhancing biocrude oil properties, reducing the carbon footprint of biocrude oil production processes, and enhancing energy efficiency. Recirculation of HTL-AP has been demonstrated to be an effective technique at a large scale, and it is currently one of the closest methods to reaching full-scale commercialization of all other HTL-AP treatment methodologies.

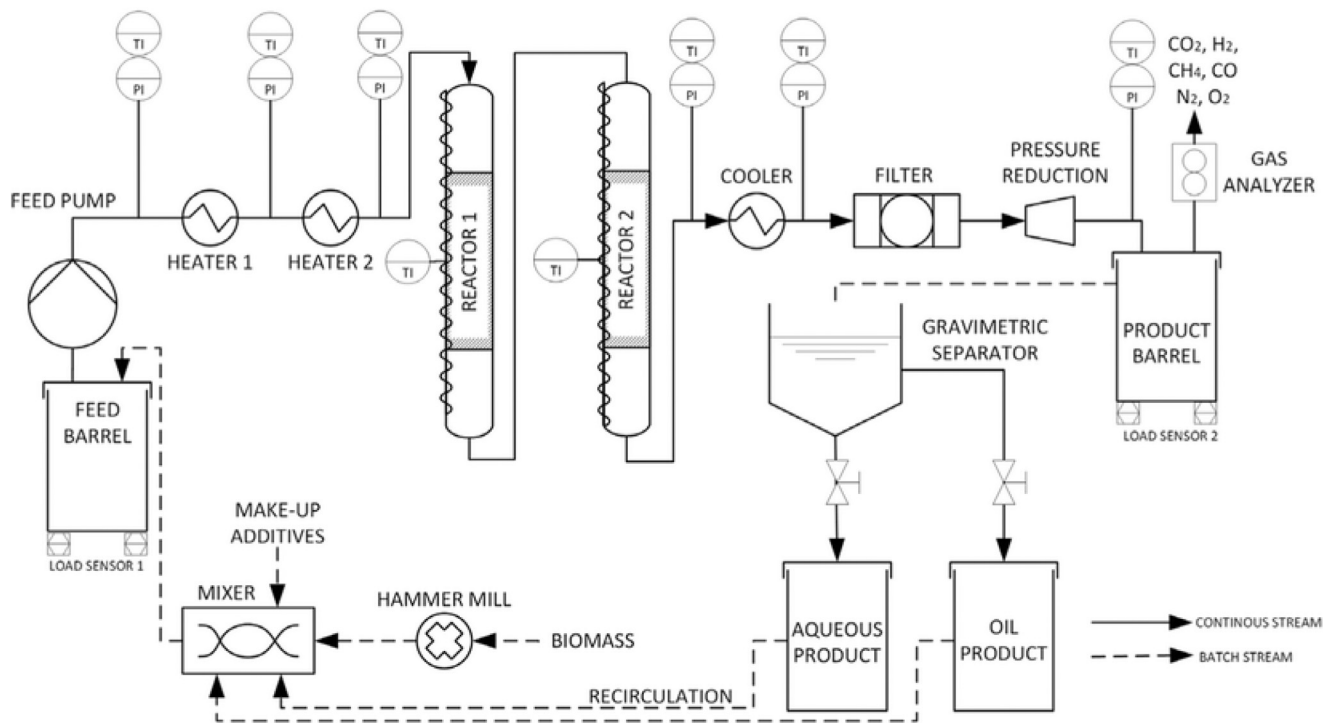


Fig. 20. Illustrative depiction of Hydrofaction™ technology, a thermochemical conversion technology which incorporates HTL-AP recirculation for drop-in biocrude production. Reprinted from [41] with permission from Springer.

6. Integrated pathways of energy and nutrients recovery for the valorization of HTL-AP

Simultaneously meeting the objectives of organics removal, nutrients recycling, value-added chemicals separation, and biofuel production can be achieved by combining multiple valorization approaches. Although each individual technique suffers from distinct drawbacks, the pitfalls of each method can be mitigated when combined into one interconnected approach, thereby limiting the individual shortcomings when only one approach is incorporated. For example, HTL-AP recycling and chemical separation valorization approaches show promise, but each needs to be further evaluated because information regarding upscale feasibility and process economics is scarce. In comparison, gasification and anaerobic digestion have demonstrated promising commercial potential towards converting HTL-AP. Specifically, commercial infrastructure of gasification technology has already been reported [273], and anaerobic digestion is a robust and efficient technology for the production of energy that has been optimized for many decades [309]. Both anaerobic fermentation and gasification can convert the organics within HTL-AP; however, subsequent nutrient recovery of the residue has not yet been achieved. Hence, an integrated system should be built up, which interlaces anaerobic fermentation/hydrothermal gasification with algae cultivation. In this manner, the inorganic nitrogen and phosphorous left over by these biological and thermochemical processes can be used as a substrate for algae cultivation, and the produced biomass could subsequently be fed back into the HTL paradigm for continued biofuels production.

6.1. Integration of anaerobic digestion and algae cultivation

Algae cultivation using the effluent from anaerobic digestion of different feedstock has been extensively studied [310–312]. These

previous studies indicated the feasibility of successfully integrating anaerobic fermentation and algae cultivation. Chen et al. confirmed that the integration of anaerobic fermentation with algae cultivation leads to benefits including reducing the process carbon footprint and managing the production cost for conventional algae cultivation [313]. In addition, toxic compounds such as phenols, furanic compounds, and N-heterocycles in HTL-AP could be partly or completely degraded during anaerobic fermentation, and this detoxification process could benefit the efficacy of algae cultivation. Yang et al. verified this hypothesis, noting that the biomass accumulation, biomass production rate, and the tolerance of HTL-AP were significantly improved after anaerobic fermentation [204].

A Sankey diagram is presented to evaluate the performance of mass, C, N and energy flows during the integration of HTL, intensified anaerobic fermentation, and algae cultivation (Fig. 21). First, the feedstock was converted to biocrude oil, solid phase, HTL-AP, and gaseous product via HTL (data based on chapter 2). The produced biocrude oil would then be further upgraded to transportation fuel through distillation combined with esterification according to a previous study [11]. The solid residue produced via upgrading could be applied as bitumen during subsequent processing [314]. HTL-AP was then converted to biogas via intensified anaerobic digestion with GAC addition according to Si et al. [21]. The polished liquid after anaerobic digestion of HTL-AP could then be further used as the medium for algae cultivation [204]. The solid product produced after HTL could be used as biochar for further application in other industries. Finally, the carbon dioxide in the HTL gaseous products and biogas could be used as a C source for algae cultivation [313].

The mass distribution showed that 30.5% of mass was transferred to algae biomass. This is because the carbon dioxide in both the gaseous product and biogas was used by algae as a C source, and most of the inorganic salts (N, P, K, etc.) were used as nutrients during algae growth. In comparison, only a limited amount of

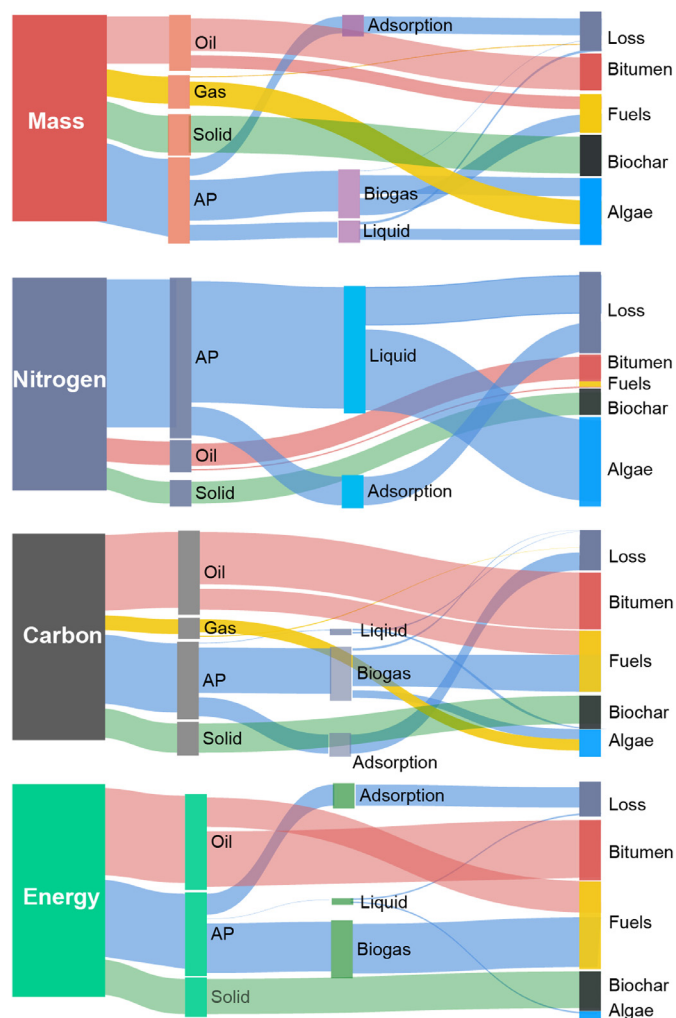


Fig. 21. Sankey diagram tracing the flows of mass, C, N, and energy by integrating HTL, intensified anaerobic digestion, and algae cultivation for HTL-AP valorization.

energy was transformed in the algae (0.6%), which predominantly came from the residue of organic acids in the liquid product of anaerobic digestion. Most of the energy (40.8%) was converted to transportation fuels which consisted of upgraded biocrude oil and methane which could be used as diesel blendstocks [11] and gas fuels in internal-combustion engines [315], respectively. It can be seen that the HTL-AP contributed a higher energy recovery through anaerobic fermentation than biocrude oil after upgrading. This is because only about 30% of the initial biocrude oil was upgraded to transportation fuels [11], and 43.8% of the energy was transferred to the biocrude oil during HTL. This trend also corresponded to the C distribution in the produced fuels, which was primarily derived from the anaerobic fermentation of HTL-AP. The N flow suggested that most of the N (40.7%) was transferred into biomass via algae cultivation. However, 34.7% of the N was lost from the liquid products after anaerobic fermentation. The lost N mainly consisted of nitrogen-containing polymers which cannot be effectively converted by anaerobic microbes, and this N loss may lead to increased environmental safety hazards. However, these recalcitrant nitrogen-containing organics can be adsorbed by activated carbon. Considering the potential commercial applications, activated carbon can be packed in a high rate reactor to act as a biofilm carrier and adsorbent. Post-treatment of the liquid products may also be an applicable pathway. For example, MEC could treat the effluents from anaerobic fermentation and

convert the compounds that were not efficiently treated, such as N-heterocyclic compounds. A similar integrated process has been applied to a process involving hydrogen gas production from cellulose by combining an anaerobic fermentation reactor and a MFC to produce power for MEC [316]. However, this integration has not been reported as a means to treat HTL-AP, so the feasibility of this methodology still needs to be further evaluated.

6.2. Integration of hydrothermal gasification and algae cultivation

The combination of HTL, hydrothermal gasification and algae cultivation was also proposed [222]. The water produced from gasification contains specific nutrients that are beneficial for algae cultivation [317–320]. Previous studies verified that almost all organics in HTL-AP were removed (57.1–98.2%) via hydrothermal gasification [77,134,317]. Li et al. found that 98.3% of N after gasification was in the form of inorganic nitrogen [134]. This suggested that a vast majority of organics in HTL-AP, including the inhibitors and nitrogen-containing organics, were converted through hydrothermal gasification. Hence, an improvement of algae cultivation using the liquid product from hydrothermal gasification could be expected.

The flows of mass, C, N, and energy by integrating HTL, hydrothermal gasification, and algae cultivation are shown in a Sankey diagram (Fig. 22). The feedstock was first converted to biocrude oil, solid phase, HTL-AP, and gaseous products via HTL (data based on chapter 2). The produced biocrude oil would be further upgraded to fuel [11], and the residue after upgrading could be applied as bitumen [314]. The HTL-AP was converted to syngas (hydrogen, methane, and carbon dioxide) via hydrothermal gasification as described based on preceding studies [77,134]. The liquid product after hydrothermal gasification could then be further used as the medium for algae cultivation. The gaseous product (mainly carbon dioxide) was used as a C source for algae cultivation, and the produced syngas from hydrothermal gasification was purified using algae in which carbon dioxide could be removed [313].

The results suggested that 39.8% of mass was transferred to the algae biomass. It should be clarified that 23.7% of C in the feedstock was transferred to algae which mainly served as the C source for photosynthesis. In addition, 43.8% of energy was converted to transportation fuels which consisted of liquid fuel and hythane. This value was slightly higher than that in the integration of anaerobic fermentation (40.8%). This could be attributed to the enhanced energy recovery from the feedstock in hydrothermal gasification compared with anaerobic fermentation. However, the extensive energy required for thermochemical conversion is not considered in this flow, so evaluation involving the energy required for heating, cooling, and reactor operation should also be considered in future studies. Of note, integration with gasification showed a different N flow pattern than that resulting from the integration with anaerobic digestion. Integration with hydrothermal gasification resulted in 62.9% of the N being fixed by algae and only 12.5% being discharged into the environment. This is due to the fact that nitrogen-containing organics were more effectively converted via hydrothermal gasification compared with anaerobic fermentation. The N in the liquid products produced after gasification existed in the form of ammonia, which is easier to be utilized by algae than the nitrogen-containing compounds in the liquid produced from anaerobic digestion. Thus, based on the above environmental implications and N recovery trends, the integration of HTL with hydrothermal gasification and algae cultivation demonstrated a greater prospect for process integration compared with anaerobic fermentation.

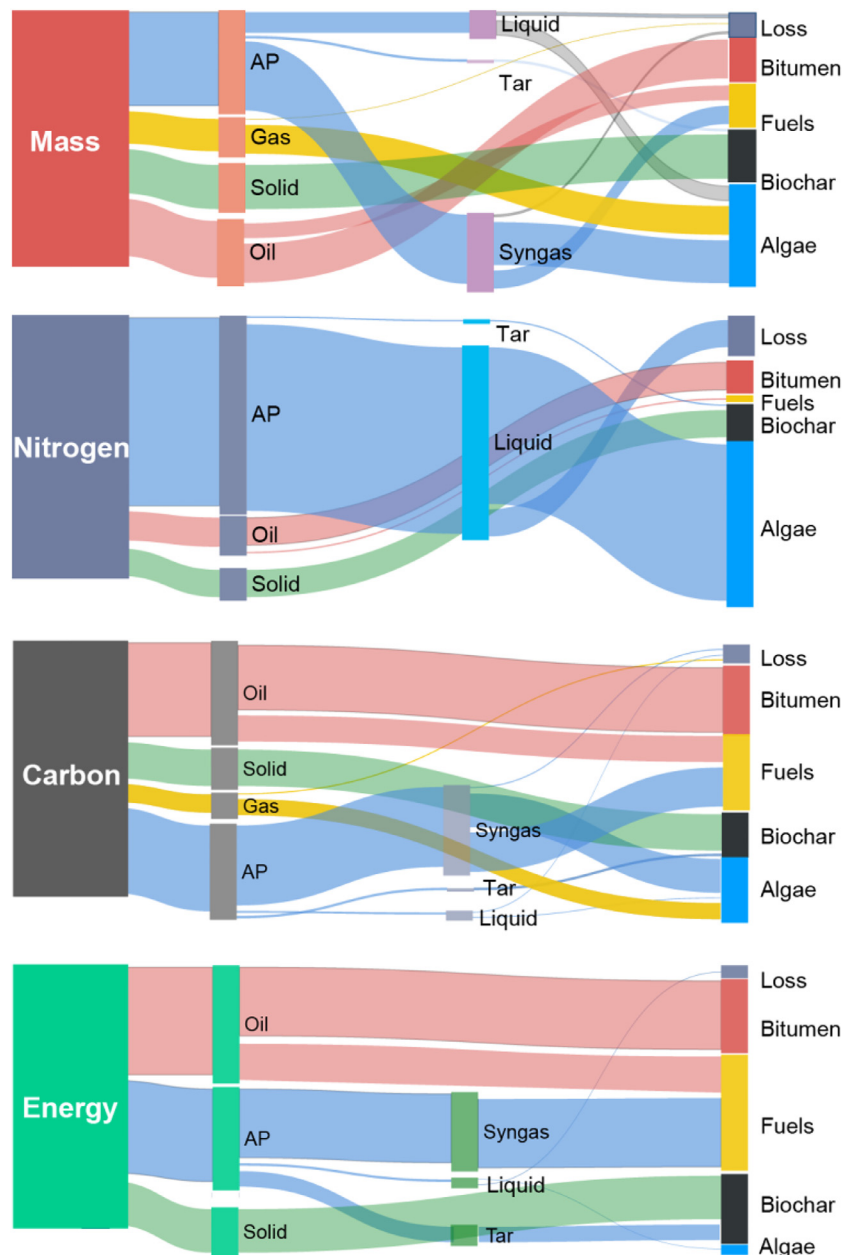


Fig. 22. Sankey diagram tracing the flows of mass of mass, C, N, and energy during the integration of HTL, intensified hydrothermal gasification, and algae cultivation for HTL-AP valorization.

7. Life cycle assessment (LCA) and techno-economic assessment (TEA)

In recent years, a myriad of analytical techniques have been incorporated to assess the commercial and industrial feasibility of selling biofuels produced via HTL of biomass. To analyze both the environmental and economic implications of this thermochemical process, LCA and TEA have been generally employed by researchers as tools to judge the potential of upscaling the HTL process to better meet the world's fuel needs. Few LCA studies have assessed the production of biocrude oil derived from feedstock other than algae, since algae-derived biocrude oil is a well-researched, mature, and holistic method to produce biocrude oil. Calculations and quantifications of the energy consumption and emissions present within HTL LCA studies can be separated into two distinct categories: feedstock production (algae growth, cultivation, and harvesting) and biocrude oil production (HTL processing, production of HTL-AP,

etc.) [321–323]. However, due to the fact that LCA involves the establishment of myriad assumptions regarding the process and due to the lack of standardization of these assumptions amongst researchers in this field, the results presented by LCA studies involve a high degree of uncertainty and the assessment of the net energy production and GHG emissions amongst different studies are difficult to compare [324].

Table 11 presents a comparison of HTL and other biomass-to-energy conversion technologies from an emissions and energy vantage point. It should be noted that HTL technology can augment its energy and LCA favorability by employing mild upgrading techniques, including distillation/esterification as opposed to traditional hydrotreating/hydrocracking [11]. Despite the reduced energy input associated with mild upgrading techniques, the current state of HTL technology still necessitates a 28% greater energy input than diesel production technology and a significantly larger input compared to traditional landfilling and incineration methods.

Table 11
Estimates of the energy demand, energy consumption ratio (ECR), and GHG emissions for different biomass-to-energy methods [11].

Process	Energy input (MJ kg ⁻¹ feedstock)	Energy recovery ratio	GHG (kg CO ₂ kg ⁻¹ product)	Product
Diesel	2.5	0.3	0.2	Fuel
Landfill	0.03–0.04	0	0.9–1.8	Methane
Incineration	0.02–0.03	2.3 × 10 ⁻⁴	2.0	Electricity
Anaerobic digestion	0.7	0.1–0.6	0.1	Methane
Lipid extraction	3.7(wet)-17(dry)	0.4(dry)-0.8(wet)	1.1(wet)-7.4(dry)	Biodiesel
HTL+hydrotreating	8.9	0.4	0.4	Diesel blendstock
HTL+distillation+ esterification	3.2	0.8	0.2	Diesel blendstock

However, HTL shows promise from an energy recovery and emissions perspective.

Specifically, HTL is optimistically able to lead to improved energy recovery ratio values compared with conventional diesel and anaerobic digestion technology depending on the type of upgrading technology utilized in the HTL process. HTL also offers distinct environmental advantages. Although HTL combined with mild upgrading was found to have similar emissions to conventional diesel and anaerobic digestion technology, HTL leads to significantly less emissions than landfilling (4.5–9x), incineration (10x), and lipid extraction (5.5–37x). Despite the promising LCA results of HTL and upgrading technology, further enhancements can be made by valorizing HTL-AP.

Juneja et al. investigated the environmental impact of upgrading biocrude oil derived from the HTL of wastewater algae and discovered that the total GHG emissions were 110 g CO₂-eq MJ⁻¹, which was less than that produced by conventional diesel when both catalytic gasification of HTL-AP and biocrude oil hydrotreating were involved [325]. Meanwhile, Ponnusamy et al. reported that 1 kg algae biodiesel produced from subcritical water fixed 0.6 kg of carbon dioxide with an energy demand of 28.23 MJ when anaerobic digestion of HTL-AP and a trans-esterification process were used in the system [326]. However, Karne et al. compared the hydrothermal conversion pathway for microalgae to biodiesel with other pathways and did not include the scenario involving the cultivation of algae, HTL-AP valorization, etc. Thus, LCA performance reports concerned with biocrude oil production are significantly influenced by the process settings and assumed performance parameters of HTL, making the comparison between different studies tedious and unreasonable. Further, since the upstream and downstream factors of HTL processing are critical for the LCA output parameters, standardization is needed to avoid large discrepancies in data outputs among different research groups [46,327].

In recent years, researchers have tried to shift their focus to utilizing other feedstock besides algae for LCA studies. Of particular interest, researchers have started to investigate utilizing wet biowaste as a HTL feedstock, mainly emphasizing sludge, manure, etc. However, the process parameters can become more complicated compared to algae when this type of feedstock is considered. Regarding the valorization of HTL-AP, previous LCA studies have focused on a couple of different approaches and valorization methods, including catalytic gasification, anaerobic digestion, recycling of HTL-AP back into the HTL paradigm, and recovery of nutrients in HTL-AP via algae cultivation [242,328]. Previous studies have indicated that the recovery, recycling, or valorization of the HTL-AP has a critical impact on the overall LCA analysis results. Fig. 23 illustrates that the GHG emissions for biowaste to biofuel studies incorporating different HTL-AP valorization pathways reported by previous LCA studies.

Techno-economic assessment (TEA) modeling has also emerged as an important tool to understand the commercial viability of biowaste-to-biofuel thermochemical techniques. Engineering related processing models with simulation software packages are generally used to estimate the investment and final selling prices

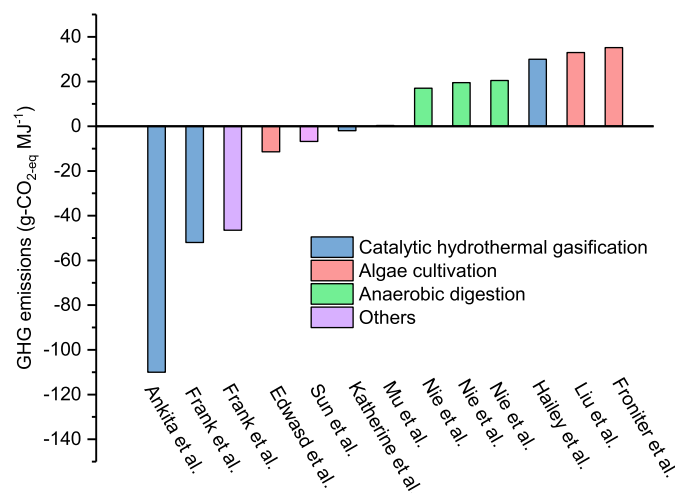


Fig. 23. GHG emissions for biowaste-to-biofuel technologies using HTL integrated with different HTL-AP valorization pathways. Results are based on previous studies involving different HTL-AP valorization methods: anaerobic digestion, algae cultivation, catalytic hydrothermal gasification, and others [322,325,328–336].

of the final product [324,337]. Previous studies have determined that not only is the biocrude oil yield an instrumental factor influencing the optimism or pessimism of TEA studies, but the capacity for sustainable production also plays a critical role in this analysis [325]. Another two influential parameters include reducing the burden of the HTL process on the environment and maximizing long-term profitability.

For biocrude oil derived from the HTL of algae, TEA studies have successfully analyzed the economic outputs as a function of the operating costs, energy efficiency, taxes, etc. Jiang et al. estimated the techno-economic uncertainty of algal-derived biocrude oil by HTL, and the results demonstrated that the minimum biocrude selling price was nearly 5–16 USD/GGE with an uncertainty level of about 12%. The large uncertainty in the overall cost was associated with the feedstock cost. In Jiang et al.'s study, it was assumed that the price of acquiring algae for HTL reactions could range from 400 USD/daf ton to 1800 USD/daf ton. This study came to the conclusion that large uncertainties are incurred in TEA analysis by both feedstock costs and biocrude oil selectivity [338]. Katherine et al. evaluated the metrics of economic viability of microalgae HTL using TEA, and a minimum selling price of 10.4 USD/GGE was reported. Katherine et al. also determined that the ash content of the algae, biomass costs, and reaction yields were regarded as the most important factors influencing the profitability of biocrude oil production according to the sensitivity analysis [333]. When a fermentation step was used to pretreat the feedstock for HTL for the fractionation of fusel alcohols, the minimum selling price of biocrude oil increased to 12.8 USD/GGE due to the high operational costs and additional taxes. Panneerselvam et al. evaluated the TEA analysis of biofuels from HTL of algae from wastewater with a hydroprocessing process, and the minimum selling price of the hydrocarbon

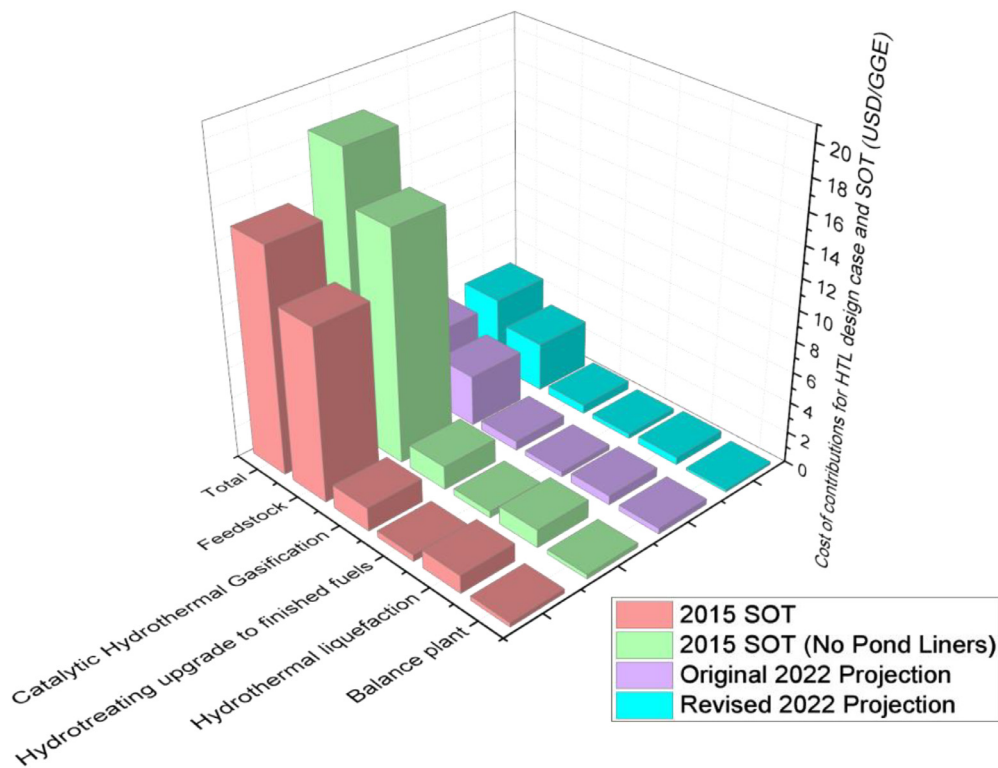


Fig. 24. Summary of cost contributions for HTL design case and state of technology (SOT). Data collected from U.S. DOE [20].

fuels was estimated to be 4.3 USD/GGE, while the algae cultivation and utility cost accounted for the majority of the capital cost and operating cost, respectively [339].

However, in Nie et al.'s study, the minimum selling price based on the production of biocrude oil derived from forest residues was reported to be 63–80% higher than that of conventional petroleum fuels. The yield of biocrude oil was the most influential parameter in determining the selling price. However, another influential factor was the transportation cost of the biocrude oil. This study determined that minimizing the transportation distance between the location of biocrude oil production and the post-production facility (biorefinery, oil pre-processing refinery, etc.) was able to reduce the operating costs; however, costs associated with transportation did not have a large impact on the overall capital investment of this expenditure [340]. Thus, maximizing the biocrude oil yield is essential to enhancing the economic performance of the HTL process. In summary, the properties of the feedstock, the employed pretreatment processes, the transportation of the biocrude oil, the capital investment, and the potential for technological advancement all have the potential to influence the TEA outputs and thereby result in large price fluctuations amongst different studies. Therefore, controlling the critical contributors to these economic uncertainties needs to be made a point of emphasis in future studies to ensure the comparability of different studies.

Fig. 24 depicts the current cost contributions calculated by the U.S. DOE for the 2015 state of HTL technology (SOT) and projected cost breakdown for the projected 2022 case of HTL technology [20]. In order to meet the projected fuel selling price of \$4.5/GGE and eventually meet the DOE's \$3.0/GGE performance goal, significant reductions in costs need to be achieved. The feedstock and processing of the HTL-AP currently account for the largest fractions of the selling price, accounting for 67–81% and 10–12% of the selling price, respectively. However, the feedstock contribution could be reduced by utilizing waste feedstock (food waste, animal excreta, etc.) as opposed to cultivated algae. Distillation

combined with esterification has also recently been proposed as an alternative biocrude oil upgrading approach which has shown promise as an inexpensive method which could further reduce the overall selling price by reducing costs associated with biocrude oil upgrading [11]. However, the DOE proposes that the fundamental issue that needs to be addressed is ensuring that the highest value is obtained from the HTL-AP in order to meet the current projected goals [20].

The selection of a HTL-AP pretreatment process has been shown to incur sizeable pecuniary costs which influence the outlook of TEA studies. Juneja et al. previously analyzed the techno-economic variables associated with the production of renewable diesel produced from algae cultivated in wastewater while concomitantly employing catalytic hydrothermal gasification as a treatment step for HTL-AP. The results demonstrated that the valorization of HTL-AP had a significant impact on the renewable diesel selling price. Sensitivity analysis from this study demonstrated that the total volume of HTL-AP produced had a significant influence on the selling price of renewable diesel [325]. Moreover, the price of renewable diesel was calculated to be 6.62 USD/GGE, and the cultivation of algae and harvesting accounted for the largest fraction of the total cost (~56%) [325]. Zhu et al. compared the economic analysis of HTL of algae coupled with three different HTL-AP valorization methods: direct recycling to the algae farm, catalytic hydrothermal gasification, and anaerobic digestion. The results suggested that anaerobic digestion and catalytic hydrothermal gasification increased the minimum fuel selling price by about 11% and 2.9% over direct recycling of HTL-AP. The main contributing factor was the high capital and operating costs. Meanwhile, anaerobic digestion for HTL-AP showed advantages over catalytic hydrothermal gasification due to the lower energy requirements and costs [341]. Si et al. previously compared benchmark commercial applications of two different HTL-AP valorization methodologies, two-stage fermentation and catalytic hydrothermal gasification, to produce biohythane [242]. The results suggested that two-stage

fermentation with conventional reactors resulted in a higher net energy return than that of catalytic hydrothermal gasification. Additionally, two-stage fermentation coupled with high-rate reactors with a high density of robust microbes resulted in a lower minimum selling price (−0.71 to 2.59 USD/GGE) than conventional fossil fuels, which demonstrates the necessity of employing HTL-AP valorization methods into the HTL paradigm to ensure financial feasibility.

Currently, research focusing on the different valorization techniques of HTL-AP in order to enhance TEA outlooks is sparse. Since the production of HTL-AP in HTL processes has been shown to negatively impact the economic prospects of HTL, future studies need to place an emphasis on HTL-AP valorization in order to assure commercial success of this thermochemical technology. However, HTL-AP also needs to be further investigated due to its environmental implications. With the increasing stringency of environmental standards, it is very important to incorporate HTL-AP into economic analysis in order to assure that the HTL process meets environmental regulations for subsequent discharge and/or reuse. In addition, the scale and industrialization potential of HTL has still yet to be elucidated. There is currently a dearth of pilot scale studies focusing on the challenges involving large-scale production of biocrude oil, and the sustainable ways of converting waste to energy and dealing with the HTL-AP is still not well understood. In conclusion, taking consideration of the way in which HTL-AP is handled, treated, and recovered

would greatly benefit the economic prospects of HTL, and more research is needed to better understand the specific avenues of HTL-AP valorization which offer the most optimistic TEA and LCA outlooks.

8. Challenges and prospects

8.1. Technologies for valorizing HTL-AP

The conversion approaches for HTL-AP detailed in this review are compared and contrasted in Fig. 25. Further, a summary regarding the technical prospects of these techniques is detailed below:

- Separation and concentration of value-added chemicals from HTL-AP remains a promising direction to improve the commercial potential of HTL. Further optimization of this pathway shows potential as a way to develop mass market sales channels for solvents, acids, and other chemical precursors. However, current research only focuses on HTL-AP with a simplistic chemical composition (e.g. extracting the phenols and organic acids from HTL-AP derived from lignocellulose). HTL-AP with a complex composition has not yet been investigated. In addition, separation and concentration also faces economic and sustainability barriers. The combination of separation and biological conversion techniques may be a promising future direction,

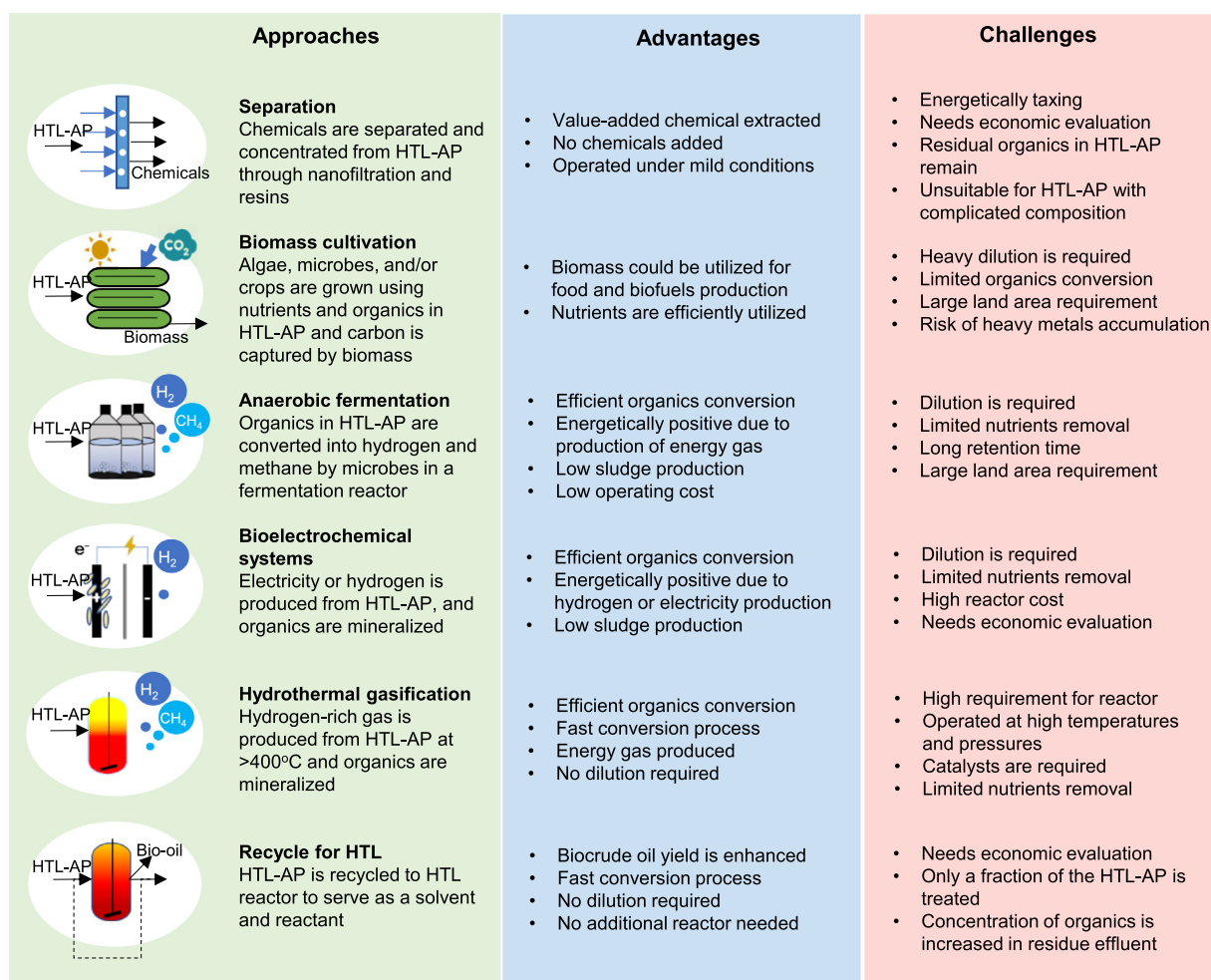


Fig. 25. Comparison of the state of technology of different HTL-AP valorization approaches. The advantages and limitation are evaluated based on the findings of previous studies.

since some value-added chemicals (phenols and nitrogen-containing organics) are regarded as inhibitors, and the residual organics after separation could serve as the feedstock for subsequent biological processing.

- Biomass cultivation using HTL-AP as a culture medium leads to a high nutrients recovery and is an economically cost-effective technique for the production of fertilizer. However, inhibition and low efficiency of organics utilization limits the application of HTL-AP with a high concentration of organics as a culture medium. In addition, the commercial application of the produced biomass also faces challenges because of the environmental risk of heavy metals accumulation and the large land area requirement.
- Bioelectrochemical systems advantageously resulted in the conversion of recalcitrant compounds (phenols, furan derivatives, and N-heterocycles). Further, energy, gas, and electricity could all be achieved. However, future studies need to focus on the full-scale commercial application of this technology in terms of efficiency and cost-effectiveness.
- Anaerobic fermentation of HTL-AP shows potential for commercial application, since it is already considered a mature technology. However, the limited conversion of nitrogen-containing organics suggested that the residual effluent needs subsequent post-treatment using other valorization approaches. In addition, pre-treatment of HTL-AP, enrichment of functional microbes, and bio-augmentation need to be emphasized to enhance the anaerobic fermentation of HTL-AP.
- The recycling of HTL-AP has demonstrated positive correlations with the biocrude oil yield and energy recovery. However, recycling results in an apparent increase in the COD and TN of the HTL-AP, which could pose grave issues for subsequent disposability, reduce the efficacy of utilizing HTL-AP for algae growth, contribute to environmental contamination if released into the environment, and reduce the long-term storability potential of this wastewater. Thus, although recycling of HTL-AP is simple to employ, cost-effective, and doesn't require much effort to scale-up, recycling exacerbates the problem associated with the toxicity of HTL-AP. Since recycling increases the concentration of organic matter in the HTL-AP, future studies should emphasize the combination of this technique with other valorization methods, such as value-added chemical separation or gasification (production of syngas/hydrothane).
- Gasification suffers from a high energy demand and incurs high capital and operating costs associated with catalyst incorporation and stringent reactor specifications. Gasification still needs to overcome issues associated with low efficiency, low yields, catalyst deactivation, and gas separation/purification before it can be viewed as a mainstream treatment technique for HTL-AP. Gasification can be easily integrated into a HTL biorefinery to enhance commercialization potential of biocrude oil production technology; however, there are still quandaries surrounding the understanding of gasification reactions, ideal reaction design, gas cleanup, and HTL-AP feeding techniques.

8.2. Constructing an interconnected energy production and waste valorization paradigm

To enhance the prospects of large-scale HTL entering the mainstream biocrude oil market, valorization of HTL-AP is a critical and necessary first step. Further research should be conducted to co-optimize the energy recovery (or ECR), the economic potential, and GHG emissions of the different paradigms associated with HTL into one, complete entity, including HTL biocrude oil production, HTL-AP valorization, biocrude oil upgrading, etc. Based on this

perspective, attractive avenues of future work concerning the interconnection of these paradigms are presented below:

From the perspective of the HTL process, future studies should focus on optimizing the energy and elemental distribution through interconnection of HTL and HTL-AP valorization. For example, recovering more C in the biocrude oil would enhance the energy recovery of the HTL process and concurrently improve the prospects of valorizing HTL-AP. In particular, lowering the concentration of organic material in HTL-AP would be beneficial for subsequent biological conversion, since this would avoid problems associated with microbial organic shock. Moreover, this would also reduce the need for serial dilution of HTL-AP, leading to economic incentives stemming from reductions in reactor volumes. The gas produced from biological conversion of HTL-AP could also be recycled back into the HTL process as a headspace gas, thereby leading to an increased energy recovery, enhanced C/H content in the oil, and elevated biocrude oil yield. In contrast, N, P, K, and S should be selectively transferred into the HTL-AP through optimization of the HTL process and reaction conditions. N and S in the biocrude oil are difficult to remove via upgrading, and current regulations restrict the allowable concentration of these heteroatoms in transportation fuels in order to circumvent the production of harmful emissions. Selectively isolating N, P, and K in HTL-AP would enhance the feasibility of utilizing this wastewater as a means to produce fertilizer or cultivate biomass. In addition, heavy metals migration should be optimized to ensure accumulation in the solid residue for safe disposal and treatment, since accumulation in HTL-AP would curtail the potential of this product to be used as a fertilizer and for biomass cultivation. The exploration of membranes as physical adsorbents of metal ions in HTL-AP should also be considered as a way to diminish the toxicity associated with this aqueous stream

Synergy also exists for the interconnection of HTL-AP valorization techniques and biocrude oil upgrading. For example, hydrogen production from gasification and anaerobic digestion of HTL-AP can be used as a headspace gas for biocrude oil hydrotreating and hydrocracking. The methane produced via anaerobic fermentation can serve as a heating source for both HTL and gasification reactors, thereby augmenting the potential for constructing a combined biocrude oil production and processing biorefinery and reducing costs associated with electricity. Additionally, value-added chemicals extracted from HTL-AP could serve as fuel additives (acetic acid, butanol, etc.), which would improve the characteristics of biocrude oil (viscosity, total acid number, pour point, etc.) and serve as a mild means of biocrude oil upgrading.

Based on the characteristics of different HTL-AP processing techniques, a process-intensification strategy could be helpful for upscaling and commercializing HTL technology. Realizing a multi-scenario optimization strategy involving the combination of multiple HTL-AP valorization techniques with traditional HTL and biocrude upgrading paradigms is needed to properly assess the synergistic and antagonistic relationships between the different scenarios. The environmental sustainability and economics of the integration process also needs further evaluation in order to achieve reductions in GHG emissions and costs. The continued analysis of these interconnected paradigms would create a driving force for more R&D focusing on co-optimizing biocrude oil production and wastewater valorization.

In order to achieve an interwoven paradigm of HTL-AP valorization pathways with HTL and biorefining, collaboration is needed among researchers in a myriad of different fields, including scientists to better control the energy recovery of the oil phase, microbiologists to investigate and manipulate the microbial community for effective anaerobic fermentation, engineers to conduct process-intensification analysis, economists to achieve multi-objective

optimization, statisticians/computational scientists to conceptualize a harmonized LCA model, and mathematicians to apply the inter-connection of these paradigms to game theory.

Declaration of Competing Interests

We wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

The authors of the review manuscript titled, "Valorization of Hydrothermal Liquefaction Aqueous Phase: Pathways Towards Commercial Viability" (No.: PECS-2019-77) have read, understood, and complied with Elsevier's ethical guidelines. The manuscript submitted on our behalf is own work and the content of our manuscript has not been copied from elsewhere. Further, our manuscript is unpublished and is not currently under review with nor submitted to another journal; all data measurements are genuine results and have not been manipulated.

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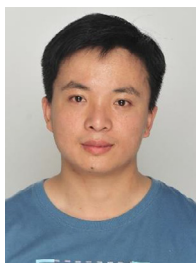
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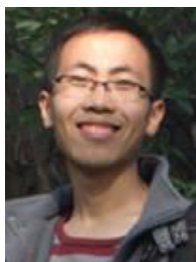
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