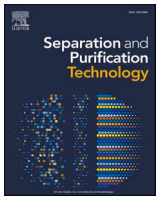
Separation and Purification Technology 378 (2025) 134493

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur



Review

# Towards sustainable bio-oil Production: Recycling and separation techniques applied to the aqueous phase byproduct of algae biomass hydrothermal liquefaction

Soorena Gharibian, Massimiliano Errico *, Knud Villy Christensen

*Department of Green Technology, Faculty of Engineering, University of Southern Denmark, Campusvej 55, 5230 Odense, Denmark*

ARTICLE INFO

*Keywords:*
Algae
HTL
Biocrude
HTL-AP
Separation
Recycle
Valorization

ABSTRACT

Valorizing or recycling the hydrothermal liquefaction aqueous phase (HTL-AP) remains a considerable challenge in commercializing the HTL process for wet biomass, especially for algae, due to the high concentration of organics and nutrients. This review focuses on separation methods for HTL-AP, with particular emphasis on membrane filtration technologies. Most HTL-AP primary separation efforts have been limited to laboratory-scale solvent extraction, which requires a secondary separation/polishing step, and upscaling these processes thus remains a challenge. Various secondary treatment processes have recently been proposed to support the development of water-closed-loop HTL systems, including the recovery of value-added products such as struvite from HTL-AP. This could improve the overall economic viability of HTL. Membrane-based separation offers a scalable and environmental friendly approach, enabling nutrient concentration, valorization, and resource recovery. However, additional research, including fouling mitigation and cost-effective cleaning strategies, is needed to assess the techno-economic feasibility of membrane applications. Integrated membrane cascades combining microfiltration, ultrafiltration, nanofiltration, and/or reverse osmosis could improve process sustainability by enhancing separation efficiency, reducing fouling, minimizing inhibitory organics, and lowering freshwater demand in algae cultivation. While a variety of secondary treatment methods have been proposed, techno-economic analyses and life cycle assessments comparing their efficiency and impacts are lacking. Such assessments should be based on identical process conditions, thereby isolating the effects of feed composition, HTL operating parameters, and primary separation techniques. Moreover, treated HTL-AP should be reused as a growth medium with the same algae strains used as HTL feed to ensure consistency across cycles.

## 1. Introduction

Global warming, along with growing environmental concerns and international efforts to reduce fossil fuel dependence, underscores the urgent need for sustainable energy alternatives. While central to economic development, conventional energy sources are major contributors to greenhouse gas (GHG) emissions, exacerbating climate change. Renewable energy technologies such as solar panels, wind turbines, hydrogen fuel cells, and biogas have emerged as possible solutions to mitigate these issues. However, their adoption faces limitations, including intermittency, high installation costs, and the extensive land and water resources they require. Against this backdrop, biocrude derived from biomass offers a compelling alternative, representing a renewable, stable, and potentially scalable source of energy [1]. Among biomass feedstocks, microalgae stand out for their exceptional productivity and minimal resource requirements as they can grow on non-arable land, in saline water, and even in industrial effluents [2].

Hydrothermal liquefaction (HTL) of algae has emerged as a highly efficient technology for converting biomass into biocrude, offering several advantages over traditional thermochemical processes such as carbonization and pyrolysis [3,4]. Unlike these methods, HTL does not require the energy-intensive dewatering or drying of wet biomass, which is a significant energy burden in other conversion technologies [1]. This makes HTL particularly suitable for algae, a naturally high-moisture feedstock [5]. Moreover, algae outperform terrestrial biomass in photosynthetic efficiency, enabling faster growth rates and enhanced $CO_2$ sequestration [6]. This ability not only supports biocrude production but also contributes to climate change mitigation by reducing

* Corresponding author.
*E-mail address:* maer@igt.sdu.dk (M. Errico).

https://doi.org/10.1016/j.seppur.2025.134493
Received 26 May 2025; Received in revised form 11 July 2025; Accepted 23 July 2025
Available online 24 July 2025

atmospheric $CO_2$ levels. Additionally, microalgae have demonstrated significant potential in wastewater treatment, where they can assimilate nutrients and pollutants, thereby coupling energy production with environmental remediation. Algae can also utilize industrial carbon emissions during mixotrophic cultivation, enhancing their potential as a sustainable and environmentally beneficial feedstock [6].

Despite its advantages, the HTL process has challenges, particularly the hydrothermal liquefaction aqueous phase (HTL-AP) by-products [1,7]. These byproducts contain high concentrations of organic compounds, nitrogen-containing substances, and heavy metals, posing substantial barriers to its reuse and disposal [7–9]. Primary separation techniques for the separation of HTL-AP from the biocrude (such as gravity settling or solvent extraction) have a direct effect on the biocrude/HTL-AP quality and properties [10]. These challenges make it difficult to achieve a closed-loop system, limiting the economic and environmental feasibility of HTL on a commercial scale.

To address these issues, researchers have proposed various valorization strategies for HTL-AP. These include extracting value-added products, such as platform chemicals and struvite [4,10], or conversion to $H_2$ and $CH_4$ through processes like anaerobic digestion (AD) or hydrothermal gasification (HTG) [11]. Another approach involves recycling HTL-AP as a reaction medium for HTL itself or as a nutrient source for algal feedstock cultivation [5]. These methods aim to enhance the overall sustainability of the process by reducing waste and maximizing resource utilization. However, the presence of heavy metals (from different sources such as: leaching from HTL reactor walls [6], algae biomass feed rich in heavy metals and arsenic [12,13], chemical agents introduced in the algae harvesting step [14], and inhibitory organic compounds (such as nitrogen-containing organics, unsaturated organics, and lignin/carboxylic-rich alicyclic molecules [15,16]) present significant obstacles. These substances not only inhibit algal growth but also accumulate during repeated recycling, thereby intensifying their inhibitory effects [10,17]. This necessitates the development of effective separation and detoxification technologies to enable safe and efficient reuse of HTL-AP.

Alternative approaches to HTL-AP valorization include chemical and biological treatments. Chemical methods, such as advanced oxidation processes (AOPs), can degrade toxic organic compounds and improve biodegradability, rendering HTL-AP more suitable for reuse [11]. Biological treatments, such as AD, can convert organic compounds in HTL-AP into biogas while simultaneously reducing its toxicity [1]. However, these methods also have limitations. Chemical treatments can be energy-intensive and costly, while biological treatments may not eliminate all inhibitory substances.

Among potential solutions, membrane separation technologies, such as membrane filtration cascades, have received attention for their ability to selectively remove contaminants from HTL-AP [18,19]. These systems can efficiently separate organic inhibitors, heavy metals, and other undesirable compounds, making the HTL-AP suitable for recycling [20]. Membrane separation technologies can also concentrate valuable nutrients, enhancing the feasibility of using HTL-AP as an algae cultivation medium [21]. Despite these advantages, the high operational costs and potential fouling of the membranes present significant challenges. Moreover, the concentrated organic inhibitors in the retentate require fractionation, safe disposal, or conversion, adding to the complexity of the process [8].

In addition to these technical challenges, the economic and environmental implications of HTL-AP recycling must be carefully evaluated through techno-economic analysis (TEA) and life cycle assessment (LCA) [22]. While recycling can reduce the need for fresh water and nutrients, it may also lead to the accumulation of salts and other non-biodegradable compounds in the cultivation system [23]. This can affect algae growth and necessitate periodic system flushing, which offsets the benefits of recycling. Addressing these issues requires a holistic approach that integrates advanced separation techniques with sustainable management practices.

The idea behind this review is to integrate relevant information on processes related to HTL using only algae as biomass feedstock. During the past decade, biocrude recovery and optimization of HTL reaction parameters have been the main aim for researchers working on algae HTL. Currently, researchers have changed their view on the valorization and recycling of HTL by-products, especially HTL-AP. Few studies have reported recovering resources from HTL-AP using membranes. Therefore, this review will provide an overview of the current primary/secondary separation techniques applied to HTL-AP for resource recovery, removal of inhibitory components for reuse, and valorization of by-products like platform chemicals.

## 2. Separation techniques for the primary separation of biocrude from algae HTL-AP

The primary separation of the final biocrude from the HTL product mixture is a key operation in the HTL process (Fig. 1). The final biocrude product should have a minimal water content if used directly or in case of further upgrading, as water may deactivate the catalyst used for upgrading [24]. According to the literature, after the reaction, the HTL product mixture readily separates into 3 phases: biocrude, AP, and solid particles (Fig. 2) [1]. In laboratory scale, vacuum filtration is often used for separating the HTL-AP and biocrude phases from these solids. Some researchers have reported the use of centrifuge equipment and vacuum filtration (Buchner filter [25]) setup using filter papers with different pore sizes, Whatman no. 4 Filter Paper [26,27], 0.2 μm glass fiber [28,29], and 1 μm glass fiber [30,31]. This method of separation is carried out mostly for experimental convenience, but should be avoided in large-scale continuous HTL systems due to the large energy requirements.

### 2.1. Gravity settling

The basic primary separation of the HTL product mixture includes gravity settling in a decantation funnel (Fig. 2) [32]. In a continuous process, gravity settling is usually carried out in two/three three-phase separator drums containing various internal devices, including weirs and corrugated plates to improve phase separation [33]. However, the separation of biocrude from the HTL-AP and solid residues requires a long settling time, and sometimes the specific polar organic compounds remain soluble in the HTL-AP [34]. A solvent-free method may have certain drawbacks, such as a lower biocrude yield, which could negatively impact the revenue of the biorefinery. Additionally, separating the biocrude from the HTL-AP byproduct might become more challenging due to the potential formation of emulsions [34].

### 2.2. Solvent extraction

To reduce separation time and improve efficiency, solvent extraction with various polar and non-polar (water-immiscible) solvents is used to remove water-soluble organics from HTL-AP and biocrude residues from solids (which contribute minimally to yield [36]). Acetone, dichloromethane (DCM), n-hexane, chloroform, methanol, ethanol, diethyl ether, cyclohexane, tetrahydrofuran, toluene, etc., have been tested. Ratha et al. [37] have extensively studied the effect of solvent type on

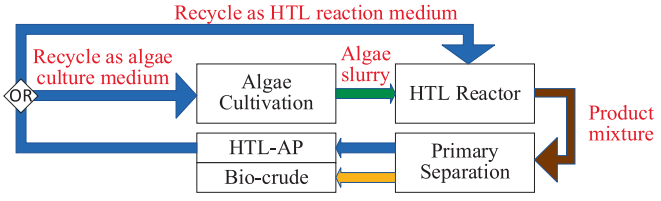



**Fig. 1.** Recycle route of primary separated HTL-AP without additional secondary treatment/separation methods.

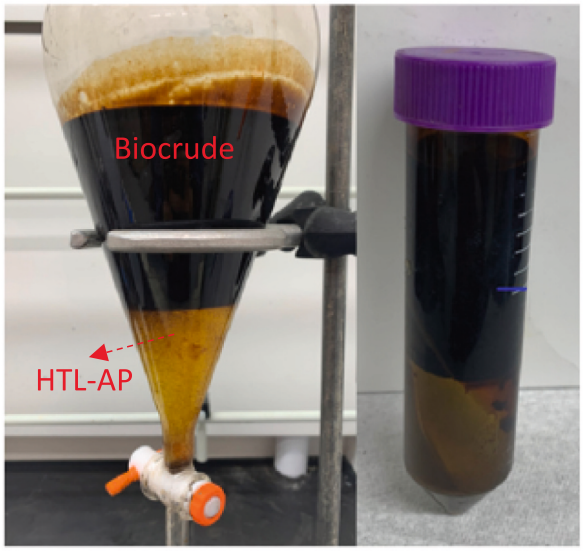



**Fig. 2.** Experimental work-up of biocrude separation from other by-products using the gravity settling method and decanter (without solvent extraction). Reprinted from [35], with permission from Elsevier.

the final biocrude based on available literature. However, authors have stated that the impact of extraction solvent on biocrude properties, such as elemental composition, remains inconclusive since feedstock biochemical composition and HTL operational parameters play a significant role in determining biocrude properties. Watson et al. [38] demonstrated that the selection of extraction solvent plays a critical role in determining both the yield and energy efficiency of biocrude from HTL. Using *Chlorella* sp., *Nannochloropsis* sp., and *Enteromorpha* pr., they reported that DCM achieved the highest yield with *Chlorella* sp. (48.8 %), toluene with *Nannochloropsis* sp. (23.3 %), and acetone with *Enteromorpha* pr. (9.8 %), with yields varying up to 20.4 %. DCM also delivered the highest energy recovery (67.1 %) and the lowest energy consumption ratio (0.06). Based on CHNS elemental analysis, DCM and toluene produced biocrude with the highest carbon, lowest oxygen, and greatest energy content across all feedstocks. However, for protein-rich feedstocks, they also extracted nitrogen and sulfur, likely due to the solvent's polarity, dipole–dipole interactions, and hydrogen bonding. The findings emphasize that solvent properties strongly influence product distribution and must be standardized when reporting HTL outcomes to ensure accurate comparisons in yield and energy metrics. Nevertheless, polar solvents, with DCM as the most popular solvent, generally produce higher quality biocrude with greater carbon content and energy density than non-polar solvents. In lab scale this method is typically conducted in the same gravity-settling decantation funnel for the final separation and reclamation of the products for experimental convenience (Fig. 3) [34,39].

Fig. 4 shows a simplified comparison of experimental workup for primary separation of biocrude from HTL-AP with gravity settling or solvent extraction. Guo et al. [34] carried out a continuous microalgae HTL using a continuous stirred reactor to demonstrate the effect of using solvent for primary separation of biocrude and HTL-AP. Their results showed that the biocrude yield using the non-solvent method was almost 20 % lower compared to using DCM solvent extraction. In addition, higher N content in the produced biocrude was achieved with the DCM extraction. Moreover, biocrude higher heating value (HHV) decreased slightly with the application of solvent extraction. The solvent extraction method did not affect the content of ions and trace elements. Similar overall trend was reported in studies conducted by Xu et al. [36] and Barriero et al. [39].

Evaporation during the process can lead to the loss of light compounds, which may impact the overall efficiency of the system [41,42]. Some organic substances initially present in the HTL-AP may migrate into the biocrude phase, increasing biocrude yields but at the cost of elevated O and N content, which can compromise fuel quality [34]. The presence of these elements reduces the HHV of the biocrude, further diminishing its energy potential [36]. Furthermore, residual organic solvents in the HTL-AP can hinder subsequent algae cultivation, posing an additional challenge [34,43]. Beyond these technical concerns, the use of organic solvents like DCM in large-scale production raises environmental, economic, and health concerns, making it a less favorable approach both environmentally and financially [25,34,39].

Based on the literature, application of solvent for the separation of biocrude and HTL-AP significantly affects the yield of the HTL-AP and

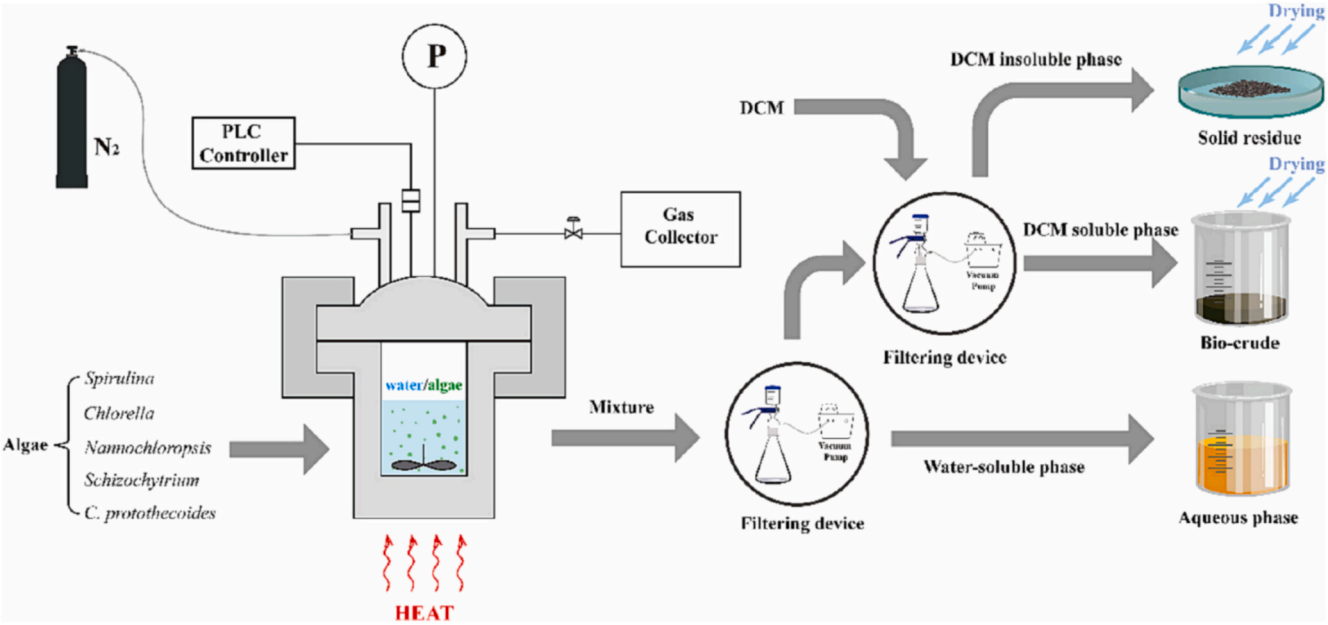



**Fig. 3.** Experimental work-up of HTL biocrude production and primary separation from other by-products using solvent extraction. Reprinted from [40], with permission from Elsevier.

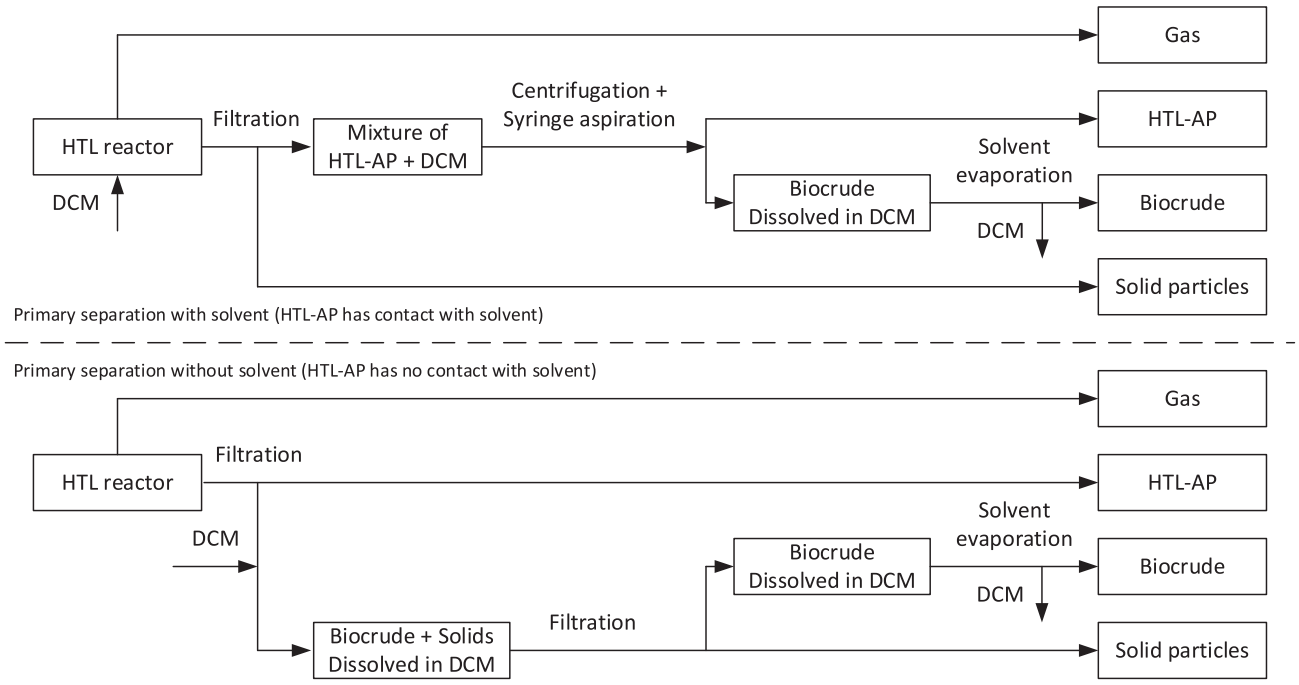



**Fig. 4.** Experimental work-up of biocrude primary separation from other by-products with/without solvent extraction. Adapted from [39].

biocrude products, including their HHV/composition. The findings emphasize the importance of creating solvent-free separation methods for full scale production and to accurately evaluate yields based on laboratory-scale experiments.

### 2.3. Membrane filtration as primary separation

For full scale production, due to the above-mentioned limitations of using solvent extraction, the economic and operational viability of a cascade/multi-step microfiltration (MF) and ultrafiltration (UF) system needs to be evaluated. The applicability of membranes for the separation of multiphase systems is a proven method in membrane bioreactor (MBR) units for wastewater treatment. In MBR systems, ultrafiltration membranes are used to separate water from a multiphase system consisting of suspended solids, microbial cells, and large extracellular polymeric substances (EPS) and soluble microbial products (SMP) secreted by microorganisms [44–46]. Based on the available literature, no study has used membranes as the primary separation method for the separation of biocrude, HTL-AP, and solids. This may be due to the fact that the majority of the available studies use small-scale HTL reactors, and the volume of the HTL product mixture is in the order of tens of milliliters while testing membrane separation requires a larger volume. During filtration, membranes are prone to fouling and thus require sophisticated setups with the ability to backwash or physical/chemical cleaning to remove fouling. It further requires an in-depth study of the membrane type, pore size, and molecular weight cut-off (MWCO).

### 2.4. Performance comparison of different primary separation techniques

Most of the available studies conduct algae HTL-AP recycling in batch scale studies using small laboratory equipment for the primary separation with enough separation time for mass transfer, and their performance cannot be compared based on the required residence time. Moreover, the performance of primary separation methods can be described/compared using biocrude yield and HHV (Section 2.2). However, the biocrude yield, HTL-AP yield, and HHV depend not only on the primary separation method but on other factors such as feed algae biochemical composition (CHNSO elemental composition and protein/lipid/carbohydrate content of the feed algae), and HTL operational parameters (feed biomass loading ratio, temperature, pressure, HTL residence time). Therefore, due to differences in the reported feed composition and reaction methods, it is not possible to quantitatively compare the biocrude yield and HHV of the different studies with different primary separation methods. Accordingly, only an overall qualitative comparison of commonly used primary separation methods in the available literature is possible. This is shown in Table 1. In a continuous large-scale HTL system, HTL-AP could be separated by gravity settling using scalable horizontal two/three-phase separator vessels with enough residence time for complete separation [47,48]. Vacuum filtration, centrifuge, and solvent extraction methods may not be suitable for continuous HTL systems due to the requirement for expensive equipment or environmental concerns regarding the application of solvents. In this context, the experience of the oil industry could prove useful for large-scale biocrude production.

## 3. Separation techniques for secondary purification, resource recovery, and valorization of algae HTL-AP

Effective utilization of HTL-AP is crucial if HTL technology is to be a viable process for wet algae biomass [8]. This can be achieved through various secondary separation/treatment methods following the primary separation (Fig. 5), including biological and chemical conversion, and extracting valuable organic and inorganic compounds as byproducts. Processes for energy recovery and valorization of HTL-AP through conversion of organics, including catalytic/noncatalytic HTG and AD, will not be covered in this review. The reason is that the energy yield of these energy recovery processes from the HTL-AP would be low due to low energy content and the presence of high content of other elements, such as P and N, which cannot be utilized during energy recovery [6,49]. Moreover, HTG requires large energy inputs and has large operating costs due to the elevated reaction pressure and temperature, and the use of catalysts including noble metals [19]. In addition, numerous studies have concluded that HTL-AP is toxic for microorganisms involved in AD due to the presence of toxic compounds such as phenols, ammonium,

**Table 1**
Comparison of common primary separation methods applied to HTL-AP.

| Method | Advantages | Disadvantages |
|---|---|---|
| Gravity Settling | • Better biocrude quality<br>• Low operating/equipment cost<br>• No solvent required<br>• Simple operation under mild conditions, resulting in lower environmental impact due to reduced energy demand<br>• Scalability | • Lower separation efficiency (in comparison with solvent extraction)<br>o Lower biocrude yield<br>o High strength HTL-AP<br>• Larger residence time requirement (in comparison with solvent extraction)<br>• Lower energy consumption |
| Filter Paper and Vacuum Filtration<br>Centrifugation | • No solvent required<br>• Lower residence time requirement (in comparison with gravity settling) | • Energy consumption<br>• Equipment cost<br>• Separation efficiency (similar to gravity settling)<br>• Environmental impacts, such as GHG emissions due to larger energy consumption<br>• Scalability issues |
| Solvent Extraction | • High separation efficiency (in comparison with other methods)<br>o Higher biocrude yield<br>o Low strength HTL-AP<br>• Lower residence time requirement (in comparison with gravity settling)<br>• Scalability | • Lower biocrude quality<br>• Equipment and safety cost<br>• Solvent safety and disposal concerns<br>• Environmental impact due to:<br>o GHG emissions due to additional energy demand for Solvent recovery<br>o Solvent toxicity and volatility<br>• Complex operation |

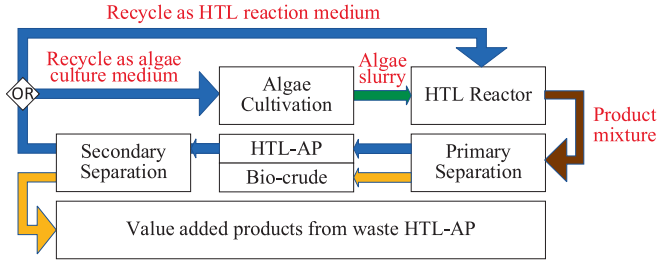



**Fig. 5.** Recycle routes of secondary treated/separated HTL-AP.

and heavy metals [19,30,50,51].

### 3.1. Membrane filtration as secondary separation

The use of membrane filtration in water and wastewater treatment has been extensively studied in the past decades [8]. Large-scale membrane setups are currently used in water polishing (MF, UF, nanofiltration (NF)), for water desalination through reverse osmosis (RO), and in MBR. This is due to high separation efficiency, high quality of the final products, chemical stability, low energy consumption, green and environmentally friendly processes, small energy footprint, and flexible scale-up. Agarwalla et al. [8] recently reviewed the application of membrane technology in microalgal harvesting and extraction of value-added products. They highlighted the lack of studies regarding the valorization of HTL-AP using membrane filtration systems. Table 2 summarizes studies that use membrane filtration in the secondary treatment of HTL-AP from different types of biomass sources. The main research objective in this context can be categorized into the following: I) Organic load reduction & water reuse, II) Chemical recovery & fractionation, III) Characterization & biodegradability assessment.

Based on Table 2 MF and UF are mainly used as a pretreatment process for HTL-AP for NF and RO systems to remove suspended solids and colloidal organic matter to reduce the fouling potential of downstream membrane systems [52]. NF systems are proposed for the separation of different fractions since HTL-AP comprises complex organic compounds with highly distributed molecular weights [50]. NF membranes cover the MWCO range of 200 to 1000 Da [8]. Although several studies have demonstrated the potential of membrane technology for HTL-AP valorization or fractionation of chemicals from synthetic HTL-AP, further research is still needed to identify/optimize operational parameters and fully explore its role in the valorization of real HTL-AP, particularly in areas such as TEA. Also, Further research is required for integrating multiple scalable membrane processes, such as membrane filtration cascades (MF, UF, NF, RO), which can help minimize membrane fouling while enabling the fractionation of value-added organic products, addressing the complexity of real HTL-AP, and reducing freshwater intake in the HTL loop.

In one of the most detailed studies on secondary separation of HTL-AP, Sayegh et al. [50] examined oil and particles from HTL-AP wastewater generated from municipal sewage sludge. HTL-AP was first separated from the HTL mixture by gravity settling. Membrane filtration of the HTL-AP was performed using ceramic ($TiO_2$) UF membranes (Inopor, Germany) in crossflow mode to separate oil droplets and particles. Fig. 6 shows the simplified flowsheet of the membrane filtration setup. The feed temperature was regulated via a thermostat and heat exchanger placed in the feed tank. Pressure and flow were adjusted using a valve installed on the retentate line. Permeate collection varied by filtration mode: without backwash, it was continuously measured on a mass balance; with backwash, it was divided between the mass balance and the backwash tank. Three membranes with different pore sizes (5, 10, and 30 nm) were tested. The effect of feed temperatures (25 and 40 °C) and backwash cycles was also studied. The 10 nm pore size membrane had the most stable performance, achieving a critical flux of 6.6 L $m^{-2}h^{-1}$ at 25 °C and maintaining a permeability around 18 L $m^{-2}h^{-1}$ $bar^{-1}$. The 5 nm membrane suffered significant fouling, particularly from surfactant adsorption. Separation of oil emulsions was effective, with a 90 % rejection of long-chain fatty acids and significant retention of anionic surfactants (85–90 %). Backwash cycles resulted in faster permeability decline due to infiltration of small molecules into membrane pores. Fouling was primarily organic, necessitating cleaning. Alkaline cleaning at pH 12had the highest efficiency among the tested physical (increasing crossflow velocity, increasing temperature, applying backwash) and chemical methods (acid cleaning at pH 2 and alkaline cleaning), achieving a recovery of up to 75 % pure water permeability. This study highlights the potential of ceramic UF membranes for HTL-AP treatment as a secondary treatment, offering effective oil and particle removal while minimizing membrane fouling through optimized conditions.

### 3.2. Struvite formation

Phosphorus is a vital element necessary for sustaining life, typically found in nature as phosphates rather than in its elemental form. Over 90 % of phosphorus consumption—an amount that continues to increase—is dedicated to agricultural use, primarily in the form of fertilizers. Human activities have exacerbated global P runoff into water bodies, contributing to nutrient-enriched environments that trigger algal and cyanobacterial blooms, which in turn create taste and odor problems, eutrophication, and dead sea beds. HTL-AP contains substantial amounts of phosphate ($PO_4^{3-}$) and ammonium nitrogen ($NH_4^+$-N), which is beneficial as a fertilizer, but must be treated before discharge to prevent eutrophication [58]. Several techniques, including biological nitrification–denitrification [59], ammonia-stripping [18,60], ion exchange [37], and struvite precipitation [42,49], have been utilized to remove $NH_4^+$ from HTL-AP [17]. Among these, chemical precipitation is commonly applied, involving reactions of hydroxides, sulfides, and carbonates with pollutants to produce insoluble precipitates. Struvite

**Table 2**
Summary of studies related to secondary treatment of HTL-AP using membrane filtration.

| Objectives | Study | Source of AP | HTL-AP primary separation Method | Membrane information: Type, product, material, manufacturer, MWCO, pore size | Process configuration | Key findings | Challenges |
|---|---|---|---|---|---|---|---|
| Chemical Recovery & Fractionation | Zhang et al. [19] | Synthetic | N/A | NF: NF90, Polyamide, DOW FILMTEC™, 200–400 Da | Single-stage, batch, dead-end | • 95 % isobutyric acid rejection.<br>• pH-sensitive selectivity.<br>• An alkaline pH resulted in greater rejection of organic solutes compared to an acidic pH. | • Synthetic model, not tested on real HTL-AP.<br>• Flux decline at high pH. |
| | Lyu et al. [52] | Rice straw | Filtration (300-mesh screen) | • UF: MW, 20 kDa<br>All membranes from General Electric Co.<br>• NF:<br>o GE, 1 kDa<br>o DL, semi-aromatic piperazine-based hydrophobic, 150 Da<br>o DK, semi-aromatic piperazine-based hydrophobic, 300 Da | • UF as pretreatment for both single-stage and two-stage NF.<br>• Single-stage NF<br>• Two-stage NF: GE + DL, GE + DK, and DL + DK<br>• Crossflow, batch | • Glucose and organic acids are separated in the 1st stage.<br>• At the first stage, DL had glucose rejection of 97.12 %.<br>• Aromatics are separated in the 2nd stage.<br>• At the 2nd stage, DK had acetic acid rejection of 5.04 %.<br>• The DL + DK process effectively fractionated hydrolysates into glucose, monophenols/cyclopentenones, and acetic acid. | Hard to completely isolate all aromatics into a single fraction due to the inconsistent rejection behavior of various aromatic compounds. |
| | Lyu et al. [53] | Synthetic | N/A | • NF:<br>o DK and DL, Polyamide, GE Osmonics<br>o NF90, Polyamide, DOW FILMTEC™<br>o NF270, Polypiperazine amide, DOW FILMTEC™<br>o XN45, Polyamide, TRISEP<br>o TS40, Polypiperazine amide, TRISEP<br>• RO:<br>o SE and SG, Polyamide, GE Osmonics<br>o BW30 and BW30FR, Polyamide, DOW FILMTEC™ | Single-stage and two-stage (DK NF + SE RO), flatsheet, crossflow, batch | • DK NF showed high selectivity for separating monophenols from glucose.<br>• SE RO effectively separated acetic acid from monophenols.<br>• Low pH helps separate monophenols from sugars and acids.<br>• The two-stage membrane process<br>• (DK NF + SE RO) effectively fractionated model HTL hydrolysates into biomass fragments, monophenol-rich concentrate, and acetic acid permeate. | Synthetic model, not tested on real HTL-AP. |
| | Teella et al. [54] | Synthetic | N/A | • NF:<br>o Desal DK, Polyamide, GE Osmonics<br>o MPF-34, Koch, 200 Da<br>• RO:<br>o AG, Polyamide, GE Osmonics<br>o CE, Cellulose acetate, GE Osmonics | Single-stage, crossflow, batch | • Guaiacol-free AP showed > 80 % glucose retention with DK NF membranes at ~ 60 bar feed pressure.<br>• Acetic acid permeation at moderate pressure ~ 40 bar. | • Synthetic model, not tested on real AP.<br>• Guaiacol degraded the membrane: A practical membrane process needs either a resistant polymer or phenolic pretreatment.<br>• High transmembrane pressure is needed for adequate glucose retention and flux. |
| | Crossley et al. [55] | Hydrothermal carbonization of spent coffee grounds | Vacuum filtration (11 μm Whatman filter paper) | NF: NF270, DOW FILMTEC™ | Single-stage, flatsheet, crossflow, batch | • NF was used to concentrate the inorganic nutrients of the HTC process water, achieving a mass concentration factor of 3.9 times.<br>• $NH_4^+$-N was also rejected by NF such that the molar ratios of Mg, $NH_4^+$-N, and $PO_4^{-3}$-P remained favorable for the precipitation of struvite.<br>• 92.8 % of aqueous phosphorus was recovered as struvite via simple pH adjustment. | • High crossflow velocity (up to 3.27 m $s^{-1}$) was used to alleviate membrane fouling due to organic compounds in the HTL-AP.<br>• Cost-benefit analysis of the process is needed to evaluate the process at an industrial scale. |

(*continued on next page*)

**Table 2** (*continued*)

| Objectives | Study | Source of AP | HTL-AP primary separation Method | Membrane information: Type, product, material, manufacturer, MWCO, pore size | Process configuration | Key findings | Challenges |
|---|---|---|---|---|---|---|---|
| Organic Load Reduction & Water Reuse | Zhang et al. [21] | Swine manure + algae | Vacuum filtration (0.45 μm) | • MF: 0.45 μm<br>• UF: Polyethersulfone, Synder Filtration:<br>o ST, 10 kDa<br>o MT, 5 kDa<br>o XT, 1 kDa<br>• NF: NF90, Polyamide, DOW FILMTEC™, 200–400 Da | • Single-stage (pretreatment with adsorbent included)<br>• Two-stage (UF + NF), batch, dead-end | • 74 % DOC rejection with coal pretreatment.<br>• Pretreatment reduced NF fouling.<br>• At pH 11, DOC rejection was high, but total ammonia–nitrogen rejection dropped, enabling organics/TAN separation.<br>• HTL-AP could be concentrated up to 90 %. | • Membrane fouling from humics and colloids.<br>• High-organics concentrated HTL-AP requires further fractionation/ valorization. |
| | Sayegh et al. [18] | Sewage sludge | Gravity settling | UF: Polyethersulfone, Millipore, 100 kDa, 10 nm | Single-stage, batch, submerged, flatsheet, with/without backwash | • 8 % total organic carbon (TOC) rejection by UF.<br>• Large oil droplets (up to 50 μm) were removed by UF.<br>• The largest droplets in the permeate were lower than 10 nm.<br>• 88 % of ammonia recovered by stripping post-treatment. | • Air scouring in the filtration cell to control fouling.<br>• Fouling was countered by backwash.<br>• Treated HTL-AP requires further fractionation/valorization. |
| | Sayegh et al. [50] | Sewage sludge | Gravity settling | UF: Ceramic, one-channel $TiO_2$, Inopor, 5/10/30 nm | Single-stage, batch, crossflow, with/ without backwash | • TOC rejection was 3 %, 6 %, and 15 % for 30 nm, 10 nm, and 5 nm membranes, respectively.<br>• >90 % fatty acids retained using 5 nm membrane.<br>• Rejection of short-chain fatty acids and cyclics stayed below 15 %.<br>• Alkaline (pH 12) cleaning is effective for removing membrane fouling. | • Organic fouling is severe at a small pore size.<br>• Treated HTL-AP requires further fractionation/valorization. |
| | Sayegh et al. [56] | Sewage sludge | Gravity settling | • UF: Ceramic, $TiO_2$, Inopor, 10 nm<br>• Membrane distillation (MD): Expanded polytetrafluoroethylene, W.L. Gore & Associates GmbH, 0.2 μm | • Two-stage (UF + MD)<br>• UF: crossflow<br>• MD: Flatsheet, feed is UF permeate | 12.4 g $L^{-1}$ $NH_4^+$ in distillate at 60 °C. | Wetting due to organic fouling is unavoidable at recovery > 60 %. |
| | Costa et al. [9] | Algal biomass from the wastewater system and harmful algal blooms | Vacuum filtration (0.45 μm) | NF: CR100, XLE, BW30, Commercial thin-film composite, DuPont FilmTec© | Single-stage, batch, dead-end, flatsheet | • Up to 99 % chemical oxygen demand (COD) rejection.<br>• Best $NH_3$-N separation/permeation at pH 11 and 45 °C.<br>• $NH_3$-N permeation increased at high pH due to $NH_3$ prevalence over $NH_4^+$.<br>• Separating $NH_3$-N from organics during NF led to almost constant N content of biocrude (preventing it from increasing) produced with recirculation of treated HTL-AP. | • Membrane fouling (caused by humic-like substances).<br>• Need for fouling mitigation strategies and TEA for scale-up.<br>• An additional $NH_3$-N removal step from NF permeate is required. |
| | Szkadłubowicz et al. [57] | Hydrothermal carbonization of sewage sludge | Filtration | ▪ Ceramic membranes (from Tami industries)<br>• UF:<br>o Ceram 5 kDa, $TiO_2$<br>o Ceram 50 kDa, $ZrO_2$<br>• MF: Ceram 0.14 μm, $ZrO_2$-$TiO_2$<br>▪ Polymeric membranes (from Mann + Hummel Water and Fluid Solutions)<br>• UF:<br>o PES 5 kDa, Polyethersulfone<br>o PES 10 kDa, Polyethersulfone | Single-stage, batch, dead-end, flatsheet | • Struvite precipitation alone before any membrane filtration led to a reduction of $P_2O_5$, $NH_4^+$, and Mg by 61–63, 47, and 62 %, respectively.<br>• In the absence of struvite pretreatment, the NPO30P membrane delivered the best filtration performance, resulting in a 24.4 % decrease in $NH_4^+$ and a 22 % reduction in nitrogen compounds.<br>• In all cases, membrane fouling progressed faster during the filtration of HTL-AP without struvite pretreatment | • Inclusion of organics in the struvite crystals requires toxicity assessment if used as fertilizer. |

(*continued on next page*)

**Table 2** (*continued*)

| Objectives | Study | Source of AP | HTL-AP primary separation Method | Membrane information: Type, product, material, manufacturer, MWCO, pore size | Process configuration | Key findings | Challenges |
|---|---|---|---|---|---|---|---|
| | | | | o PES 30 kDa, Polyethersulfone<br>o PES 50 kDa, Polyethersulfone<br>o PES 150 kDa, Polyethersulfone<br>o C 5 kDa, Regenerated cellulose<br>o C 10 kDa, Regenerated cellulose<br>o C 30 kDa, Regenerated cellulose<br>o C 100 kDa, Regenerated cellulose<br>• NF:<br>o NPO10P, Polyethersulfone<br>o NPO30P, Polyethersulfone | | than when struvite precipitation was applied beforehand. | |
| Characterization & Biodegradability Assessment | Kizza and Eskicioglu [20] | Sewage sludge | Vacuum filtration (0.45 μm) | UF: Polyethersulfone, MilliporeSigma:<br>• PES300, 300 kDa<br>• YM100, 100 kDa<br>• YM10, 10 kDA<br>• YM1, 1 kDa | Cascaded, dead-end, batch, flatsheet | • Unfiltered HTL: lowest methane production rate.<br>• 1 < MW < 10 kDa: 8 % (lowest) of organics.<br>• <1 kDa fraction: highest methane production rate. | • 45 % of the total COD remains recalcitrant to AD and methane production, even after 1 kDa UF.<br>• Residual inhibitors: Although UF improved anaerobic degradation rate of the < 1 kDa HTL fraction, methane yield reached only 55 % of the theoretical maximum. |

N/A: Not Applicable.

formed through this process ($NH_4MgPO_4{\cdot}6H_2O$) has demonstrated potential as a slow-release fertilizer for crops [17,58]. This method works particularly well in wastewater streams with high levels of N and P, such as anaerobically digested wastewater and baker's yeast wastewater, ensuring effective nutrient removal [49]. In cases where wastewater lacks sufficient $Mg^{2+}$, additional supplementation is required to enhance the removal efficiency of $PO_4^{3-}$ and $NH_4^+$. Struvite crystallization depends on specific pH conditions and occurs when $Mg^{2+}$, $PO_4^{3-}$, and $NH_4^+$ are present in equimolar proportions under alkaline conditions [6]. Nearly all $PO_4^{3-}$ and $NH_4^+$ can be recovered as struvite, which can then be reused to support HTL algal feedstock growth [6,61]. However, industrial-scale adoption faces obstacles such as the production of sludge and high chemical costs, highlighting the need for further research [17]. One potential strategy to address these issues involves concentrating nutrients through membrane processes before initiating chemical precipitation, which should be explored further. In addition, the precipitation process requires optimization to minimize the adsorption of organics onto the solid precipitates [62].

### 3.3. Adsorption

Numerous investigations have examined adsorption as a secondary treatment method for HTL-AP, with some studies highlighting its potential to remove organic and inorganic pollutants, thereby reducing the environmental impact of HTL-AP [5]. Various porous adsorbents such as Granular Activated Carbon (GAC) [49,51,63], zeolite [30,31,51,64], and hydrochar/biochar [21,65,66] have been applied for secondary treatment of HTL-AP. Specific compounds, such as phenolic substances, are known to impede algae and microbial growth, posing challenges during the biological valorization of HTL-AP or when released into the environment [17]. The use of porous materials for adsorption offers an efficient and cost-effective approach to wastewater detoxification, with activated carbon demonstrating exceptional efficacy, achieving over 90 % removal of toxic compounds like phenols and nitrogen organics [10,64], while also enhancing methane production by mitigating toxicity to anaerobic microbes [59,63]. Zeolite, a naturally occurring mineral with a well-defined pore structure, supports ion exchange due to its loosely bound water molecules and cations such as $K^+$, $Na^+$, and $Ca^{2+}$ [31,67]. However, adsorption primarily relocates inhibitory substances to the adsorbent, necessitating further treatment methods such as wet oxidation or incineration for adsorbent regeneration, though these options present economic and operational challenges [1]. Consequently, alternative adsorbents like biochar waste derived from solid HTL residues [51,68,69] have been proposed as cost-effective substitutes for commercial activated carbon. Moreover, the treatment efficiency of adsorbents in the presence of competing compounds will be affected [70,71]. In addition to the adsorption stage, the desorption or regeneration steps must also be included, especially when the goal of the adsorption process is to recover value-added compounds from HTL-AP [16,70,72]. Addressing cost factors, including adsorbent procurement, regeneration, disposal, and energy needs for water recycling, is essential, alongside ensuring that adsorbents effectively eliminate toxic organics from HTL-AP without removing the beneficial nutrients in recycled water [5].

### 3.4. Overall comparison of different secondary separation techniques

The final goal for all secondary separation/treatment methods is to improve the properties of HTL-AP wastewater and the overall HTL process economy by producing reusable water and value-added products via resource recovery. Table 3 presents a comparison of commonly reported HTL-AP secondary separation/treatment methods from a process engineering point of view. Currently, biological/chemical conversion processes, including widely studied AD and HTG, suffer from process complexity, high energy demand, and related environmental impacts such as GHG emission [1,11]. Regarding the secondary separation

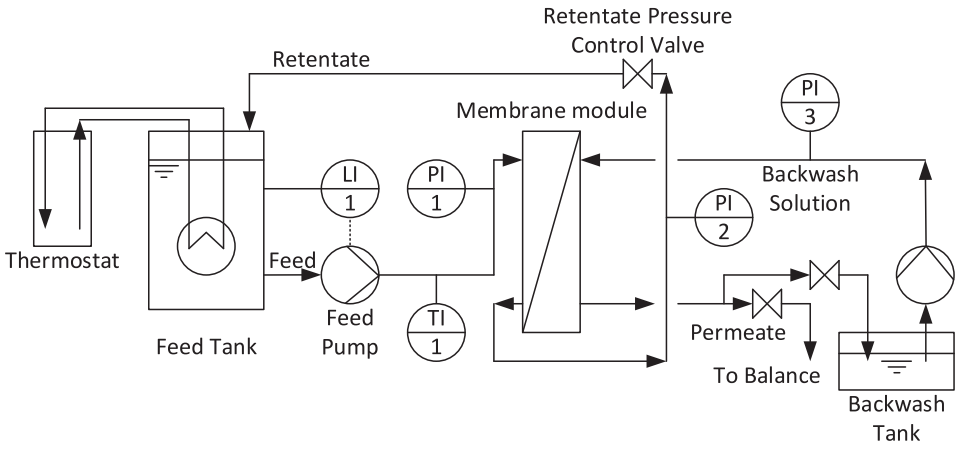



**Fig. 6.** Schematics of the membrane filtration setup for the treatment of HTL-AP. Adapted from [50].

processes, adsorption faces downsides such as regeneration issues and selective removal efficiency for specific target compounds. However, membrane processes have shown potential for resource recovery, significantly reducing negative wastewater properties while having high scalability. Coupling membrane filtration cascades with chemical precipitation (i.e., struvite) could further recover nutrients from HTL-AP, improving overall process economy [55,57,73].

Comparisons provided in Table 3 are qualitative, and a comprehensive evaluation using quantitative indicators, such as treatment efficiency, capital and operating costs, and environmental impact, requires explicit TEA and LCA studies. These studies should be conducted under identical process conditions to isolate the effects of algae biomass feedstock type, HTL reaction parameters, and the primary separation step on the performance of secondary treatment, separation, or valorization pathways for HTL-AP [4,74]. The recent study by Jiang et al. [7] compared five options for the treatment of HTL-AP from sewage sludge before directing it to a downstream wastewater treatment facility (i.e., activated sludge process). The HTL-AP was obtained from the sludge (slurry with a solid loading of 25 wt%) of the same wastewater treatment facility using a continuous-flow HTL at 350 °C and 20 MPa using gravity settling as primary separation. Treatment options were:

1- Baseline process (no COD reduction): Ammonia stripper ($NH_3$ product) + Thermal oxidizer ($N_2$ product)
2- Moderate COD reduction of HTL-AP (sulfur-tolerant catalytic hydrothermal gasification) + Ammonia stripper + Thermal oxidizer
3- Deep COD reduction (catalytic hydrothermal gasification) + Ammonia stripper + Thermal oxidizer
4- Deep COD reduction (steam-phase catalytic reduction of wastewater) + Ammonia stripper + Thermal oxidizer
5- Deep COD reduction (ambient-pressure catalytic upgrading) + Ammonia stripper + Thermal oxidizer

The ambient-pressure catalytic upgrading pathway was indicated as giving the best performance, reducing the minimum selling price of the fuel by 20 % and GHG emissions by 39 %. These results highlight the importance of using mild treatment methods that recover valuable by-products, such as fertilizers, to improve the economic and environmental performance of the HTL.

## 4. Application of HTL-AP

### *4.1. Effect of HTL-AP recycling as the reaction medium of the HTL process*

The HTL reaction typically uses water as its medium, and numerous researchers have suggested the recirculation of HTL-AP (Fig. 7), at specific concentrations mixed with pure water due to its cost efficiency, financial practicality, ease of implementation, and scalability, which collectively minimizes the need for fresh water [11,75]. Based on Table 4, which summarizes key studies dedicated to the reuse of HTL-AP as the HTL reaction medium in consecutive recycle steps, this approach generally increases the biocrude yield (reaching up to 50 %) and energy recovery [51]. Additionally, the biocrude produced using recycled HTL-AP exhibits slightly better or comparable properties, such as HHV and N or O content, while the volume of HTL-AP generated progressively declines after each cycle. It is worth mentioning that usually the HTL-AP is recycled to the HTL reactor without secondary treatment. Also, it should be noticed that recycled HTL-AP is diluted with fresh water in some studies. The enhanced biocrude yield is primarily attributed to acylation and polymerization reactions, in which low molecular weight compounds facilitate biomass degradation during HTL, promoting the transfer of light polar organics from the aqueous phase to the oily phase [75,76]. Despite these benefits, the accumulation of components such as S and N in HTL-AP can impair the reaction system [59]. Repeated recycling may lead to an increase in N content in the biocrude due to Maillard reactions between reducing sugars and protein derivatives in the HTL-AP [51]. The presence of nitrogenous compounds in HTL-AP can lead to formation of harmful NOx gases during the combustion of the biocrude produced from recycled HTL-AP, posing additional environmental risks [4,51]. Further, inorganic impurities resulting from reactor wall corrosion (e.g., Ni from INCOLOY 825 alloy) can accumulate through repeated HTL-AP recycling [10,43]. These components can deactivate heterogeneous catalysts through fouling and poisoning, while also causing undesirable enrichment of these elements in the biocrude product. As highlighted by Rajan et al. [51], pretreatment or employing a blowdown stream to remove accumulated components, evidenced by increased TOC levels, can improve the performance of HTL-AP recirculation. On the other hand, the concentrated organics in HTL-AP become more recalcitrant to further conversion in the HTL reactor after multiple recycling and can facilitate subsequent valorization processes such as AD or microalgae cultivation [6,10]. Additionally, when concentrated compounds like phenols and carboxylic acids in recirculated HTL-AP may be recovered via methods such as solvent extraction [77], adsorption [5], cation exchange [78], or membrane separation [19]. Therefore, a sustainable recirculation cycle must account for

**Table 3**
Comparison of common secondary separation and treatment methods applied to HTL-AP.

| Method | Advantages | Disadvantages |
|---|---|---|
| Anaerobic Digestion (AD) | • High treatment efficiency (biological conversion)<br>• Energy recovery (hydrogen and methane)<br>• Low environmental impact | • Limited nutrient recovery/removal<br>• Operational complexity<br>o Long residence time<br>o Toxic organics in HTL-AP induce an inhibitory effect on microorganisms<br>• Equipment cost<br>• Scalability and large footprint requirement |
| Gasification (HTG) | • High treatment efficiency (thermochemical conversion)<br>• Rapid reaction<br>• Produces syngas and char (potential energy/fuel value) | • Limited nutrient recovery/removal<br>• High operational demands due to elevated temperature and pressure<br>• Equipment cost<br>• Product gas separation/purification is required<br>• Environmental impacts, such as GHG emissions due to larger energy consumption<br>• Catalyst requirement and deactivation |
| Adsorption | • Use of cost-efficient and green adsorbents (e.g., biochar)<br>• Operation under mild conditions, resulting in lower environmental impact due to reduced energy demand<br>• Scalability | • No energy recovery<br>• Selective removal efficiency for specific target compounds and competing contaminants (organic/inorganic)<br>• Adsorbed compounds require desorption in the form of a concentrate stream, which adds process complexity<br>• Concentrate stream requires further separation/purification<br>• Adsorbed compounds may transfer to the regeneration waste stream<br>• Environmental impacts related to the disposal of spent adsorbent and regeneration waste may not be negligible |
| Membrane Filtration | • High removal efficiency of both organic and inorganic compounds<br>• Wide range of MWCOs (MF, UF, NF, RO) allows selective separation of compound fractions<br>• High nutrient recovery<br>• Operation under mild conditions, resulting in lower environmental impact due to reduced energy demand<br>• Scalability | • No energy recovery<br>• Concentrate/reject stream requires further separation/purification<br>• Maintenance costs due to fouling mitigation strategies, such as backwash and cleaning |
| Chemical Precipitation (Struvite Production) | • High nutrient recovery in fertilizer form to support algae cultivation<br>• Operation under mild conditions, resulting in lower environmental impact due to reduced energy demand<br>• Scalability | • No energy recovery<br>• Minimal removal efficiency towards organics<br>• pH adjustment/control complexity<br>• High environmental impact due to chemical handling<br>• Additional reactant cost |

multiple factors, including the trade-offs between the costs of separation, treatment, blowdown, heat transfer, improvement/deterioration of biocrude yield, HHV, N/O content, and the final management of highly concentrated HTL-AP.

### 4.2. *Effect of HTL-AP recycling as cultivation medium on algae growth*

For the cultivation of microalgae as the HTL feedstock fresh water and nutrients are a direct cost for the HTL biocrude production. Accordingly, many studies have investigated the application of various wastewater streams as the nutrient source for algae cultivation [6,86]. Since nutrient-rich HTL-AP is produced in large amounts as a by-product of the HTL reaction, its application either as an algae cultivation medium rich in nutrients or the HTL reaction medium could significantly improve the economy of the HTL system and solve the problem of HTL-AP disposal.

The chemical composition of HTL-AP (C, O, and N content of cyclic compounds) and concentration of heavy metals vary depending on the type of microalgae biomass used and the operating conditions [87]. Approximately 20 % of C and over 50 % of N from the feedstock are transferred into the HTL-AP [6,34]. N primarily exists as ammonium or ammonia, while C is present as organic acids like acetic acid, propanoic acid, as acetamide, and as methylpyrazine [88]. Utilizing the HTL-AP as a nutrient source for microalgal cultivation in a closed-loop system could significantly lower nutrient costs [11]. The available studies in this regard are summarized in Table 5. Overall, algae cultivation in HTL-AP demonstrates higher/comparable biomass concentrations than conventional synthetic media [51]. However, most of the research studies report pH adjustment and dilution of HTL-AP (with large dilution factors, i.e., 1000) without any secondary separation/treatment. Nutrient components such as N, P, and short-chain organic acids can promote microalgal growth [89], with P being particularly critical for forming adenosine triphosphate (ATP), phospholipids, RNA, and DNA in microalgae [51]. High concentrations of organic compounds in HTL-AP can enhance mixotrophic microalgal growth [39,90]. However, HTL-AP also contains toxic compounds such as phenols, cyclic amines, amides, and amino phenols that can inhibit algal growth, though their toxicity varies with concentration and algae species [10]. Ammonia in the growth medium is known to suppress algal growth, necessitating pH adjustments to maintain neutral conditions when recycling HTL-AP for algae cultivation [10,91]. Heavy metals, such as nickel, originating from reactor materials, flocculants like aluminum, and biomass contaminated during cultivation, further inhibit microalgal growth. Toxicity from high concentrations of organic molecules also necessitates the dilution of HTL-AP [92]. However, growth inhibition in some studies has also been attributed to the absence of essential nutrients rather than inadequate dilution [51,93]. Nutrient composition in HTL-AP can also be affected by the separation method employed during HTL processing, such as solvent-based transfer of organophosphates. The accumulation of organic molecules and toxic compounds that cannot be degraded by microalgae necessitates pretreatment of the HTL-AP to reduce inhibitory effects and ensure safe disposal, as it would else accumulate over successive cycles [6,10].

Accordingly, due to algae growth inhibition effects and the requirement of large dilution factors, cultivation of HTL algal feedstock as a standalone recycle process might not be feasible, and combination with other HTL-AP valorization methods should be considered in future studies for closed-loop HTL-AP biocrude production. In addition, some studies (Table 5) cultivate algae strains different from those used in the HTL process, which might not be useful for scale-up. For example, one species is converted into biocrude, and then a different species is used to grow on the resulting HTL-AP as part of a toxicity assessment. However, for the process to be truly sustainable and circular, the same species should ideally be cultivated on the HTL-AP.

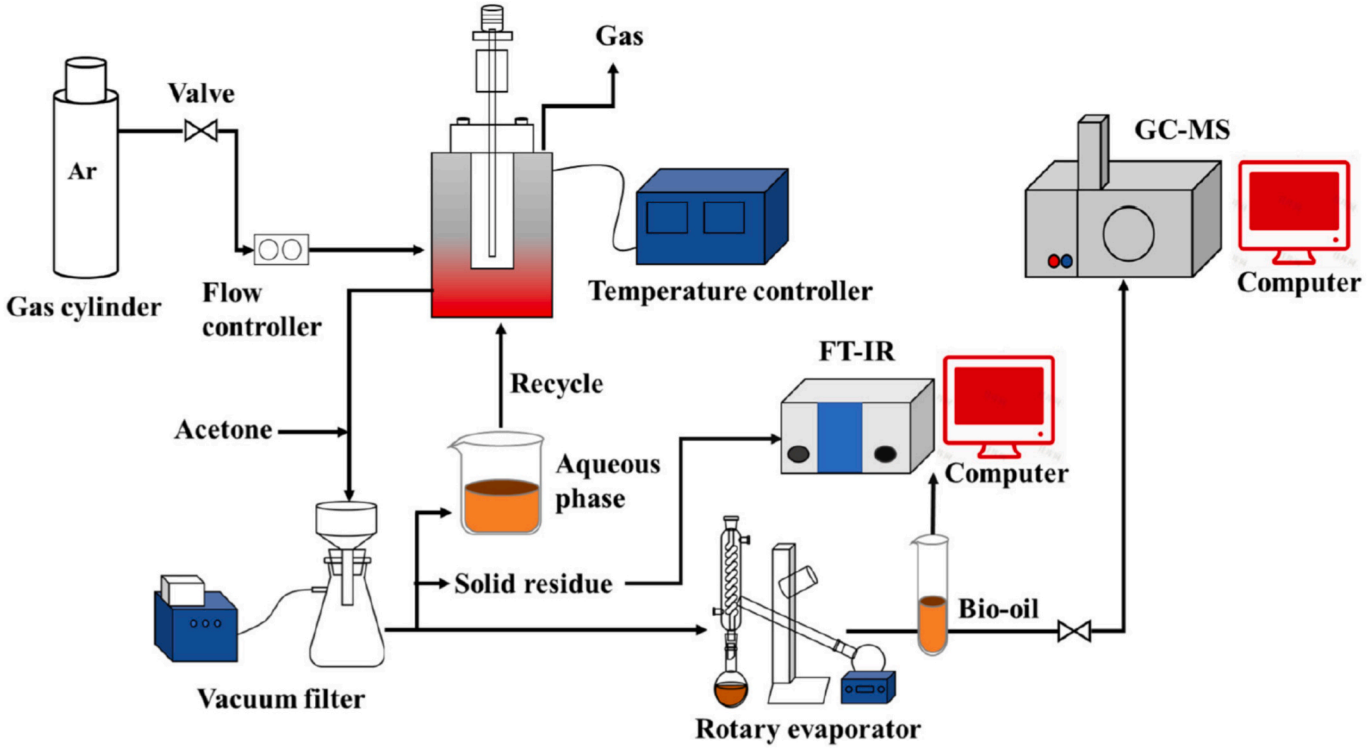



**Fig. 7.** Experimental work-up of HTL biocrude production/separation from other by-products using the solvent extraction method and recirculation of HTL-AP as HTL reaction medium. Reprinted from [79], with permission from Elsevier.

## 5. Synthetic HTL-AP and prediction of HTL-AP properties

The use of synthetic wastewater is a common strategy in treatment research to evaluate process performance and investigate underlying mechanisms under controlled conditions. In the context of HTL-AP, many studies focused on separation processes have either built costly HTL systems or relied on aged samples [9,21], highlighting a gap in the development of synthetic HTL-AP. A well-designed synthetic alternative could reduce the need for resource-intensive HTL runs conducted solely for HTL-AP generation, while providing realistic aqueous matrices for downstream treatment/separation investigations. Studying synthetic wastewater offers certain advantages, but creating a realistic synthetic version of HTL-AP is particularly challenging due to its highly complex composition. Some studies have attempted to generalize wastewater properties such as TOC, COD, and $NH_4^+$-N. While the type of biomass is typically known in these studies, details regarding its exact composition, such as the ratio of proteins, lipids, and carbohydrates, and the specific HTL reaction conditions, remain unclear. Although techniques like gas chromatography-mass spectroscopy (GC–MS) have been used to determine the chemical composition of HTL-AP, only a limited number of studies have quantified the concentration of these compounds, often relying on peak area for qualitative comparisons rather than calibration curves. On the other hand, one challenge lies in the fragmentation of larger compounds during GC–MS analysis, primarily due to the high injector and oven temperatures, which can thermally degrade thermolabile molecules. This degradation often mimics, to some extent, the harsh thermal conditions of the HTL reactor, potentially leading to secondary fragmentation that does not accurately represent the original compound composition. As a result, the GC–MS data may reflect breakdown products rather than the intact target molecules, complicating structural identification and quantification [6]. In general, there is a lack of comprehensive studies that in detail explore the properties of HTL-AP. Research by Madsen et al. [105] demonstrated that key wastewater parameters, including TOC, TN, pH, and individual compound concentrations, often can be predicted based on the HTL of biomass mixtures. Additionally, some researchers have developed predictive fitted models to estimate HTL-AP properties. Leng et al. [106] used a machine learning (ML) approach and provided new insights into understanding HTL-AP formation and properties, which reduced the need for time-consuming experiments.

## 6. Conclusions, perspectives, and future prospects

Initially, research on algae HTL has been centered on optimizing biocrude recovery, with by-products such as biochar, HTL-AP, and gaseous products being recovered as secondary outputs. However, there has been a shift toward valorization and recycling of HTL by-products. Despite this, resource recovery from HTL-AP using environmentally friendly methods with high scale-up potential, particularly membrane technology, has hitherto received limited attention in research.

Based on the recent advancements in this field, there is still considerable room for improvement in primary and secondary separation techniques, particularly in their efficiency, scale-up strategies, and the overall treatment and valorization of HTL-AP. Researchers should try to specify their exact primary separation method applied for the separation of HTL-AP and biocrude with full details, as this information is crucial for scale-up studies and elucidating the effect of separation/treatment on the HTL-AP toxicity and algae growth inhibition. Comparative studies with a focus on the effect of the primary separation methods effect on biocrude yield, HHV, and composition of organic compounds in the HTL-AP using identical algae feed biomass strain and HTL operational parameters are required. Also, Comparative investigations regarding the type of primary and secondary separation/treatment processes' effect on treated HTL-AP's toxicity and inhibition of algae growth using the same algae as HTL feedstock and the same HTL-AP characteristics are required. Although research has shown that solvent extraction for the separation of biocrude from HTL-AP leads to higher yield, future studies should focus on developing primary HTL-AP separation methods without solvents to reduce operating costs and environmental concerns. A few available studies have shown the potential

**Table 4**
Performance of HTL reactors using recycled HTL-AP.

| Algae type | HTL-AP primary separation method | HTL-AP secondary separation/treatment method | HTL-AP dilution factor | Number of recycles | Biocrude yield (%) (before/after recycle) | Biocrude HHV (MJ/kg) (before/after recycle) | Effect observed | Reference |
|---|---|---|---|---|---|---|---|---|
| *Chlorella vulgaris* | Solvent extraction (DCM) | None | No dilution | 3 | 29.39/38.87 | 33.87/33.46 | • Energy Recovery increased from 41.13 to 53.75 %.<br>• Biocrude N content reduced from 8.20 to 7.69 %. | [75] |
| *Spirulina platensis* | Solvent extraction (DCM) | None | From 0:30 to 30:30 (HTL-AP/water concentration) | 3 | 30.07/39.77[a] | 34.67/30.15[a] | • Energy recovery increased from 56.32 to 64.78[a].<br>• Biocrude N content increased from 9.79 to 15.37 %[a].<br>• As the number of recycling cycles increased, certain organic compounds in the aqueous phase may have approached saturation, diminishing their enhancing effect on bio-oil yield. | [80] |
| *Chlorella* sp. + Aspen wood sawdust | Solvent extraction (DCM) | None | No dilution | 1 | 11.13/9.16 | 30.86/34.75 | • Biocrude N content increased from 4.50 to 4.57 %. | [81] |
| *Gracilaria gracilis*<br>*Cladophora glomerata* | Solvent extraction (DCM) | None | No dilution | 2 | 16.9/24.6<br>15.71/25 | 33.06/NA<br>36.01/NA | • The effect of HTL-AP recycling on other parameters, such as HHV and energy recovery, was not studied. | [82] |
| *Scenedesmus abundans* | Solvent extraction (Hexane) | None | Partial dilution | 3 | 43/47.91 | 39.1/38.03 | • Biocrude N content increased from 2.12 to 2.23 %.<br>• pH of HTL-AP increased from 6.26 to 6.83. | [83] |
| *Spirulina platensis* | Solvent extraction (DCM) | None | No dilution | 1 | 41.3/49.2 | 35.3/32.4 | • Energy recovery increased from 77.3 to 81.1 %.<br>• Biocrude N content increased from 7.4 to 8.3 %. | [84] |
| *Chlorella vulgaris* | 6 μm filter paper[b] | None | No dilution | 7 | 14.3/42.2 | 34.8/32.3 | • Energy recovery increased from 25 to 68 %.<br>• Biocrude N content increased from 4.7 to 8.9 %.<br>• pH of HTL-AP decreased from 6 to 4. | [76] |
| C-Phycocyanin[c] | Solvent extraction (DCM) | None | Water to HTL-AP mass ratio of 1:5 | 1 | 32.2/37.4 | NA | • The content of nitrogen-containing compounds increased from 49.12 to 59.26 %. | [85] |
| Algae from a pilot algal wastewater treatment system | Solvent extraction (DCM) | None | 0.94 g HTL-AP per g biomass | 1 | 22.87/31.28 | 35.5/35 | • Heteroatom content was increased slightly in the biocrude produced with recirculation of untreated HTL-AP.<br>• Biocrude N content increased from 6.6 to 6.8 %.<br>• Energy recovery increased from 35.9 to 48.5 %. | [9] |
| | Solvent extraction (DCM) | NF | 0.61 g NF retentate per g biomass | | 22.87/39.5 | 35.5/35.8 | • Separating $NH_3$-N from organics during NF led to almost constant N content of biocrude produced with recirculation of treated HTL-AP.<br>• Biocrude N content increased from 6.6 to 6.8 %.<br>• Energy recovery increased from 35.9 to 62.6 %. | |

NA: Not available.
[a] Obtained after 1 cycle using an HTL-AP to water concentration of 25:5.
[b] Oily solid residues after filtration were washed with DCM.
[c] Model compound representing the microalgae protein.

**Table 5**
Performance of microalgae cultivation systems using recycled HTL-AP.

| Algae type for HTL/for cultivation tests using recycled HTL-AP | HTL-AP primary separation method | HTL-AP secondary separation/treatment method | HTL-AP contents (prior to dilution) (mg $L^{-1}$) | HTL-AP Dilution factor | pH adjustment/ Nutrient make-up | Remarks | Reference |
|---|---|---|---|---|---|---|---|
| *Nannochloropsis* sp./*(Chlorella vulgaris 1067, Chlorella regularis* var. *minima, Chlorella pyrenoidosa, Scenedesmus quadricauda,* and *Maeruginosa)* | Filter paper and solvent extraction (ethyl ether) | None | TOC: 35319.30<br>$NH_3$-N: 8291<br>Total phosphorus (TP): 554 | 10, 20, 30, 40 | Yes/no | • No comparison with an HTL-AP free culture medium.<br>• Algae were able to grow on HTL-AP nutrients.<br>• Performance was strain dependent. | [94] |
| *Tetraselmis* sp. | Solvent extraction (DCM) | None | TOC: 13,917<br>$NH_3$-N: 1803<br>TP: 504.7 | 0–1000 | No/yes | • Biomass yield was slightly better than that of the control culture medium.<br>• A dilution factor of 300 was selected for the best result.<br>• 50 % nutrient requirement was replaced by HTL-AP.<br>• 3 cultivation cycles. | [89] |
| *Nannochloropsis gaditana* | Centrifugation and filtration (no solvent) | None | TOC: 3072<br>Total nitrogen (TN): 767<br>TP: 117 | NA | No/yes | • Results show that *Nannochloropsis gaditana* was able to grow in AP medium, almost comparable to f/2 medium. | [95] |
| *Chlorella sorokiniana*, *Chlorella vulgaris*, *Galdieria sulphuraria* | Filter paper (2.5 μm) | None | TN: 3700<br>$NH_4^+$-N: 403<br>Total $PO_4^{3-}$-P: 1460 | 0, 15, 20, 25, 30 | No/no | • There were no significant differences in lipid contents and composition of algae grown on HTL-AP compared to the standard media.<br>• The results indicate that nutrient recovery is species-dependent | [29] |
| *Chlamydomonas reinhardtii* | Vacuum filtration | None | TOC: 32,700<br>$NH_4^+$-N: 2400<br>$PO_4^{3-}$: 5300 | 140 | No/yes | • Microalgae growth was inhibited significantly, indicating that the AP must be treated before recycling to the culture medium. | [25] |
| *Scenedesmus* sp. | Solvent extraction (DCM) | None | TOC: 9150<br>$NH_3$: 668<br>$PO_4^{3-}$: 729 | Various (5–136), the nutrient replacement percentage was the target | No/yes | • Ammonia toxicity at lower dilutions.<br>• Up to 50 % nutrient replacement using AP was achieved. | [96] |
| *Oocystis* sp. | Solvent extraction (DCM) | None | TOC: 10,550<br>$NH_4^+$-N: 1550<br>$PO_4^{3-}$: 920 | | | | |
| *Scenedesmus almeriensis* | Filter paper | None | TOC: 12,565<br>$NH_4^+$-N: 3514.6<br>$PO_4^{3-}$: 113.7 | Various (313–667), the nutrient replacement percentage was the target | No/yes | • Microalgae showed comparable growth to the standard medium, even when 75 % of the nutrients were replaced with HTL-AP.<br>• Algal tolerance to AP varied depending on the strain.<br>• Using AP derived from the SCWG process did not result in noticeably better algal growth compared to HTL-AP.<br>• HTL-AP required a higher dilution level than SCWG-AP to be usable. | [91] |
| *Nannochloropsis gaditana* | | | TOC: 13,259<br>$NH_4^+$-N: 4509<br>$PO_4^{3-}$: 3393 | | | | |
| *Scenedesmus almeriensis* | | Supercritical water gasification (SCWG) | TOC: 9181<br>$NH_4^+$-N: 4232.7<br>$PO_4^{3-}$: 187.1 | | | | |
| *Nannochloropsis gaditana* | | | TOC: 7665<br>$NH_4^+$-N: 5240.7<br>$PO_4^{3-}$: 2442.4 | | | | |
| *Desmodesmus* sp. | Solvent extraction (DCM) | None | TOC: 9000<br>$NH_4^+$-N: 956<br>$PO_4^{3-}$: 160 | 250 | No/yes | • Cells preferentially utilized $NH_4^+$-N rather than $NO_3$-N.<br>• In the fifth cycle, *Desmodesmus* sp. exhibited the same growth with diluted HTL-AP and half the nutrients of the COMBO medium as it did in the standard medium. | [93] |

(*continued on next page*)

**Table 5** (*continued*)

| Algae type for HTL/for cultivation tests using recycled HTL-AP | HTL-AP primary separation method | HTL-AP secondary separation/treatment method | HTL-AP contents (prior to dilution) (mg $L^{-1}$) | HTL-AP Dilution factor | pH adjustment/ Nutrient make-up | Remarks | Reference |
|---|---|---|---|---|---|---|---|
| | | | | | | • A total of five HTL-AP recycling cycles were investigated.<br>• Over the cycles, inhibitory compounds (e.g., pyrrolidones, phenols, cyclic dipeptides) accumulated and retained much of the AP-nitrogen, indicating that long-term recycling would require additional pretreatment. | |
| *Desmodesmus* sp. | Solvent extraction (DCM) | None | TOC: 9000<br>$NH_4^+$-N: 956<br>$PO_4^3$: 160 | Various (20–623), the nutrient replacement percentage was the target | No/yes | • A substantial reduction in growth was observed when using water-diluted HTL-AP (without combination with standard medium).<br>• Growth of *Desmodesmus* sp. with diluted HTL-AP and 50 % of the nutrients of the standard medium was identical to that of the standard medium.<br>• External nutrients (such as Mg) must be supplied upon HTL-AP recycling to avoid growth reduction. | [43] |
| *Chlorella vulgaris* | Filter paper | None | TOC: 22,300<br>$NH_4^+$: 3550<br>$PO_4^3$: 3130 | 50–1000 | Yes/yes | • Acclimation to the AP is effective in improving microalgal growth rates, reducing the initial inhibitory effects.<br>• The addition of AP resulted in lower-quality biomass for biofuel production via HTL.<br>• Prolonged cultivation periods led to improved biomass quality.<br>• Performance was strain dependent. | [97] |
| *Dunaliella salina* | Centrifugation and filtration (no solvent) | None | TOC: 10,240<br>$NH_4^+$-N: 3040<br>TP: 1510 | 400 | No/yes | • Utilization of HTL-AP mixed with seawater enhanced the biomass productivity by 16.7 % due to mixotrophic growth by using the HTL-AP organics.<br>• Utilization of HTL-AP for algae cultivation showed an insignificant difference in the biocrude yield.<br>• Biocrude quality improved when using recycled HTL-AP for algae cultivation, with a 60.7 % reduction in N-compounds and increases in hydrocarbons (1.7 × ) and fatty acids/esters (12.6 %). | [98] |
| *Chlorella vulgaris* | Gravity settling | None | TOC: 16,778<br>$NH_4^+$-N: 1943<br>$PO_4^3$: 1370 | 15 | No/yes | • Growth stopped in the beginning period, and no change was observed. | [34] |
| | | Activated carbon[a] | TOC: 2136<br>$NH_4^+$-N: 1981<br>$PO_4^3$: 21.38 | | | • Better growth than the algae cultivated with standard medium. | |
| *Phaeodactylum tricornutum* | Gravity settling | None | TOC: NA[b]<br>$NH_4^+$-N: 8440<br>$PO_4^3$: 2415 | 25 | Yes/yes | • The growth achieved with the diluted HTL-AP was equal to standard medium, although a 4-day adaptation period was observed. | [99] |
| *Ammi visnaga/Chlorella minutissima* | Solvent extraction (Diethyl ether) | None | TOC: 64155 ± 17631<br>$NH_4^+$-N: NA<br>$PO_4^3$: NA | 50, 25, 12.5, 6.25 | Yes/no | • A dilution factor greater than 12.5 appeared to have a detrimental effect on microalgae. | [100] |

(*continued on next page*)

**Table 5** (*continued*)

| Algae type for HTL/for cultivation tests using recycled HTL-AP | HTL-AP primary separation method | HTL-AP secondary separation/treatment method | HTL-AP contents (prior to dilution) (mg $L^{-1}$) | HTL-AP Dilution factor | pH adjustment/ Nutrient make-up | Remarks | Reference |
|---|---|---|---|---|---|---|---|
| *Scenedesmus obliquus* | Solvent extraction (DCM) | None | COD: 742<br>$NH_3$: 478<br>$PO_4$: 5.89 | 1, 2, 1.5, 3, 4 | No/yes | • Maximum biomass yield was obtained from a mixture with a 1.5 dilution factor. | [101] |
| *Chlorella sorokiniana NIES 2173/(Chlorella sorokiniana NIES 2173, Chlorella vulgaris NIES 227 and CCALA 256, Parachlorella kessleri CCALA 251 and 253)* | Filtration (50 μm sieve) | None | Total carbon (TC): 33,400<br>$NH_4^+$: 3750<br>$PO_4^3$: 2850 | 200 | Yes/yes | • A total of five HTL-AP recycling cycles were investigated.<br>• Recycling HTL-AP led to biomass with suboptimal properties.<br>• Slow accumulation of lipids occurred.<br>• A reduced overall energy content of the biomass was observed. | [58] |
| *Chlorella* sp. | Solvent extraction (DCM) | None | TOC: 20,000<br>$NH_4^+$-N: 4800<br>TP: 330 | 10 | No/no | • Growth of algae in HTL-AP decreased and reached almost 0 after 8 days. | [15] |
| *Nannochloropsis* sp./*Chlorella vulgaris 1067*<br><br>*Chlorella* sp./*Chlorella vulgaris 1067*<br><br>*Nannochloropsis* sp./*Chlorella vulgaris 1067*<br><br>*Chlorella* sp./*Chlorella vulgaris 1067* | Vacuum filtration<br><br><br><br>Solvent extraction (ethyl ether) | None | TOC: 35,480<br>TN: 12,888<br>TP: 968<br>TOC: 14,626<br>TN: 1729<br>TP: 82<br>TOC: 80,000<br>TN: 6867<br>TP: 453<br>TOC: 52,180<br>TN: 2473<br>TP: 16 | Various, to obtain 4 different levels of TN concentrations (50, 150, 250, and 500 mg $L^{-1}$) the HTL-AP was diluted with distilled water. | Yes/no | • The results showed that both the type of feedstock and the method used to separate biocrude from the aqueous phase affect biomass yield and nutrient recovery.<br>• *Chlorella vulgaris* exhibited the highest growth in a 28.6 % concentration of HTL-AP, which was derived from *Chlorella* sp. using vacuum filtration.<br>• For the *Nannochloropsis* sp., HTL-AP separated using ethyl ether proved to be more suitable for the growth of *Chlorella vulgaris*, whereas for the *Chlorella* sp. feedstock, HTL-AP obtained through vacuum filtration was more favorable for its growth. | [102] |
| *Picochlorum* sp. | NA | None | TOC: 34,920<br>$NH_4^+$: 8966<br>$PO_4^3$: 3072 | 1000 (0.1 v%) | No/yes | • 8.6x increase in exponential cells grown with 0.1 v% HTL-AP compared to controls.<br>• Algae grown on 0.1 v% HTL-AP had 2.1x higher protease activity. | [103] |
| *Spirulina* sp./mixture of: *Spirulina* sp., *Scenedesmus* sp., *Chlorella vulgaris*, and *Nannochloropsis oculata* | NA | Adsorption (Zeolite) | NA | 20 and 100 | No/yes | • The average Soluble COD removal of the cultivation reactor was 70.3 and 77 % without and with zeolite, respectively.<br>• The average $NH_4^+$ removal of the cultivation reactor was 83.5 and 96.2 % without and with zeolite, respectively.<br>• The long-term existence of zeolites also efficiently promoted microalgal growth. | [104] |
| *Chlorella* sp./*Scenedesmus* sp. | Gravity settling | I) First struvite precipitation, then HTG, then adsorption using activated carbon<br><br>II) First struvite precipitation, then ammonia stripping<br>III) First struvite precipitation, then ammonia stripping, then adsorption using activated carbon | TOC: NA<br>$NH_3$: 11600—13900<br>$PO_4^3$: 7700—9800 | 125, 250, and 500<br><br>125 | Yes/yes | The best specific growth rate (1.2 $d^{-1}$) was achieved with a 125 dilution factor. A growth rate of 0.7 $d^{-1}$ was achieved (1.2 $d^{-1}$ for standard medium). A growth rate of 1.2 $d^{-1}$ was achieved (1.2 $d^{-1}$ for standard medium). Decreasing organic concentration: HTL-AP > HTL-AP(I) > HTL-AP(II) > HTL-AP(III) | [60] |

NA: Not available.

[a] SCWG was tested for secondary treatment of HTL-AP; however, due to the low yield of HTL-AP from SCWG, only the activated carbon-treated HTL-AP was used for algae cultivation experiments.

[b] 15 % of the feedstock carbon ended up in the HTL-AP.

for cost-effective yet efficient treatment of HTL-AP. More studies regarding the potential applications of membrane technology are required. These should include TEA and LCA studies of the membrane filtration sequence that also take the environmental impacts of the whole process and expenses related to membrane fouling mitigation strategies, such as backwash and physical/chemical cleaning, into account. Recycling of membrane effluents from membrane filtration as the secondary separation step, for either HTL reaction medium or algae culture medium, should be investigated. Future research should include process integration with the aim of: I) Combining multiple green processes, such as membrane filtration cascades (MF, UF, NF, RO) for minimum membrane fouling and fractionation of value-added organic products. II) Maximizing inorganic resource recovery using processes such as chemical precipitation of concentrated HTL-AP (i.e., struvite production). III) Maintaining nutrient levels required for the growth of algal feedstock. IV) lowering the concentration of organics with growth inhibition effects if recycling the HTL-AP as HTL reaction medium or algae growth medium. V) Minimizing freshwater intake (make-up) into the whole algae HTL loop. After primary or secondary separation, HTL-AP is usually diluted, which requires a large freshwater intake. In order to close the loop, future studies should be directed towards the highest possible valorization and elimination of excess nutrients/inhibitory organics to lower the HTL-AP dilution factor during the recycling step and minimize wastewater discharge. Moreover, if solvent extraction is used as the primary separation method, the presence of trace organic solvents in the HTL-AP should be taken into account in toxicity studies. While previous studies have investigated the effects of HTL operating parameters and biomass source on HTL-AP characteristics, a gap remains in efficient and cost-effective methods for quantifying correlations between biomass composition, HTL parameters, and AP properties. Further research using advanced mathematical modeling, including ML techniques, empirical correlations, mechanistic modeling based on reaction kinetics and thermodynamics, and data-driven statistical analyses e.g., principal component analysis or regression modeling is necessary to incorporate biomass constituents, HTL reaction parameters (such as temperature, pressure, and residence time, and primary separation methods like solvent extraction) to predict HTL-AP properties. This would be particularly valuable in HTL-AP treatment studies, where generating reliable synthetic HTL-AP could reduce the need for costly and resource-intensive HTL experiments solely for AP production. By accurately predicting HTL-AP composition, researchers could simulate realistic aqueous matrices for downstream treatment testing without having to operate the full HTL setup.

## CRediT authorship contribution statement

**Soorena Gharibian:** Writing – original draft, Methodology, Formal analysis, Data curation, Conceptualization. **Massimiliano Errico:** Writing – review & editing, Supervision, Project administration, Methodology, Funding acquisition, Data curation, Conceptualization. **Knud Villy Christensen:** Writing – review & editing, Supervision, Methodology, Data curation, Conceptualization.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Acknowledgments

This project has received funding from Horizon Europe, the European Union's Framework Programme for Research, and Innovation, under Grant Agreement No. 101122363 (SUSTEPS).

## Data availability

No data was used for the research described in the article.

## References

[1] J. Watson, et al., Valorization of hydrothermal liquefaction aqueous phase: pathways towards commercial viability, Prog. Energy Combust. Sci. 77 (2020) 100819.
[2] S.R. Ravichandran, et al., A review on hydrothermal liquefaction of algal biomass on process parameters, purification and applications, Fuel 313 (2022) 122679.
[3] T. Nguyen, et al., Valorization of the aqueous phase from hydrothermal carbonization of different feedstocks: challenges and perspectives, Chem. Eng. J. 472 (2023) 144802.
[4] M. Usman, et al., From biomass to biocrude: Innovations in hydrothermal liquefaction and upgrading, Energy Convers. Manage. 302 (2024) 118093.
[5] W. Farooq, Sustainable production of microalgae biomass for biofuel and chemicals through recycling of water and nutrient within the biorefinery context: a review, GCB Bioenergy 13 (6) (2021) 914–940.
[6] L. Leng, et al., Use of microalgae to recycle nutrients in aqueous phase derived from hydrothermal liquefaction process, Bioresour. Technol. 256 (2018) 529–542.
[7] Y. Jiang, et al., Aqueous-phase product treatment and monetization options of wet waste hydrothermal liquefaction: Comprehensive techno-economic and life-cycle GHG emission assessment unveiling research opportunities, Bioresour. Technol. 397 (2024) 130504.
[8] A. Agarwalla, K. Mohanty, A critical review on the application of membrane technology in microalgal harvesting and extraction of value-added products, Sep. Purif. Technol. (2024) 127180.
[9] T. Costa, et al., Valorizing Hydrothermal liquefaction aqueous phase via nanofiltration: Enhancing biocrude production from algal biomass, Bioresour. Technol. (2025) 132456.
[10] L. Leng, et al., Bioenergy recovery from wastewater produced by hydrothermal processing biomass: progress, challenges, and opportunities, Sci. Total Environ. 748 (2020) 142383.
[11] A. Swetha, et al., Review on hydrothermal liquefaction aqueous phase as a valuable resource for biofuels, bio-hydrogen and valuable bio-chemicals recovery, Chemosphere 283 (2021) 131248.
[12] H. Li, et al., Hydrothermal liquefaction accelerates the toxicity and solubility of arsenic in biowaste, J. Hazard. Mater. 418 (2021) 126341.
[13] S. Munasinghe-Arachchige, et al., Biofertilizer recovery from organic solid wastes via hydrothermal liquefaction, Bioresour. Technol. 338 (2021) 125497.
[14] M. Bagnoud-Velásquez, et al., Continuous catalytic hydrothermal gasification of algal biomass and case study on toxicity of aluminum as a step toward effluents recycling, Catal. Today 223 (2014) 35–43.
[15] J. Chen, et al., A novel strategy to simultaneously enhance bio-oil yield and nutrient recovery in sequential hydrothermal liquefaction of high protein microalgae, Energy Convers. Manage. 255 (2022) 115330.
[16] P.H. Chen, et al., Nutrient recycle from algae hydrothermal liquefaction aqueous phase through a novel selective remediation approach, Algal Res. 46 (2020) 101776.
[17] Y. Gu, et al., Advances in energy systems for valorization of aqueous byproducts generated from hydrothermal processing of biomass and systems thinking, Green Chem. 21 (10) (2019) 2518–2543.
[18] A. Sayegh, et al., Treatment of hydrothermal liquefaction wastewater with ultrafiltration and air stripping for oil and particle removal and ammonia recovery, J. Water Process Eng. 44 (2021) 102427.
[19] X. Zhang, et al., Advanced treatment of hydrothermal liquefaction wastewater with nanofiltration to recover carboxylic acids, Environ. Sci. Water Res. Technol. 4 (4) (2018) 520–528.
[20] R. Kizza, C. Eskicioglu, Ultrafiltration fractionation of potentially inhibitory substances of hydrothermal liquefaction aqueous phase derived from municipal sludge, Water Res. 257 (2024) 121703.
[21] X. Zhang, et al., Fouling mitigation and carbon recovery in nanofiltration processing of hydrothermal liquefaction aqueous waste stream, J. Membr. Sci. 614 (2020) 118558.
[22] Y. Zhu, et al., Techno-economic analysis of alternative aqueous phase treatment methods for microalgae hydrothermal liquefaction and biocrude upgrading system, Algal Res. 39 (2019) 101467.
[23] X. Zhuang, et al., A review on the stepwise processes of hydrothermal liquefaction (HTL): Recovery of nitrogen sources and upgrading of biocrude, Fuel 313 (2022) 122671.
[24] J.A. Ramirez, R.J. Brown, T.J. Rainey, A review of hydrothermal liquefaction bio-crude properties and prospects for upgrading to transportation fuels, Energies 8 (7) (2015) 6765–6794.
[25] C. Hognon, et al., Comparison of pyrolysis and hydrothermal liquefaction of Chlamydomonas reinhardtii. growth studies on the recovered hydrothermal aqueous phase, Biomass Bioenergy 73 (2015) 23–31.
[26] Zhou, Y., et al. Environment-enhancing energy: A novel wastewater treatment system that maximizes algal biofuel production and minimizes greenhouse gas emissions. in WEFTEC 2011. 2011. Water Environment Federation.
[27] Y. Zhou, et al., A synergistic combination of algal wastewater treatment and hydrothermal biofuel production maximized by nutrient and carbon recycling, Energy Environ. Sci. 6 (12) (2013) 3765–3779.

[28] M. Pham, et al., Chemical and biological characterization of wastewater generated from hydrothermal liquefaction of Spirulina, Environ. Sci. Technol. 47 (4) (2013) 2131–2138.
[29] L. Chen, et al., Recycling nutrients from a sequential hydrothermal liquefaction process for microalgae culture, Algal Res. 27 (2017) 311–317.
[30] M. Zheng, et al., Anaerobic digestion of wastewater generated from the hydrothermal liquefaction of Spirulina: Toxicity assessment and minimization, Energy Convers. Manage. 141 (2017) 420–428.
[31] L. Ruirui, et al., Application of zeolite adsorption and biological anaerobic digestion technology on hydrothermal liquefaction wastewater, Int. J. Agric. Biol. Eng. 10 (1) (2017) 163–168.
[32] H. Song, et al., Hydrothermal liquefaction of sewage sludge into biocrude: effect of aqueous phase recycling on energy recovery and pollution mitigation, Water Res. 226 (2022) 119278.
[33] Monnery, W.D. and W.Y. Svrcek, Successfully specify three-phase separators. Chem. Eng. Prog., 1994. 90: p. 29-29.
[34] B. Guo, et al., The effect of dichloromethane on product separation during continuous hydrothermal liquefaction of Chlorella vulgaris and aqueous product recycling for algae cultivation, Energy Fuels 36 (2) (2022) 922–931.
[35] Z. Cui, et al., Co-hydrothermal liquefaction of wastewater-grown algae and crude glycerol: a novel strategy of bio-crude oil-aqueous separation and techno-economic analysis for bio-crude oil recovery and upgrading, Algal Res. 51 (2020) 102077.
[36] D. Xu, P.E. Savage, Characterization of biocrudes recovered with and without solvent after hydrothermal liquefaction of algae, Algal Res. 6 (2014) 1–7.
[37] S.K. Ratha, et al., Hydrothermal liquefaction of algal feedstocks: the effect of biomass characteristics and extraction solvents, Renew. Sustain. Energy Rev. 156 (2022) 111973.
[38] J. Watson, et al., Effects of the extraction solvents in hydrothermal liquefaction processes: Biocrude oil quality and energy conversion efficiency, Energy 167 (2019) 189–197.
[39] D.L. Barreiro, et al., Hydrothermal liquefaction of microalgae: effect on the product yields of the addition of an organic solvent to separate the aqueous phase and the biocrude oil, Algal Res. 12 (2015) 206–212.
[40] S. Dong, Z. Liu, X. Yang, Exploration of hydrothermal liquefaction of multiple algae to improve bio-crude quality and carbohydrate utilization, Appl. Energy 361 (2024) 122861.
[41] L. Garcia Alba, et al., Hydrothermal treatment (HTT) of microalgae: evaluation of the process as conversion method in an algae biorefinery concept, Energy Fuels 26 (1) (2012) 642–657.
[42] Y. Li, et al., Quantitative evaluation of an integrated system for valorization of wastewater algae as bio-oil, fuel gas, and fertilizer products, Environ. Sci. Technol. 52 (21) (2018) 12717–12727.
[43] L.G. Alba, et al., Microalgae growth on the aqueous phase from hydrothermal liquefaction of the same microalgae, Chem. Eng. J. 228 (2013) 214–223.
[44] S. Gharibian, H. Hazrati, Towards practical integration of MBR with electrochemical AOP: improved biodegradability of real pharmaceutical wastewater and fouling mitigation, Water Res. 218 (2022) 118478.
[45] S. Esteki, et al., Combination of membrane bioreactor with chemical coagulation for the treatment of real pharmaceutical wastewater: Comparison of simultaneous and consecutive pre-treatment of coagulation on MBR performance, J. Water Process Eng. 60 (2024) 105108.
[46] Judd, S., The MBR book: principles and applications of membrane bioreactors for water and wastewater treatment. 2010: Elsevier.
[47] Z. Borazjani, et al., Computer-aided Exergy Evaluation of Hydrothermal Liquefaction for Biocrude Production from Nannochloropsis sp, Bioenergy Res. (2022) 1–13.
[48] Jones, S.B., et al., Process design and economics for the conversion of algal biomass to hydrocarbons: whole algae hydrothermal liquefaction and upgrading. 2014, Pacific Northwest National Lab.(PNNL), Richland, WA (United States).
[49] S.R. Shanmugam, S. Adhikari, R. Shakya, Nutrient removal and energy production from aqueous phase of bio-oil generated via hydrothermal liquefaction of algae, Bioresour. Technol. 230 (2017) 43–48.
[50] A. Sayegh, et al., Treatment of hydrothermal-liquefaction wastewater with crossflow UF for oil and particle removal, Membranes 12 (3) (2022) 255.
[51] P. SundarRajan, et al., Insights into valuing the aqueous phase derived from hydrothermal liquefaction, Renew. Sustain. Energy Rev. 144 (2021) 111019.
[52] H. Lyu, et al., Two-stage nanofiltration process for high-value chemical production from hydrolysates of lignocellulosic biomass through hydrothermal liquefaction, Sep. Purif. Technol. 147 (2015) 276–283.
[53] H. Lyu, et al., Monophenols separation from monosaccharides and acids by two-stage nanofiltration and reverse osmosis in hydrothermal liquefaction hydrolysates, J. Membr. Sci. 504 (2016) 141–152.
[54] A. Teella, G.W. Huber, D.M. Ford, Separation of acetic acid from the aqueous fraction of fast pyrolysis bio-oils using nanofiltration and reverse osmosis membranes, J. Membr. Sci. 378 (1–2) (2011) 495–502.
[55] O.P. Crossley, et al., Phosphorus recovery from process waste water made by the hydrothermal carbonisation of spent coffee grounds, Bioresour. Technol. 301 (2020) 122664.
[56] A. Sayegh, et al., Membrane distillation as a second stage treatment of hydrothermal liquefaction wastewater after ultrafiltration, Sep. Purif. Technol. 285 (2022) 120379.
[57] K. Szkadłubowicz, et al., Removal of contaminants from liquid after the hydrothermal carbonization of sewage sludge using a combination of membrane techniques and struvite precipitation, Water Resour. Ind. 33 (2025) 100285.
[58] A. Ramírez-Romero, et al., Aqueous phase recycling: impact on microalgal lipid accumulation and biomass quality, Environ. Sci. Pollut. Res. (2024) 1–15.
[59] L. Leng, et al., Valorization of the aqueous phase produced from wet and dry thermochemical processing biomass: a review, J. Cleaner Prod. 294 (2021) 126238.
[60] P.J. McGinn, et al., Strategies for recovery and recycling of nutrients from municipal sewage treatment effluent and hydrothermal liquefaction wastewaters for the growth of the microalga Scenedesmus sp, AMDD. Algal Res. 38 (2019) 101418.
[61] E. Barbera, et al., Recycling minerals in microalgae cultivation through a combined flash hydrolysis–precipitation process, ACS Sustain. Chem. Eng. 5 (1) (2017) 929–935.
[62] H. Sudibyo, et al., Thermodynamics and kinetics of struvite crystallization from hydrothermal liquefaction aqueous-phase considering hydroxyapatite and organics coprecipitation, Ind. Eng. Chem. Res. 61 (20) (2022) 6894–6908.
[63] L. Yang, et al., Continuous treatment of hydrothermal liquefaction wastewater in an anaerobic biofilm reactor: potential role of granular activated carbon, J. Cleaner Prod. 276 (2020) 122836.
[64] M. Erkelens, A.S. Ball, D.M. Lewis, The application of activated carbon for the treatment and reuse of the aqueous phase derived from the hydrothermal liquefaction of a halophytic Tetraselmis sp, Bioresour. Technol. 182 (2015) 378–382.
[65] J. Arun, et al., Enrichment of bio-oil after hydrothermal liquefaction (HTL) of microalgae C. vulgaris grown in wastewater: Bio-char and post HTL wastewater utilization studies, Bioresour. Technol. 261 (2018) 182–187.
[66] B. de Caprariis, et al., Pyrolysis wastewater treatment by adsorption on biochars produced by poplar biomass, J. Environ. Manage. 197 (2017) 231–238.
[67] Z. Liu, et al., Influence of Fe/HZSM-5 catalyst on elemental distribution and product properties during hydrothermal liquefaction of Nannochloropsis sp, Algal Res. 35 (2018) 1–9.
[68] K.Z. Benis, J. Soltan, K.N. McPhedran, Electrochemically modified adsorbents for treatment of aqueous arsenic: Pore diffusion in modified biomass vs. biochar, Chem. Eng. J. 423 (2021) 130061.
[69] F. Marrakchi, et al., Bio-crude oils production from wheat stem under subcritical water conditions and batch adsorption of post-hydrothermal liquefaction aqueous phase onto activated hydrochars, Chem. Eng. J. 452 (2023) 139293.
[70] K. Aktas, H. Liu, C. Eskicioglu, Treatment of aqueous phase from hydrothermal liquefaction of municipal sludge by adsorption: comparison of biochar, hydrochar, and granular activated carbon, J. Environ. Manage. 356 (2024) 120619.
[71] O.M. Adedeji, K. Jahan, Removal of pollutants from aqueous product of Co-hydrothermal liquefaction: Adsorption and isotherm studies, Chemosphere 321 (2023) 138165.
[72] T. Zhang, et al., Ammonium nitrogen recovery from digestate by hydrothermal pretreatment followed by activated hydrochar sorption, Chem. Eng. J. 379 (2020) 122254.
[73] Z. Anari, et al., Pressure-driven membrane nutrient preconcentration for down-stream electrochemical struvite recovery, Sep. Purif. Technol. 309 (2023) 122907.
[74] P. Karka, I. Johannsen, S. Papadokonstantakis, Hydrothermal liquefaction integrated with wastewater treatment plants–life cycle assessment and technoeconomic analysis of process system options, Sustain. Energ. Fuels. 8 (15) (2024) 3438–3451.
[75] Y. Hu, et al., Investigation of aqueous phase recycling for improving bio-crude oil yield in hydrothermal liquefaction of algae, Bioresour. Technol. 239 (2017) 151–159.
[76] E.A. Ramos-Tercero, A. Bertucco, D. Brilman, Process water recycle in hydrothermal liquefaction of microalgae to enhance bio-oil yield, Energy Fuels 29 (4) (2015) 2422–2430.
[77] H. Chen, et al., Biogas production from hydrothermal liquefaction wastewater (HTLWW): focusing on the microbial communities as revealed by high-throughput sequencing of full-length 16S rRNA genes, Water Res. 106 (2016) 98–107.
[78] K. Chen, et al., Chromatographic separation of glucose, xylose and arabinose from lignocellulosic hydrolysates using cation exchange resin, Sep. Purif. Technol. 195 (2018) 288–294.
[79] C. Hong, et al., Effects of aqueous phase circulation and catalysts on hydrothermal liquefaction (HTL) of penicillin residue (PR): Characteristics of the aqueous phase, solid residue and bio oil, Sci. Total Environ. 776 (2021) 145596.
[80] H. Chen, et al., Effects of the aqueous phase recycling on bio-oil yield in hydrothermal liquefaction of Spirulina Platensis, α-cellulose, and lignin, Energy 179 (2019) 1103–1113.
[81] Y. Hu, et al., Improvement in bio-crude yield and quality through co-liquefaction of algal biomass and sawdust in ethanol-water mixed solvent and recycling of the aqueous by-product as a reaction medium, Energy Convers. Manage. 171 (2018) 618–625.
[82] M. Parsa, et al., Hydrothermal liquefaction of Gracilaria gracilis and Cladophora glomerata macro-algae for biocrude production, Bioresour. Technol. 250 (2018) 26–34.
[83] P.S. Rajan, et al., Hydrothermal liquefaction of Scenedesmus abundans biomass spent for sorption of petroleum residues from wastewater and studies on recycling of post hydrothermal liquefaction wastewater, Bioresour. Technol. 283 (2019) 36–44.
[84] A. Taghipour, et al., Aqueous phase recycling in catalytic hydrothermal liquefaction for algal biomass and the effect on elemental accumulation and energy efficiency, J. Cleaner Prod. 289 (2021) 125582.

[85] B. Zhang, Z. He, Z. Xu, Effect of organic aqueous phase recycling on hydrothermal liquefaction of C-Phycocyanin, Biomass Bioenergy 165 (2022) 106573.
[86] P. Biller, et al., Nutrient recycling of aqueous phase for microalgae cultivation from the hydrothermal liquefaction process, Algal Res. 1 (1) (2012) 70–76.
[87] P. Biller, et al., Effect of hydrothermal liquefaction aqueous phase recycling on bio-crude yields and composition, Bioresour. Technol. 220 (2016) 190–199.
[88] B. Maddi, et al., Quantitative characterization of the aqueous fraction from hydrothermal liquefaction of algae, Biomass Bioenergy 93 (2016) 122–130.
[89] P. Das, et al., A feasibility study of utilizing hydrothermal liquefaction derived aqueous phase as nutrients for semi-continuous cultivation of Tetraselmis sp, Bioresour. Technol. 295 (2020) 122310.
[90] C. Gai, et al., Characterization of aqueous phase from the hydrothermal liquefaction of Chlorella pyrenoidosa, Bioresour. Technol. 184 (2015) 328–335.
[91] D.L. Barreiro, et al., Cultivation of microalgae with recovered nutrients after hydrothermal liquefaction, Algal Res. 9 (2015) 99–106.
[92] T. Selvaratnam, et al., Algal biofuels from urban wastewaters: Maximizing biomass yield using nutrients recycled from hydrothermal processing of biomass, Bioresour. Technol. 182 (2015) 232–238.
[93] L. Garcia Alba, et al., Recycling nutrients in algae biorefinery, ChemSusChem 6 (8) (2013) 1330–1333.
[94] Z. Li, et al., Effects of strain, nutrients concentration and inoculum size on microalgae culture for bioenergy from post hydrothermal liquefaction wastewater, Int. J. Agric. Biol. Eng. 10 (2) (2017) 194–204.
[95] A. Teymouri, et al., Integration of biofuels intermediates production and nutrients recycling in the processing of a marine algae, AIChE J 63 (5) (2017) 1494–1502.
[96] C. Talbot, et al., Cultivation of microalgae using flash hydrolysis nutrient recycle, Algal Res. 18 (2016) 191–197.
[97] A. Ramírez-Romero, et al., Microalgae adaptation as a strategy to recycle the aqueous phase from hydrothermal liquefaction, Bioresour. Technol. 371 (2023) 128631.
[98] A.W. Almutairi, Full utilization of marine microalgal hydrothermal liquefaction liquid products through a closed-loop route: towards enhanced bio-oil production and zero-waste approach, 3 Biotech 12 (9) (2022) 209.
[99] M. Bagnoud-Velásquez, et al., First developments towards closing the nutrient cycle in a biofuel production process, Algal Res. 8 (2015) 76–82.
[100] H. Durak, et al., Hydrothermal liquefaction process of Ammi visnaga and a new approach for recycling of the waste process water: cultivation of algae and fungi, Biomass Convers. Biorefin. 14 (5) (2024) 7149–7165.
[101] J. Mahima, et al., Effect of algae (Scenedesmus obliquus) biomass pre-treatment on bio-oil production in hydrothermal liquefaction (HTL): biochar and aqueous phase utilization studies, Sci. Total Environ. 778 (2021) 146262.
[102] L. Zhang, et al., Nutrient recovery and biomass production by cultivating Chlorella vulgaris 1067 from four types of post-hydrothermal liquefaction wastewater, J. Appl. Phycol. 28 (2016) 1031–1039.
[103] S. Wang, X. Shi, B. Palenik, Characterization of Picochlorum sp. use of wastewater generated from hydrothermal liquefaction as a nitrogen source, Algal Res. 13 (2016) 311–317.
[104] M. Wang, et al., Zeolite-amended microalgal-bacterial system in a membrane photobioreactor for promoting system stability, biomass production, and wastewater treatment efficiency to realize Environmental-Enhancing Energy paradigm, J. Appl. Phycol. 31 (2019) 335–344.
[105] R.B. Madsen, et al., Predicting the chemical composition of aqueous phase from hydrothermal liquefaction of model compounds and biomasses, Energy Fuels 30 (12) (2016) 10470–10483.
[106] L. Leng, et al., Machine learning predicting wastewater properties of the aqueous phase derived from hydrothermal treatment of biomass, Bioresour. Technol. 358 (2022) 127348.