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Abstract

Hydrothermal liquefaction (HTL) is an evolving technology that can convert waste with high moisture and low energy content to electricity, heat, hydrogen and other synthetic fuels more efficiently. The lee side is that the HTL process produces enormous amounts of wastewaters (HTWW), having high organic and nutrient load. The discharge of the HTWW would contaminate the environment and result in the loss of valuable bioenergy sources. The valorization of HTWW has drawn considerable interest. Therefore, this review highlights the valorization of wastewater during the HTL of biomass. The review paper begins with the discussion of the role of microalgae in valorizing the HTWW. The survey illustrates that the selection of appropriate technology is dependent on biomass characteristics of the microalgae. Finally, potential research opportunities are recommended to improve the viability of the HTL wastewater valorization for bioenergy production. Overall, this review concludes that combining various processes, such as microalgae-anaerobic digestion, and bio-electrochemical system – microalgae-anaerobic digestion would be beneficial in maximizing HTWW valorization.

Keywords: Hydrothermal liquefaction, Wastewater from HTL (HTWW), Bioenergy, Microalgae, Valorization

1 Introduction

The International Energy Outlook forecasts that the global energy demands will increase by about 48% by 2040 [1, 2]. To meet the exceedingly high energy demand, the international community is committed to environmentally friendly renewable and sustainable energy research [3, 4]. Among various renewable energy options, biomass including feedstocks with high-moisture content have been identified as an alternative renewable energy source to produce bioenergy and biofuels via thermochemical conversion process [5–8]. To convert biomass into energy, thermochemical conversion processes appear to be a promising route for producing renewable H_2, methanol and synthetic biofuels (biodiesel or dimethyl ether)[9].

In recent literatures several treatment technologies are used for bioenergy and biofuels production and nutrient recovery including thermochemical (pyrolysis, gasification, and combustion), chemical (hydrolysis) and microbiological (anaerobic digestion and fermentation technologies) conversion processes [8, 10–13]. Processing wastewater via thermochemical processes has several advantages over chemical or biological conversion routes such as shorter conversion time, pathogens elimination and is quite adaptable to different kinds of waste [14, 15]. Hydrothermal conversion technologies are one of the thermochemical methods and unlike traditional thermal conversion technologies it can handle diverse range of feedstocks. Although, hydrothermal processes have been regarded as sustainable, energy efficient and innovative technology to produce biofuels from renewable (wet) feedstocks such as black liquor, lignocellulosic and biomass sewage sludge while addressing to the societal, environmental, and economic concerns. Moreover, the hydrothermal process also generates a huge amount of wastewater (HTWW) which retains high organic matter (up to 45%), over 80% of nutrients (N-P-K) present in the feedstock and is highly toxic toward microorganism and the environmental challenge [16–18]. Therefore, it is imperative to develop an innovative solution that can process the huge amount of wastewater while being compliant with latest environmental regulations. The US Department of Energy's report stressed that the optimisation of valorisation of wastewater from HTL can play a critical role in making HTL-derived oil competes with overall market fuel selling price of \$3.7/gallon gasoline equivalent [19, 20].

Hydrothermal technologies can be categorized on the basis of temperature and pressure into three categories. Hydrothermal carbonization (HTC) which carried out at mild temperatures (180-260°C) and low pressures (2-5MPa), to produce carbon rich solid fuel called hydrochar [21, 22]. Hydrothermal liquefaction (HTL) is another wet thermochemical conversion process in which the macromolecules of the feedstock undergo dehydration and decarboxylation reactions to produce the liquid product of bio-oil, solid residue and gas products. HTL occurs in the presence of water at slightly elevated temperatures (200-400°C) and pressures (5-20 MPa) and the average residence time varies between from 10 to 60 min to produce biochemicals [23, 24] or bio-oils [25–27]. Supercritical water gasification (SCWG) or hydrothermal gasification works under more extreme conditions, at temperatures >374°C and pressures beyond 22.1MPa to produce syngas (mixture of H_2, CO_2, CH_4, CO and small fractions of C^{2+} compounds) [16, 28–30]

HTL process can be divided roughly into three key stages: depolymerisation, decomposition and reformation. The process is optimally conducted with lower temperatures, 200-350°C and heating rates in comparison to pyrolysis [31]. It employs pressures (5-20 MPa) to encourage decomposition of the biomass as well as reformation [32]. As the temperature increases to approach that of the critical point of water, a significant change in its properties occur, accommodating fast and efficient, homogenous reactions. Particle size and rate of heating have minimal effect on HTL due to the role that subcritical water plays in both the heat transfer and extracting medium. Physiochemical properties and yield are predominantly affected by feedstock nature and the process conditions [33]. In addition to the desirable energy dense oil, HTL produces hydrochar, gas and inevitably large quantities of aqueous phase (AP) as a result of the reaction medium, from which the oil self-separates as depicted in Figure 1 [34, 35].

In case of HTWW generation per unit processing of biomass, few studies have done. HTL of algal biomass (*Monoraphidium* sp. KMC4) at different temperature condition generated variable amounts of HTWW. At 275°C generated aqueous phase was 60% and at 325°C amount of aqueous phase was 43%. Whereas in case of domestic sewage sludge (DSS) the generated aqueous phase varies from 34–40%. co-HTL of domestic wastewater treatment derived microalgal biomass and domestic sewage sludge (DSS) varied from 50% to 38% with reaction temperature of 275°C and 350°C, respectively. In this study, at optimal level of co-HTL at 325°C for 45 min with 75:25% feedstock ratio resulted an aqueous phase yield of 37% [36].

*** * Insert Figure 1 * ***

Valorizing wastewater generated from hydrothermal process (HTWW) has gained considerable interest among the research community and are being developed and integrated with biorefinery process to produce renewable biofuels, building blocks for chemicals and nutrients. Valdez et al. examined the effect of temperatures and residence time during HTL of *Nannochloropsis* sp. [37]. The authors have reported that shorter residence time and low temperature yielded higher aqueous phase due to reduced depolymerisation reaction. Furthermore, about 67% N and up to 85% of the P associated in the aqueous phase which can be recovered and used as an organic fertiliser. Jena et al. proposed an algal based biorefinery concept by combining algae cultivation integrated with HTL process by utilising nutrient from aqueous phase for microalgae cultivation [38]. An integration of HTL with super critical water gasification (SCWG) was demonstrated to improve the energy recovery from algal biomass. It was reported that 14.3-36.34% energy algal biomass distributed in HTL process water. Authors have also claimed a 35% SCWG efficiency even at as lower as 3.3 g/L organic loading which was attributed to higher oxygen and nitrogen containing compounds or lower amide contents and total acids in HTL aqueous phase [39]. Several contemporary researchers have exploited various valorisation technologies for energy and nutrient recovery and as a result it improved the HTL process, enhanced energy and nutrient recovery, improved economic viability and make the process more environmentally friendly [17, 40, 41].

Despite the availability of various technologies for valorising the wastewater generated from hydrothermal process the performance efficiency of most of the employed technologies are not satisfactory as the mechanism of HTL is not thoroughly elucidated due to the complexity of the products and feedstocks. Moreover, a comprehensive summary of the AP valorization techniques (microalgae mediated) is limited. Therefore, the primary objective of this paper is to undertake a systematic review of the microalgae mediated valorization technologies currently engaged for AP valorization. This review highlights and discusses the valorization of wastewater and its utilization in algae cultivation by utilizing nutrient from wastewater and microalgae reactor to produce biofuels via HTL. This paper particularly focused on pros and cons of technological advancements pertaining to microalgal mediated valorization of wastewater originated from HTL/HTC or SCWG process. Finally, current trends and development and future research possibilities are discussed to improve the viability of wastewater valorization for biofuel production and nutrient recovery.

Several studies have shown simultaneous remediation of HTWW generated from hydrothermal treatment of different subsrate and microalgal cultivation [42, 43]. Mostly used algal innoculam for treatment were *Chlorella* sp.

[44, 45], *Chlorella minutissima* [46], *Botryococcus braunii* [46], *Nannochloropsis gaditana* [47], *Phaeodactylum tricornutum* [47], *Chlorella vulgaris* [47–49] and *Scenedesmus almeriensis* [47], *Tetraselmis sp.* [50], Chlorella sp. [50], *Chlorella minutissima* [51, 52], *Scenedesmus abundans* [51, 52], *Chlorella singularis* UUIND5 [51, 52], *Chlorella sorokiniana* UUIND6 [51, 52], *Desmodesmus armatus* [49] etc. The cultivated algal biomass can further be subjected for value added products like bio-oil [44], biodiesel [46], biofuel [47, 48, 50] and biomass and lipid for the realization of circular bioeconomy [51–55].

Algae-oleaginous yeast co-cultivation using HTWW was also explored by several research groups. This system was found to be very efficient for overall biomass and lipid productivity. In the co-culture, microalgae operate as an oxygen generator for aerobic yeast growth, while the yeast supplies the CO_2 essential for microalgal growth, yeast and microalgae both then produce lipids. Yen et al. reported an increase in biomass production of about 40-50% and lipid production of 60-70% by co-culturing yeast-*Rhodotorula glutinis* and microalgae-*Scenedesmus obliquusas* compared to the single culture batches [56]. Similarly, the co-culture of microalga-*Isochrysis galbana* 8701 and yeast-*Ambrosiozyma cicatricose* resulted in an increased productivity of around 20.71 g/m^3 [57]. The co-culture of oleaginous yeast-*T. spathulata*, and microalgae- *C. vulgaris* var. TISTR 8261 generated biomass of 12.2 g/L and 47% mass fraction of the dried cells was observed to be lipid [51, 58]".

2 Microalgae cultivation using wastewater generated from hydrothermal process

Various studies used for characterisation of HTWW have reported that although the composition of HTWW varies depending on the input biomass but it mainly contains organic compounds like sugars, hydrocarbons, phenols, alcohols, carboxylic acids etc [5, 17, 18, 59–62]. Due to the presence of these chemicals in HTWW there is potential toxicity to different life forms including various microorganisms [18, 63]. Valorisation of HTWW could achieve the twin target of recovery of valuable materials and reduction of toxic effect [40, 41]. Summary of SCWG mediated valorization of wastewater generated from the hydrothermal processes of different algal biomass are presented in Table 1. Various microalgal species has been shown to grow in HTWW using nutrients like nitrogen and phosphorous and organic carbon present in this wastewater [35, 38, 64–67]. Algal biomass grown using HTWW can be further used for biofuel production and various bioactive compounds production [68]. Studies on HTL of various algal strains including *Spirulina*, *Nannochloropsis*, *Chlorella*, *Dunaliella* and *Botryococcus braunii* under different process conditions have been reported by several researchers [37, 38, 69–74]. The reported yield of bio-oil was in the range of 40-60%. HTL was employed on *Nannochloropsis* sp. and was experimentally studied in stainless-steel reactor at temperature range of 200-500°C. The authors reported that maximum bio-oil yield of 43% with heating value of 39 MJ/kg [70]. Biller and Ross exploited HTL process using model biochemical components of *Nannochloropsis oculata*, *Chlorella vulgaris*, *Spirulina* and *Porphyridium cruentumin* in a batch reactor using catalyst of Na_2CO_3 or HCOOH [71, 75]. The study concluded that the bio-oil formation is due to degradation of lipids, protein and carbohydrates leads. Jena et al. studied HTL of *Spirulina platensis* in agitated reactor and reported that bio-crude oil (maximum yield of 39.9%) has fuel characteristics comparable to crude petroleum and could further be refined to a liquid transportation fuel [38]. Bio-oil production from algae feedstock via HTL route and optimizing the process have been extensively studied [76, 77].

As already discussed algal biomass is one of the most commonly used raw material for hydrothermal liquification, Figure 2 summarizes how the wastewater generated from HTL process can be used for growing further algal biomass could enhance net energy, building a closed loop economically and environmentally sustainable system [32, 78]. This section will focus on the latest development in using algal biomass in treating HTWW and highlight various challenges in the valorisation pathway.

*** * Insert Table 1 * ***

*** * Insert Figure 2 * ***

Growing algae using in HTWW has been classified majorly into four different ways depending on the type of nutrient algae is using from the wastewater, first being the mixotrophic growth mode wherein algae can utilise the organic carbon present in HTWW along with inorganic atmospheric CO_2, second and third being the one is where algae is grown using nitrogen and phosphorous source, respectively from HTWW by supplementing it in standard algal medium, lastly diluted HTWW can be used solely for growing microalgae for meeting multiple nutrient requirements.

2.1 Using HTWW as carbon source for growing microalgae

Different microalgal species have proven metabolic flexibility to utilize organic carbon from wastewater and inorganic carbon in the form of CO_2 from atmosphere to demonstrate mixotrophic growth [79]. Out of these mixotrophic microalgal species monoculture of *Chlorella* [80], *C. vulgaris* [64], *S. dimorphous*, *S. platensis*, *Chlamydomonas reinhardtii* [81], *C. sorokiniana* [82], *Galdieria sulphuraria* [83], *N. gaditana* [84] and mixed culture of various algal species have shown promising results [65]. Especially *Chlorella vulgaris* grown in media blended with different dilution ratio of HTWW showed reduction in COD from around 2700 to 1100 mg/L, 1330 to 510 mg/L, or 640 to 300 mg/L. The reduction was dependent on the dilution factor of HTWW [44]. In another study higher algal biomass productivity of *Galdieria sulphuraria* was seen when standard algal growth media BG-11 was blended with HTWW [83].

2.2 Using HTWW as nutrient source for growing microalgae

Source of phosphorous in HTWW is chiefly found in orthophosphate form. *Chlorella vulgaris* removed total phosphorous from 2.0-6.3 mg/L to <0.5 mg/L (almost 85-95 %) in medium blended with HTWW which when compared with standard BG-11 media was only 40% [44]. In another study, total phosphorous was lessened from 22 mg/L to less than 1 mg/L [85]. Nitrogen utilisation from HTWW varies greatly depending on the type of nitrogen sources [86]. For example, microalgal species like *Phaeodactylum tricornutum* and *Desmodesmus* sp. desired ammonium to nitrate [69, 87]. Ammonium which is the major form of nitrogen in HTWW is more bioavailable than nitrate as shown by consortium of *Chlorella* sp.when grown in coculture with bacteria [26, 88, 89]. However, high concentration of total nitrogen in media shows inhibitory effect towards growth of microalgae mostly attributed to ammonium inhibition [90]. As a rich source of nutrients, HTWW can be solely used for growing microalgae without any supplement of synthetic media. However, HTWW might contain some compounds which can inhibit the growth thus appropriate dilution is required before inoculation. The dilution range of HTWW plays a critical role in growth of microalgae as some species like *Chlorella vulgaris* 1067 can be cultivated in media containing wide range of dilution starting with 1.9% and can go up to 28.6% [90]. Other than the macronutrients like carbon, nitrogen and phosphorous, HTWW can also contain trace amount of micronutrients required for algal growth like Mg, Fe, Co, Mo etc [91]. However, if the HTWW is found to be lacking in these nutrients, these micronutrients need to be externally supplied for supporting optimal growth.

3 Challenges in using HTWW to grow microalgae

As discussed earlier, optimum dilution of HTWW is essential to support growth of microalgae which is majorly owing to the presence of recalcitrant and toxic compounds such as phenol and its derivatives, heterocyclic nitrogenous compounds, heavy metals, emerging contaminants like dibutyl phthalate known to inhibit the growth [66, 92]. Phenol derivatives with chlorine, methyl and ethyl groups have shown higher toxicity than phenol in the culture of *Pseudokirchneriella subcapitata* [93]. Polyphenolic compounds like catechol and hydroquinone can cause formation of reactive oxygen species through auto oxidation process which has been reported to suppress the growth of *Microcystis aeruginosa* [94]. HTWW derived from lignocellulosic biomass like wood and corn stove are known to contain polyphenols [60]. Similarly, heterocyclic nitrogenous compounds are very toxic to algal proliferation in 0.052 to 139 mg/L concentration range [18]. Among heavy metals high amount of Ni (240 mg/L) was reported in HTWW produced from HTL of *Chlorella vulgaris* biomass which is inhibitory to algal growth when media was supplemented with Ni^{2+} ions [95] and also shows toxicity to many microalgae species isolated from soft or hard water environment [96]. Other heavy metals like Cu, Al, Cr, Pb, Cd, and Zn could be present in significant amount in HTWW if the input biomass for HTL is rich in these metals [97]. A study has already shown that 0.02 mg/L of aluminium ions could inhibit up to 70% of the growth of *Chlorella vulgaris*[98].

4 Strategies to overcome growth inhibition by HTWW

Valorisation of HTWW is crucial in achieving better economic and environmental sustainability to the entire process. However, growth inhibition of various microalgal species by recalcitrant compounds present in HTWW is still a bottleneck and needs to be addressed. In this direction several strategies have been developed to overcome the growth inhibitory effect of HTWW which are briefly discussed in this section. Overall, the strategies could be divided into two broad categories one in which the hydrothermal liquification process and resulting HTWW can be optimised to reduce the toxicity. Moreover, several physical/chemical or biological processes can be combined or sequentially integrated with algal culturing to achieve better results. The second category can combine strategies which are aimed at improving microalgal resistance to HTWW by strain selection, genetic/metabolic engineering to enhance growth rate, polymicrobial cultures like bacteria-algal coculturing or combining various species of algae.

4.1 Process centric approaches

4.1.1 Optimisation of HTL process

The quality and composition of HTWW is highly dependent on process parameters of HTL like biomass composition, operating conditions like temperature, retention time, feeding rate etc. Therefore, understanding the detailed mechanisms of HTL along with input biomass composition can greatly enhance the prediction of HTWW composition [99]. This has been shown in a study where controlling the HTL temperature and manipulating the properties of sludge biomass could affect the presence of heavy metal in HTWW [100, 101]. However, these optimization of process parameters needs to carefully traded as it may affect the yield of HTL process itself. A study by Patel et al. shows that HTL of *Nannochloropsis* sp. for producing bio-oil when operated at 275°C with a residence time of 30 min resulted in production HTWW which was supporting algal growth well but the bio-oil yield was unsatisfactorily low [102].

4.1.2 Pretreatment of HTWW

Studies have demonstrated that some of the recalcitrant growth inhibiting substances present in HTWW can be removed effectively using certain pretreatment processes before growing microalgae in it. Adsorbent like activated carbon and zeolite have been used for pretreatment of HTWW which can remove nitrogenous compounds [103] furfural [104] etc. Phenol and its derivatives can be removed using specialized resins [105]. Removal of these compounds could also be achieved by precipitation and membrane filtration methods but the cost involved in these processes make them less attractive currently and rarely being reported.

4.1.3 Combining/ integration of various processes

Valorization of HTWW could also be achieved by other methods e.g., anaerobic digestion (AD). Combining these processes with microalgal cultivation has been quite promising in lab scale studies. When HTWW is subjected to AD for biogas production nutrients like nitrogen and phosphorous are still left in the HTWW which can be utilized by microalgae for growth [48]. Another advantage of combing AD with microalgal cultivation would be to reduce the toxicity of the HTWW by degradation during the AD process [63].

4.2 Culture centric approaches

4.2.1 Strain selection

Microalgal strains vary greatly in their abilities to tolerate toxic compounds. Strain selection should aim at selecting strains which can tolerate recalcitrant compounds without compromising with the growth rate, ease of harvesting and biomass usability [106]. Many algae-based treatment studies have been carried out employing either monocultures of microalgae or microalgal–bacterial consortia. Algae strains that are found in leachates are very tolerant to high amounts of contaminants such as ammonia nitrogen, salts, and recalcitrant organic debris. Because of their ability to tolerate varied substances or environmental parameters, strains from diverse niche can be isolated. They were thought to have adapted to the high levels of ammonia-nitrogen, phosphate, and other contaminants found in leachate. Paskuliakova et al. found *Chlamydomonas* sp. SW13aLS to be most tolerant for cultivation and remediation of leachates having similar conditions [107]. Chen et al. selected two strains, *Chlorella vulgaris* FACHB-8 and *Chlorella* sp. FACHB-31, based on their enhanced growth performances, higher tolerance to wastewater components and better nutrient sequestration abilities. Both of the strains were found to be very adaptive against concentrated wastewater [108]. A significant drawback of monoculture is that it is more species-dependent in many circumstances, and when microbial diversity varies according to seasonal variations, it has a considerable impact on wastewater remediation efficiency [109].

4.2.2 Use of mixed consortia

Studies shows that mixed consortia of microalgal culture which have complementary metabolic pathways and growth requirements are able to better tolerate toxicity of pollutants compared to single or mono-cultures. Study by Godwin et al. showed that when species of *Ankistrodesmus falcatus*, *Chlorella sorokiniana*, *Pediastrum duplex*, *Scenedesmus acuminatus*, *Scenedesmus ecornis*, and *Selenastrum capricornutum* in media containing HTWW were grown together they can withstand 10% of HTWW supplementation compared to only 2% by monocultures of these species [65, 110]. Sharma et al. found two algal consortia viz. MAC1 and MAC2 to be effective for waste water nutrient sequestration. MAC1 was found to be consisted of *Chlorella* sp., *Nannochloropsis* sp., *Scenedesmus bijugatus*, *Chlamydomonas reinhardtii*, and *Oscillatoria* whereas MAC2 consisted of *Chlorella* sp., *Nannochloropsis* sp., *Scenedesmus dimorphus*, *Kirchnella* and *Microcoleus*.[111]. In another study, Fallahi et al. found similar findings using algal consortia of *Chlorella vulgaris*, *Scenedesmus obliquus* and *Nannochloropsis* sp.[112, 113]. Similarly, Mahapatra et al. found mixotrophic algal consortia to be most efficient for wastewater remediation which was comprised of several algal species including *Cyclotella meneghiniana*, *Nitzschia palea*, *Chlorococcum* sp., *Scenedesmus quadricauda*, *Scenedesmus obliques*, *Arthrodesmus curvatus*, *Golenkinia radiata*, *Kirchneriella lunaris*, *Chlorella vulgaris*, *Chlorella pyrenoidosa*, *Chlorococcum humicola*, *Chroococcus* sp., *Monoraphidium* sp., *Ankistrodesmus falcatus*, *Oocystis* sp., *Phormidium tenue*, *Spirulina maximus*, *Trachelomonas* spp., *Euglena* spp., *Phacus longicauda* and *Phacus caudatus* [114]. These findings demonstrated the prospect of mixed microalgae production for better nutrient removal and microalgal biomass production in an attractive and cost-effective manner.

4.2.3 Co-culture of algae-bacteria

Microalgae thrive in natural habitats as part of a microbial consortium, which comprises a variety of microorganisms such as bacteria, viruses, protozoa, and fungi. Because of the significant risk of contamination, mixed cultures are often used in the wastewater industry. Bacterial and algal interactions are critical factors that affect the treatment efficacy of a mixed culture system. Microalgae consume carbon dioxide(CO_2) released by bacteria and release oxygen through photosynthesis, which is consumed by bacteria in this system. As a result, bacteria and algae form a synergistic biomechanism that aids in wastewater bioremediation [109]. Other than mixed algal culture researchers have also looked at the possibilities of developing algal bacteria co-culture systems as bacteria like *E. coli*, *Pseudomonas putida* have shown higher tolerance to toxicity of HTWW and can grow in 40% HTWW [40]. Zhou et al. have tested the feasibility of algae-bacteria consortium in HTWW containing wastewater and it resulted in net positive energy yields [26]. In another study, it has been also found that algae-bacteria cocultures can degrade organic pollutants which algal strain alone couldn't degrade [115].

4.2.4 Genetic/ Metabolic engineering approach

With the advancement in genetic engineering tools it is now possible to incorporate genes coding for enzymes and pathways helpful in degrading pollutants into microorganisms. In this direction expression of ascorbate peroxidase (AsPOX) which detoxifies peroxides utilising ascorbate as a reductant in ascorbate-glutathione cycle in *Picochlorum* sp. to detoxify peroxidase has shown to enhance algae toxicity tolerance in HTWW media [116]. Genetic engineering has already contributed to increasing lipid content in certain microalgal species, similar efforts can go a long way in developing genetically modified strains with enhanced toxicity tolerance and higher growth rate.

5 Integrated systems for HTWW valorization

The presence of recalcitrant organics in HTWW requires cost-effective and novel treatment methods for degradation and valorisation [8]. All the systems discussed in the preceding sections have their advantages and disadvantages. Figure 3 detailed various pros and cons of each approach. Since the valorisation process has multi-dimensional objectives regarding nutrient recycling, biofuel generation, chemicals separation, etc., integrating various valorisation systems would complement each other. The combined systems can utilize the positives of individual techniques, resulting in higher valorisation efficiency and higher effluent quality [117, 118]. The following section discusses the integration of a biological system with physicochemical processes. The subsequent section discusses the integration of two or more biological systems. A separate section then discusses the combination of biological and thermochemical process in valorising HTWW.

*** * Insert Figure 3 * ***

5.1 Anaerobic digestion-microalgae

Integrating anaerobic digestion (AD) and microalgae cultivation is highly efficient in harnessing the renewable energy potential of organic waste by utilizing the biodegradable portion of the waste into biogas and capturing CO_2 present in the biogas through microalgae, simultaneously producing valuable biofuels/biochemicals. Microalgae can also efficiently use the AD digestate as a nutrient for their growth. Several authors have explored the combination of AD and microalgae in neutralizing organic wastes [119–122]. Li et al. found that integrating the AD process and microalgae accomplished high methane production and a significant synergistic effect [123]. It was also able to recycle 91% of the total nitrogen and 86% of the soluble organics. Yang et al. integrated AD process and microalgae cultivation to produce a high methane yield [48]. The integration was also able to achieve high algal biomass productivity of 2.3 g/L, more prominent than that achieved using untreated HTTW as the growth medium. Some of the significant studies pertaining to anaerobic digestion mediated valorization of wastewater generated from thermochemical treatment of algal biomass are summarized in Table 2.

*** * Insert Table 2 * ***

A high COD removal rate by microalgae was also observed using AD treated HTWW. The energy yield was also noticeably more elevated in the combined process. HTWW valorisation by microalgae alone produced a 3.44 kJ/g COD energy yield. On the other hand, the combined AD and microalgae for the same HTWW yielded 20.7 kJ/g COD, thus a six-fold increase. Yang et al. also integrated the AD-microalgae process with granular activated carbon (GAC) adsorption and ozone treatment [48]. The pre-treatment with adsorption and ozonation eliminated inhibitors, enhancing methane production and energy yield. The energy yield significantly increased to 565 kJ/g COD with GAC pre-treatment. Even the ozone treatment increased the energy yield to 50.8 kJ/g COD for the integrated AD and microalgae process. The integrated approach was also able to neutralize nutrients such as nitrogen and phosphorous. The removal rate of ammonia was 80%, and phosphorus was completely removed from HTWW after microalgal treatment, whereas without pre-treatment, ammonium removal was only 53.3% [48]. Zheng et al. also demonstrated the effectiveness of AD of HTWW in providing optimal nutrients for downstream algal cultivation [63]. The AD process coupled with adsorption could mitigate phenol and benzene. They are toxic to algal growth [26, 124, 125]. Integration of AD and microalgae for HTWW valorisation has all-round potential, and the process could also benefit from coupling either advanced oxidation process or adsorption. As discussed earlier, Advanced oxidation processes (AOPs) and adsorption could neutralize inhibitors in various ways and facilitate the development of microbes with high valorising efficiency. The treated wastewater from the algal process could also be recycled back to the HTL system, alleviating wastewater discharge [126].

5.2 Anaerobic digestion/Microalgae Bio-electrochemical system

Bio-electrochemical system – anaerobic digestion (BES-AD) system is gaining significant attention due to the syntrophic interactions between exoelectrogens and anaerobic microbes [127, 128]. The metabolites generated from the AD process are much more amenable to electroactive microorganisms, creating an inclusive thermodynamically favourable fermentation process [129]. The system is studied in great details for various biomass such as waste slurry [130], corn silage [131], livestock manure [132], waste sludge [133] etc. Feng et al. examined the effect of applied voltage on the combined The Microbial electrolysis cell (MEC) assisted anaerobic digester (MEC-AD) system for sewage sludge [134]. A nominal 0.3–0.5V enhanced methane production and volatile solids removal. *Cloacamonas* was found to be the influential species. Similarly, Marone et al. integrated MEC and AD to treat wastewater from olive processing industries [135]. Their work generated maximum methane production of 701 mL/L of wastewater. On the other hand, individual AD of the wastewater could not generate methane. The process also had the potential to produce various biofuels [136]. The microalgae developed from HTWW can be coupled with microbial fuel cell (MFC) for electricity generation, carbon capture and biomass production. Algae have been utilized frequently in MFCs as a substrate for bacteria [137–139]. It is a sustainable technology as it does not consume any energy, simultaneously producing extra electricity. It also has the potential to reduce sludge production, minimizing sludge disposal cost. The process's high infrastructure cost and energy demand are some of the major issues in coupling BES and microalgae [140, 141].

6 Bottlenecks and Perspectives

Valorization of wastewater produced during the hydrothermal processes of biomass via microalgal cultivation is reviewed. It can be inferred from the review that achieving efficient valorization of HTWW using a single conversion technology is challenging. The use of integrated systems where the limitations of the individual technologies can be bridged appears as promising alternatives for effective HTWW valorization. However, the majority of the alternative valorization technologies investigated/proposed, are in lab-scales, lacking the commercial scale implementation feasibility information. Additionally, performance efficiency of most of the employed technologies are not satisfactory as the mechanism of HTL is not thoroughly elucidated due to the complexity of the products and feedstock. So, a suitable valorisation approach of HTWW should target to achieve the twin benefit of resource recovery and reduction of toxic effects of HTWW before discharging it to the environment. The prevalent challenges and related research directions are as follows:

red

Despite progressive developments in HTWW valorization technologies, significant limitations still exist, necessitating future research for the realization of a holistic HTWW valorization approach.

1. The development of new analytical techniques for the complete composition profiling of HTWW is essential to figure out the energy generation as well as inhibitor effects of the constituents of HTWW.

2. Some of the recalcitrant growth inhibiting substances present in HTWW can be removed effectively using certain pre-treatment processes like adding adsorbents, for instance activated carbon to remove the toxic compounds before growing microalgae in it.

3. Replacing pure or mono culture with mixed microbial consortia enhances the tolerance to toxic compounds due to mixed microbial consortia's complementary metabolic pathways and growth requirements.

4. Commercial scale studies of HTWW valorization are limited, which needs further investigation as the variable HTWW compositions and properties may lead to the performance uncertainties of the valorisation processes during scaling-up process.

5. Systematic techno-economic analysis of HTWW valorisation approaches is very much essential to find out the technical and economic feasibility of the valorising techniques and their integration thereof.

7 Conclusions

This review offers a bird's eye on the valorization of wastewater produced during the hydrothermal processes of biomass via microalgal technologies. Various microalgal species can be grown in HTWW using the organic carbon and nutrients present in this wastewater and the cultivated algal biomass can further be utilised for biofuel generation with the reported yield of bio-oil in the range of 40-60%. Similarly, the integration of AD and microalgal cultivation achieved high algal biomass productivity and energy yield was six-fold higher than that achieved by microalgae cultivation alone using untreated HTWW as the growth medium. Integrated systems are thus found to be most appropriate for valorisation of HTWW from economic and environmental points of view.

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List of Tables:

Table 1 Summary of SCWG mediated valorization of wastewater generated from the hydrothermal processes of different algal biomass

Source of wastewater	Process conditions	Catalyst	H_2 (%v/v)	CH_4 (%v/v)	CO_2 (%v/v)	CO (%v/v)	Carbon conversion efficiency (%)	Ref
Chlorella vulgaris	350°C, 35 MPa, 0–60 min,	None	37.6	20.3	30.2	2.8	51.9	[142]
		NaOH	71.1	23.4	0	0 .2	98.7	[142]
Chlorella vulgaris	300°C, 325°C, 350°C, 375°C, and 400°C, 24 MPa, 15 min	None	-	-	-	-	-	[143]
Chlorella sp. and *Scenedesmus* sp	350°C, 240min	Ru/C	53.4	24.4	15.0	0.0	-	[144]
Auxenochlorellapy renoidosa	600°C, 30-50 MPa, 120min	None	27.78	37.35	15.26	9.76	84.15	[39]
Arthrospira platensis	600°C, 30-50 MPa, 120min	None	30.11	32.40	26.46	0.46	69.05	[39]
Schizochytriumlim acinum	600°C, 30-50 MPa, 120min	None	27.83	35.11	33.91	0.27	93.52	[39]
Nannochloropsiso ceanica	600°C, 30-50 MPa, 120min	None	34.48	36.20	17.30	0.63	91.11	[39]
Arthrospira platensis (ArP)	350 ± 5°C, 19-20 MPa, 1h	1 wt% Ru	-	-	-	-	-	[145]
Ulva prolifera	600°C, 30-50 MPa, 120min	None	28.17	35.95	28.30	0.0	54.18	[39]
Saccharina japonica	600°C, 30-50 MPa, 120min	None	31.37	29.35	25.90	6.65	90.54	[39]
Chlorella vulgaris	400°C and 600°C, 25 MPa, 30s	None	-	-	-	-	-	[146]
Zostera marina	600°C, 30-50 MPa, 120min	None	33.72	26.68	33.81	0.27	61.83	[39]
Gracilariaeucheu moidesharvey	600°C, 30-50 MPa, 120min	None	21.05	25.73	38.35	12.40	83.57	[39]

Table 2 Anaerobic digestion mediated valorization of wastewater generated from thermochemical treatment of algal biomass

Source of wastewater	COD content of wastewater	Anaerobic digestion conditions	Methane production (mL/GCOD)	COD removal efficiency	Possible inhibitors	Remarks	Ref
HTL, algae, 260–320°C, 60 min	0.28 g/g TVS	Batch, 35°C, 45 d	182.8–365.1 mL/g VS	44-61%	Phenols and cyclic hydrocarbons	More than 7 days of lag period was observed, and butyrate oxidation was likely impaired	[17]
HTL, *Nannochloropsis* sp., 320°C, 30 min	1 g/L	Batch, 37°C, 13 d	182	59%	Total ammonia nitrogen (TAN)	Struvite crystallization mediated removal of TAN, approximately 3.5 times higher CH_4 production after inhibitor removal	[103]
HTL, modeled biomass, 200–350°C, 20 min	4 g/L	Batch, 37°C, 30 d	41–314	31.4–52.8%	5-hydroxymethylfurfural (5-HMF) and levulinic acid	Inhibition can be minimized by lowering lignin content and at low HTL temperature	[41]
HTL, *Spirulina*, 300 °C, 30 min	5.788 g/L	Two-stage batch, 213 d	123	33%	Ammonia and N & O-heterocyclic compounds	Activated carbon and zeolite can adsorb N & O-heterocyclic compounds	[63]
HTL, *Tetraselmis*	22.2% AP	Semi-continuous, 37°C, 89 d	313.2	-	Ammonia, chloride salts, pyridine and pyrrolidine compounds	Adopting a continuous AD process, the toxicity effect can be significantly reduced	[147]
HTL, *Nannochloropsis* sp., 320°C, 30 min	4.26 g/L	Batch, 37°C, 32 d	296	85%	-	-	[148]
HTL, *Chlorella*	26.5% AP	Semi-continuous, 37°C, 89 d	243.9	-	Ammonia, chloride salts, pyridine and pyrrolidine compounds	Adopting a continuous AD process, the toxicity effect can be significantly reduced	[147]
HTL, *Chlorella* 300°C, 30min	2–7 g/L	Batch, 35°C, 50 d	78.0–331.3	14.4–61.1%	Ammonia and N-heterocyclic compounds	On adsorption of AP by zeolite to remove inhibitors, the lag phase was reduced from 8-12 days approximately 1 day	[149]

AP- aqueous phase, **HTL**- hydrothermal liquefaction, **AD**- anaerobic digestion, **COD**- chemical oxygen demand

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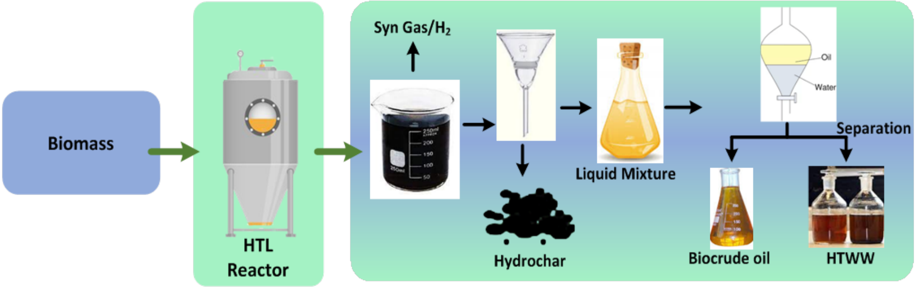

Fig. 1 Overview of hydrothermal liquefaction of biomass

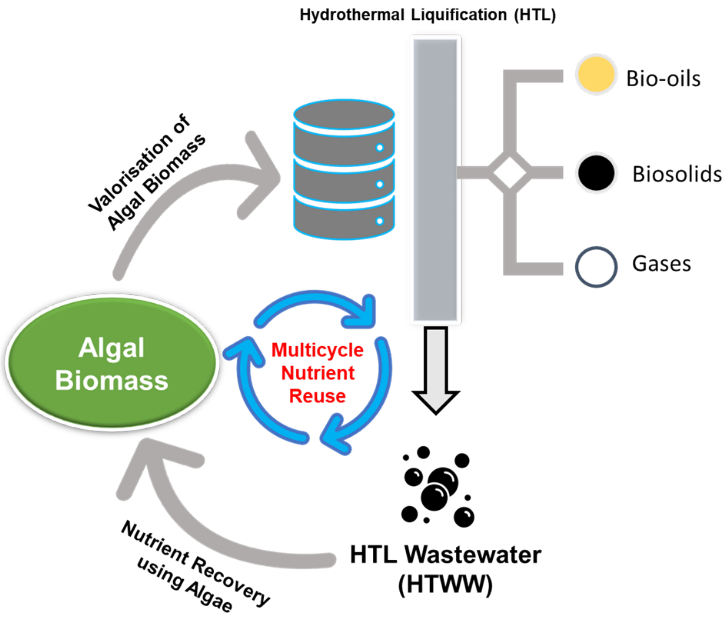

Fig. 2 Schematic representation of a closed loop cyclic process of using HTWW to grow microalgae which can be used as biomass for HTL process to recover value added products

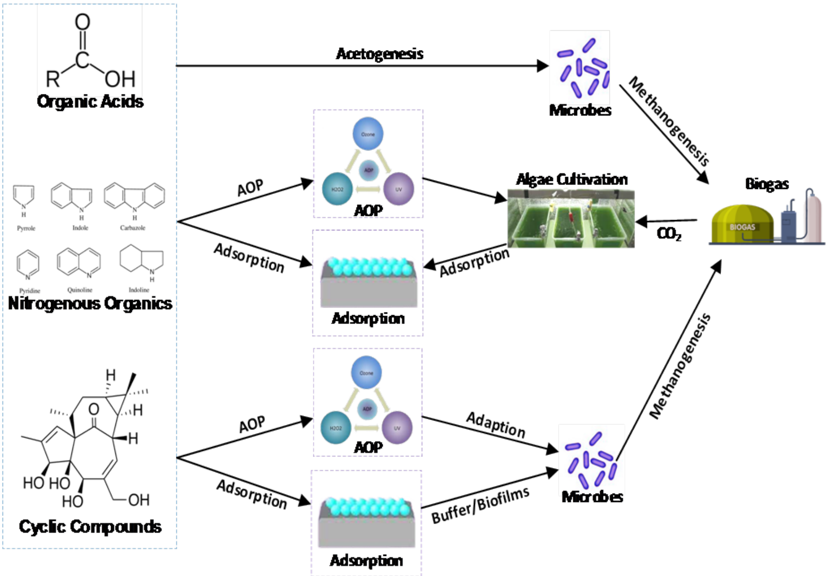

Fig. 3 The mechanism of various organics' valorization using integrated AD and microalgae