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Review

Hydrothermal processing of microalgal biomass: Circular bio-economy perspectives for addressing food-water-energy nexus

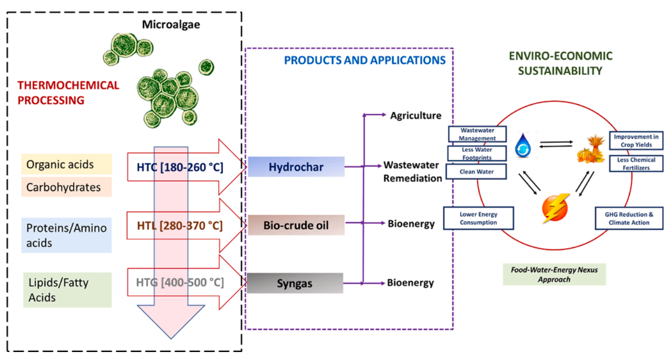
Bunushree Behera *, Mari Selvam S, Paramasivan Balasubramanian

Agricultural & Environmental Biotechnology Group, Department of Biotechnology and Medical Engineering, National Institute of Technology Rourkela, India

HIGHLIGHTS

- Process, mechanisms and product portfolio for algal HTC/HTL/HTG were reviewed.
- Research on HTL of algal biomass has been more focused compared to HTC/HTG.
- Enviro-economic feasibility constraints to be addressed for scale-up.
- Process optimization, integration and supply chain management must be emphasized.
- Holistic thermochemical engineering perspectives promote food-water-energy nexus.

GRAPHICAL ABSTRACT



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ABSTRACT

Hydrothermal processing of microalgae is regarded as a promising technology to generate multitude of energy based and value-added products. The niche of hydrothermal technologies is still under infancy in terms of the technical discrepancies related to research and development. Thus, the present review critically surveyed the recent advancements linked to the influencing factors governing the algal hydrothermal processing in terms of the product yield and quality. The sustainability of hydrothermal technologies as a standalone method and in broader aspects of circular bio-based economy for energy and value-added platform chemicals are comprehensively discussed. Process optimization and strategic integration of technologies has been suggested to improve efficiency, with reduced energy usage and environmental impacts for addressing the energy-food-water supply chains. Within the wider economic transition and sustainability debate, the knowledge gaps identified and the research hotspots fostering future perspective solutions proposed herewith would facilitate its real-time implementation.

1. Introduction

Recent research arena on sustainable environment perspectives focus to alleviate the harmful effects of non-renewable energy sources. In this regard, the pressing need for the alternative strategies for fossil fuel consumption are being explored in terms of utilizing biomass as one of the energy resources since it is abundant and low cost in nature. The conversion of biomass into biofuels is likely carried out by the means of

* Corresponding author.
E-mail address: bunushree1991@gmail.com (B. Behera).

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thermochemical or biochemical reactions to produce different bio-products. Classification of biofuels is based on the biomass source being used as 1st, 2nd and 3rd generation biofuels. 1st and 2nd-generation biofuels are obtained from food and non-food crops respectively whereas third generation biofuels point to utilization of microalgae as feedstock to produce various bioenergy products. Among these feed-stocks, the focus on microalgae as source of drop-in-fuels/ advanced biofuels and value-added products has been increased dramatically over past years (Behera et al., 2022). Microalgal biotechnology is bounded by cost and energy intensive upstream and downstream processes and there is a requirement of paradigm shift for multi-product recovery where the significant development of technology also increases its market value (Sankaran et al., 2020). Biorefinery approach of utilizing microalgal biomass involves the integrated upstream and downstream processes to derive multiple products by reducing residual component and favouring sustainable economics. Microalgal biorefinery concepts has been previously elaborated by Hemalatha et al. (2019) and Banu et al. (2020) where it could be interpreted that maximum resource recovery of microalgae is concerned by interlinking eco-friendly and cost-effective bioprocessing techniques in perspective of feasible scale up and bioeconomy.

Hydrothermal treatment of microalgae is one of the superior bio-processing technology which does not require cost and energy intensive downstream process and it is gaining attention as a viable route for multi-product recovery (Biller and Ross, 2011; Barreiro et al., 2014). Hydrothermal processing of microalgae to produce different forms of product like hydrochar, biocrude/bio-oil, syngas and nutrients enriched aqueous phase possesses multiple applications and follows the holistic hybrid biorefinery approach ensuring circular economy as proposed by Mohan et al. (2016).

The enhancement in solvation property of water under high temperature and pressure during hydrothermal processing of feedstock is attributed to reduction in hydrogen bonding, increasing the miscibility, dielectric constant and decreasing the mass transfer constraint arising from potential phase boundary resulting in enhancement of heat capacity (Patel et al., 2016). During hydrothermal processing, critical factors like temperature, pressure and residence time variation makes water a better heat carrier, resulting in significant change in molecular structure causing fractionation of biochemical components of microalgal biomass. Hydrothermal pre-treatment is commonly utilized for lignocellulosic biomass, however the process is still at infancy and limited studies have been done with microalgal biomass. Acid hydrothermal pre-treatment of 20% *Chlorella* sp., biomass with 1.5% sulphuric acid at 117 °C, 20 min resulted in maximal ethanol yield (5.62 g/L), which was 3.5 times more than untreated process. Further, hydrolysing the acid pre-treatment crude slurry with glucoamylase was found to increase ethanol yield by 7 times compared to control without pre-treatment (Ngamsirisomsakul et al., 2019). An advancement as a part to reduce the energy consumption linked with hydrothermal processing, Xiao et al. (2019) proposed a solar driven continuous hydrothermal pre-treatment with a parabolic trough collector resulting in 4 MPa pressure and 200 °C temperature, leading to 7.4 and 3.7 times higher yield of carbohydrates and proteins respectively, thereby enhancing the anaerobic digestion efficiency by 57%. A similar study by Li et al. (2022) utilized N, N Dimethylformamide for pre-treating *Chlorella* sp., at temperature of 180 °C – 220 °C, resulting in 41.59% sugar and 63.57% nitrogenous components in pyrolysis bio-oil. Conventional acid/alkali based pre-treatment strategies not only results in equipment corrosion due to harsh chemical reagents but also leads to the generation of toxic components inhibitory to the microbial biomass, thereby causing low product recovery. Hydrothermal pre-treatment is a better approach compared to the conventional chemical pre-treatment as it offers possibility of generating lesser toxic by-products owing to the use of only water as the solvation medium without any chemical addition, thereby have low capital investments and environmental impacts (Aparicio et al., 2021). More insights into the relevance and applicability of hydrothermal pre-treatment for processing the hydrolysates can be obtained from the reviews by Ruiz et al. (2020) and Morales-Contreras et al. (2022).

Many researchers had reviewed the hydrothermal liquefaction (HTL) of microalgae that used feedstock with approximately 80% moisture content to produce biocrude oil having greater calorific value (Barreiro et al., 2013a; Hu et al., 2019). These studies have detailed the characteristics of HTL products, reaction conditions and mechanism emphasizing it as feasible technology for biofuel production in comparison to pyrolysis on the basis of product quality and energy yield (Masoumi et al., 2021a; Masoumi et al., 2021b). Patel et al. (2016) described the hydrothermal treatment of microalgae through carbonization, liquefaction and supercritical water gasification reactions along with the life cycle analysis of algal biofuel supply chains. The transformation behaviour and mechanism of metal uptake on hydrochar was emphasized by Li et al. (2020) summarizing the studies on feedstock characteristics and process conditions over the hydrochar properties and its applications. Aliyu et al. (2021) has reviewed the thermochemical conversion of microalgae wherein the authors had elaborated the hydrothermal reaction conditions and suggested it to be effective in reducing energy and costs associated with harvesting and drying. Sahoo et al. (2021) had summarized the potential of algae and lignocellulosic biomass for co-hydrothermal liquefaction (Co-HTL). The reaction kinetics along with mechanism, the role of catalyst in Co-HTL and the application of by-products were also discussed. Chen et al. (2022) has recently reviewed the hydrothermal hydrolysis of algae wherein the associated mechanism and the influence of process parameters on biomethane production were elucidated.

Nevertheless, in spite of these comprehensive reviews, the effect of process parameters during microalgal hydrothermal processing (carbonization, liquefaction, gasification) on product yield and characteristics is scarcely discussed. Comprehensive discussion on hydrothermal reaction parameters influence on product yields using the severity factor for microalgal processing is sporadic. The reviews focusing on hydrothermal processing of microalgae emphasizing the research hotspots are also limited. Process pathways of different hydrothermal reactions considering the multi-product recovery and description of product along with market portfolio has been rarely reported. In that regard, three types of hydrothermal reactions of microalgae along with process pathways for multi-product recovery has been illustrated in this review. A hybrid Sankey diagram explaining the major research themes of the research field has been annotated. Market status of different hydrothermal products along with their environmental sustainability has been assessed. Besides the technical aspects, the review aids to understand the microalgal biorefinery in establishing energy-food-water nexus for promoting circular economy.

2. Thematic areas of microalgal hydrothermal treatment

The thematic areas assessment related to microalgal hydrothermal processing illustrates the current research scenario. The global collaboration network with their contribution in research themes could be visualized by hybrid Sankey diagram. Sahoo et al. (2021) described the potential of Co-HTL of lignocellulosic and algal biomass through hybrid Sankey diagram containing country, journal, year of publication. Here in this review, the knowledge domain of microalgal hydrothermal process has been mapped through country, major research themes and mean year through hybrid Sankey diagram (Fig. 1). Each node in the diagram corresponding to the country represents its frequency and in case of research theme, it refers to the size of the respective cluster formed.

It could be inferred that China, United States of America (USA), India, England, Australia, Canada has higher frequency of publications related to microalgal hydrothermal treatment process. These countries along with others have led the research development in various aspects to ensure the process feasibility in large scale and sustainability. The major research theme is “biocrude oil” which depicts the potential of

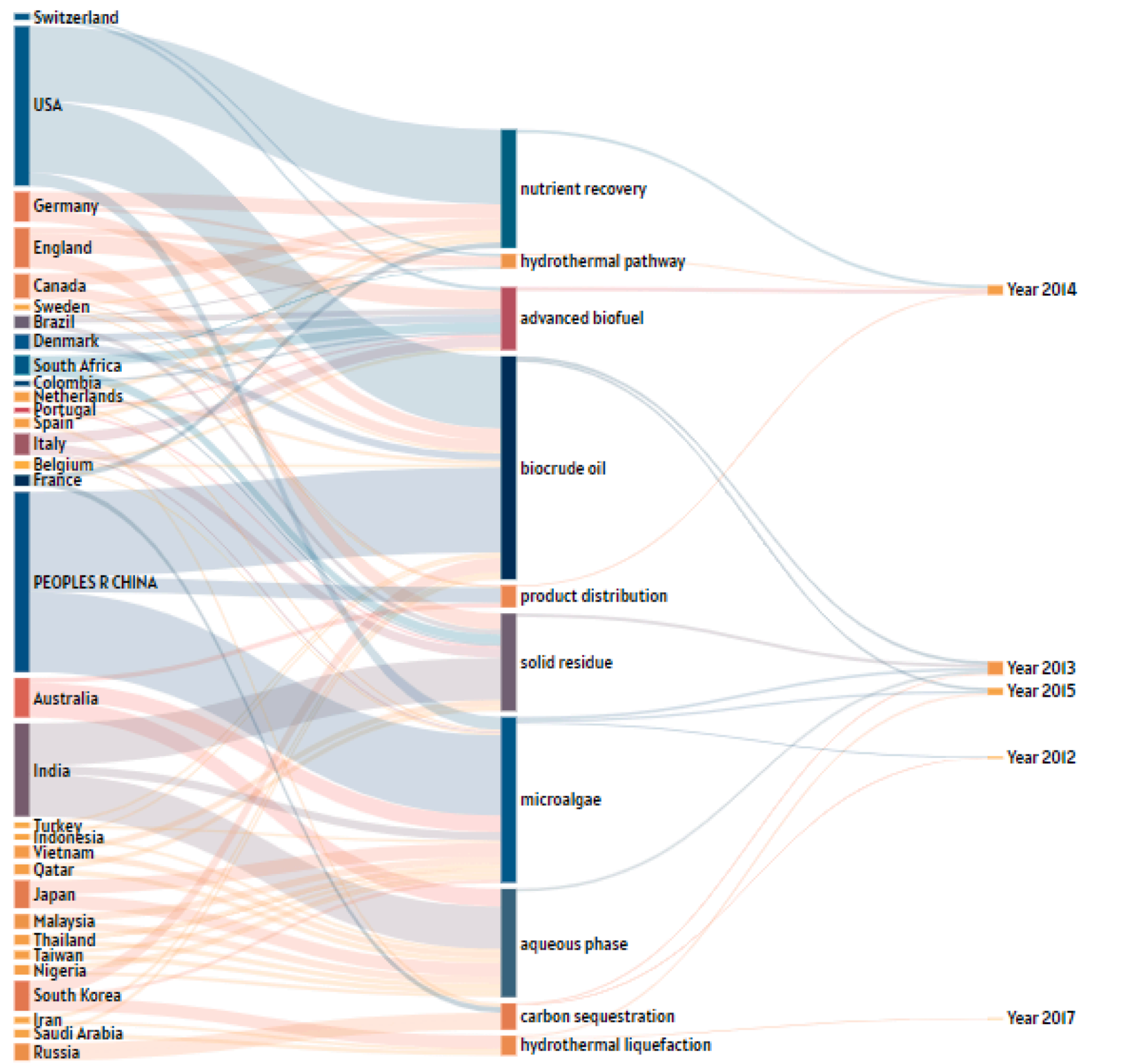

Fig. 1. Thematic research evolution of microalgal hydrothermal process.

microalgae for producing liquid biofuel through hydrothermal liquefaction having higher heating value (Biller and Ross, 2011; Eboibi et al., 2014a; Sharma et al., 2021). The catalytic upgradation of biocrude to be used as advanced biofuel has also been addressed over years (Panahi et al., 2019). Besides, the reaction pathways of hydrothermal liquefaction, product distribution has been widely discussed by many researchers (Vo et al., 2017; Matayeva et al., 2019). Furthermore, the upstream processing of microalgae for hydrothermal treatment like strain selection and specific conditions (Barreiro et al., 2013b), biochemical composition analysis (Liu et al., 2019) and biomass load optimization is also crucial for maximum product and energy recovery. The solid residue obtained after hydrothermal carbonization (HTC) of microalgae is carbon enriched hydrochar that has recently received more attention due to its multifunctional characteristics. It has been used as adsorbent for heavy metals or contaminants (Saber et al., 2018), crop improvement (Chu et al., 2021), catalyst (Masoumi and Dalai, 2021), bioenergy (Lee et al., 2019) and in carbon sequestration. These are the major thematic areas observed where more research is focussed towards HTL than HTC and hydrothermal gasification (HTG). Hence, there is a need for comparative assessment of three reaction pathways to delineate the research gaps that limits the bioeconomy of microalgal hydrothermal process.

3. Hydrothermal processing of microalgae: Process pathways and multi-product description

3.1. Hydrothermal carbonization (HTC)

Hydrothermal carbonization (HTC), a thermochemical conversion technique converting microalgal biomass carbohydrates into carbon rich solid in a hydrothermal aqueous medium. Initially, Heilmann et al. (2010) analysed the potential of microalgae for combustion and soil amendment through hydrothermal carbonization reaction. The carbon content of algal char was found to be greater than lignocellulosic char. The mechanism proposed for carbonization includes dehydration reaction, increased oxygen content in filtrate owing to fragmentation of carbohydrate polyol materials and formation of water soluble oxidized products. In HTC process, the yield and energy of products is influenced by process parameters like temperature ranging from 180 °C to 260 °C and retention time of 5 min–60 min. The thermal stability and yield of hydrochar could be enhanced by aqueous phase recirculation (Leng et al., 2020). It has also been reported that hydrochar prepared from HTC of de-washed algae has better physicochemical properties and higher heating value (HHV) compared to that of unprocessed microalgae. Owing to removal of ash, the energy yield of hydrochar will be enhanced following the mechanism of decarboxylation and dehydration (Liu et al., 2019).

3.2. Hydrothermal liquefaction (HTL)

The conventional production of biofuel from microalgae involves the extraction of lipids and chemical conversion into biodiesel, which is energy intensive because of the dewatering step needed to reduce 80–90% moisture content in the algal biomass. Alternatively, microalgal wet biomass can be hydrothermally converted into bio-crude oil at sub-critical temperature between 280 °C and 370 °C and, pressure in range of 10–25 MPa. Along with bio-crude oil, other secondary products like solid residue, aqueous and gaseous phase are also generated. Sub-critical water is a low-cost reaction medium facilitating the wet biomass conversion via dehydration, dehydrogenation, de-oxygenation and decarboxylation reactions into unstable and potentially reactive smaller molecules which thereby reorder through a series of reactions to form bio-oil with much wider molecular weight (Gollakota et al., 2018). Hydrothermal processing producing bio-crude oil utilizes not only lipids but also the fraction of carbohydrate and proteins. This strategy is especially useful in case of microalgae having lower amount of lipids where the other metabolic constituents are also completely being utilized to produce bio-based products (Biller and Ross, 2011). However, the complexity of biochemical constituents makes the process complicated and the reactions difficult to understand. The HTL of wet algal biomass proceeds through the three basic steps as detailed by Mathimani and Mallick, (2019) including 1). Depolymerisation: Disintegration of cellulose, hemi-cellulose via solvolysis into micellar structure followed by depolymerisation into individual small molecules; 2). Decomposition: Removal of water, carbon dioxide and amine via dehydration, decarboxylaton and deamination respectively; 3). Recombination: Re-polymerization and recombination of high molecular weight compounds like char/coke due to the lack of hydrogen and higher free radical content. HTL of microalgae has several advantages compared to pyrolysis, basically because of its better process efficacy and quality of bio-oil (Raheem et al., 2018). Several researchers have highlighted the importance of influencing factors like the microalgae ultimate composition (Koley et al., 2018) and loading characteristics (Guo et al., 2015), reaction temperature and pressure (Barreiro et al., 2013a), residence time (Ji et al., 2017), and catalyst content (Masoumi and Dalai, 2021) on the product yield and quality.

3.3. Hydrothermal gasification (HTG)

Hydrothermal gasification (HTG), a thermochemical conversion reaction which occurs at 400 °C – 500 °C, at a pressure of 24 MPa–36 MPa in the presence of sub-critical water (<374 °C and 22.1 MPa pressure) resulting in the production of combustible gases consisting of methane (CH_4), hydrogen (H_2), carbon monoxide (CO) and carbon dioxide (CO_2) (Mathimani and Mallick, 2019). Depending on the process conditions and the prominent gaseous product yield HTG can be broadly classified as 1). H_2 based HTG, where biomass is treated at temperature of more than 500 °C; 2). CH_4 based HTG, with thermochemical treatment carried between the critical temperature and 500 °C. HTG mainly progresses through a series of reactions including water–gas shift, steam reforming and methanation, where apart from temperature, several other process parameters along with cultivation conditions of microalgae influences the product yield The study by Fozer et al. (2019) reported hydrogen yield of 9.34 mol/kg via HTG in tubular reactor operated at 30 MPa, 550 °C and 120 s retention time using *Chlorella vulgaris* grown under optimal light conditions. HTG yields gaseous products with better yield and performance efficacy with lower tar/soot than conventional gasification, thereby finds application as a source of electricity, fuel cell or for chemical synthesis (Canabarro et al., 2013). A recent study by Nurcahyani and Matsumura, (2021) reported that the effluent produced from HTG of *Chlorella vulgaris* at 600 °C can be recycled into the cultivation medium leading to 2.5 times higher phosphate accumulation thereby facilitating algal growth. The effluent was reported to be superior in terms of quality compared to that obtained during HTL process.

4. Effect of factors on product yield during hydrothermal processing of microalgae

Hydrothermal processing of microalgae involving chemical transformation of biomass is governed mainly by the reaction temperature and time. Severity factor (SF) is often utilized to establish the relationship between the combination of temperature and time to reaction extent through a kinetic model (Ruiz et al., 2021). SF assumes first order reaction in isothermal processing with Arrhenius equation and it is being used to evaluate and compare the different hydrothermal pre-treatment (HTP) conditions as given in Eq. (1) (De Farias Silva et al., 2022).

$$\text{Severity factor}(Ro) = e^{\frac{T-Tr}{\omega}}t \tag{1}$$

where, T and T_r is the treatment temperature and reference temperature (100 °C) respectively. ω is an empirical parameter containing the value of 14.75 based on the assumption of first order kinetic reaction. t is the holding time. The determination of SF provides the opportunity to select the hydrothermal processing conditions achieving higher product yield with desired characteristics (Jiang and Savage, 2017). Several researchers have utilized SF for analysing the correlation of reaction parameters like hydrothermal treatment temperature, time and acid concentration on product yield to optimize the reaction conditions (Faeth et al., 2013; Ruiz et al., 2020). The correlation analysis between the severity of different HTL conditions for biocrude aids to identify the suitable conditions for obtaining higher yield and desired characteristics. The reaction ordinate, $Ro = 10^9$–10^{11} was reported to be suitable conditions for biocrude production with reduced iron content from *Nannochloropsis* sp. (Jiang and Savage, 2017). The higher biocrude yield is obtained with shorter reaction time leading to lower log *Ro* (which increases with temperature and time) as reported by Eboibi et al. (2014b) who obtained biocrude yield of 65% with energy density of 35 MJ/kg at SF of 5.21 which was lower than other related studies. However, biocrude yield decreases after a certain severity of hydrothermal process owing to the gasification reactions. Hence, the determination of optimal range of reaction ordinate prevents the longer reaction time that limit the biocrude yields (Faeth et al., 2013).

Jeong and Kim, (2021) utilized combined severity factor (CSF) to analyse the catalytic performance of hydrothermal conversion of *Chlorella* sp. into 5-hydroxymethylfurfural (5-HMF) and levulinic acid (LA). The effect of CSF on 5-HMF and LA yield follows non-linear sigmoidal model where high CSF conditions significantly affects both the yields (Jeong and Kim, 2020, 2021). Besides the significant role of SF in predicting the hydrothermal processing conditions for product recovery and the effectiveness of HTP applicable for lignocellulosic biomass, macroalgae (Ruiz et al., 2021; Morales-Contreras et al., 2022), its contribution in microalgal hydrothermal processing is less explored. Based on the severity of process, hydrothermal processing is categorized as HTC, HTL, HTG (Morales-Contreras et al., 2022) as detailed in previous section. Besides temperature and reaction time, product yield and characteristics is also governed by process conditions during HTC, HTL and HTG which has been detailed in the subsequent sections and also represented in Table 1.

4.1. Feedstock composition

Microalgae has varied biochemical composition including lipids, proteins, and carbohydrates that determines the yield and product composition obtained via thermochemical processing. Compared to lignocellulosic biomass, microalgae could rapidly decompose because of its lower thermal stability (Ji et al., 2017). Furthermore, due to lower sulphur content in microalgae, the issues of corrosion in hydrothermal

Table 1
Comparative assessment of reaction parameters and product characteristics of different hydrothermal processing of microalgae.

Microalgae	Hydrothermal reaction	Biomass composition (%)	Process conditions	Product Yield (%)	Product composition (%)	HHV (MJ kg^{-1})	Energy yield (%)	References
Chlorella vulgaris	HTC	VM – 82.43; FC – 11.99; Ash – 5.57	B/W ratio: 25% Temp: 220 °C; HR: 4.6 °C min^{-1}; Time: 45 min	Hydrochar: 30.26	VM: 71.55; FC: 21.95; Ash: 6.5	18.87	33.5	Sztancs et al. (2021)
Sewage sludge + *Chlorella vulgaris*	Co-HTC	MC – 4.32; VM – 74.55; Ash – 14.32; FC – 11.13	B/W ratio: 1:1 Temp: 180 °C- 270 °C; Time: 30 min	Hydrochar: 45.98 – 93.97	VM: 63.52–72.37; FC: 9.82–12.53; Ash: 15.10–26.66;	21.71–24.30	–	Lee et al. (2019)
Microalgal consortium	HTC	C – 50.44; H – 8.51; N – 6.03; O – 34.5	B/W ratio: 1:10 Temp: 130 °C- 170 °C; Pressure: 1–6 bar; Time: 10–50 min	Hydrochar: 67–77	C: 53.01–58.54; H: 8.81–9.98; N: 4.31–5.77; O: 24.93–32.99	16.99–17.47	68.30–78.21	de Siqueira Castro et al. (2021)
Spirulina sp.	HTL	Carbohydrate: 11; Lipids: 18; Protein: 53	Temp: 300 °C; Time: 5 min; B/W ratio: 16%	Biocrude: 67; Solid: 14	C: 83.8; H: 9.5; N: 4.6; S: 0.6; O: 1.5	40.4	79	Eboibi et al. (2014a)
Chlorella pyrenoidosa	HTL	C: 40.32; H: 5.99; N: 9.14; O: 27.74	B/W ratio: 1:10; Temp: 350 °C; Time: 30 min	Biocrude: 31.7	C: 72.59; H: 8.88; N: 6.91; S: 0.75	35.3	64.65	He et al. (2018)
Chlorella pyrenoidosa	HTG	C: 53.12; H: 7.38; N: 8.80; O: 27.31; FC: 19.92; Ash: 4.62	B/W ratio: 1:1; Pressure: 2–13 MPa; Temp: 430 °C; Time 60 min	H_2: 5.6 mmol g^{-1}; CH_4: 8.22 mmol g^{-1}	–	–	–	Jiao et al. (2017)
Spirulina sp.	HTG	MC: 7.8; Ash: 7.6	B/W ratio: 1:15; HR: 30 °C min^{-1}; Temp: 500 °C; Pressure: 36 MPa; Time: 30 min	Gas: 69; Tar: 15; Solid: 7;	H_2: 21.1; CO: 4.26; CO_2: 36.2; CH_4: 21.2; C_2-C_4: 16.9	27.9 MJ/m^3)	–	Onwudili et al. (2013)

*Abbreviations: HTC: Hydrothermal Carbonization; HTL: Hydrothermal Liquefaction; HTG: Hydrothermal Gasification; Temp: Temperature: HR: Heating Rate; B/W ratio: Biomass/water ratio; VM: Volatile Matter; FC: Fixed Carbon; MC: Moisture Content; C: Elemental Carbon; H: Elemental Hydrogen; N: Elemental Nitrogen; O: Elemental Oxygen; S: Elemental Sulphur; HHV: Higher Heating Value.

reactors is relatively less compared to lignocellulosic feedstock (Thakkar and Kumar, 2019). Also, depending on the biochemical constituents, the range of reaction parameters needed for hydrothermal processing might also vary (Guo et al., 2015). *Chlorella* sp., *Desmodesmus* sp., *Scenedesmus* sp., *Dunaliella* sp., *Phaeodactylum* sp., *Spirulina* sp., and *Nannochloropsis* sp., are most commonly utilized for hydrothermal processing into hydrochar, biocrude oil and gaseous by-products (Mathimani and Mallick, 2019). Biller and Ross, (2011) performed hydrothermal processing at 350 °C, 20 MPa, 60 min for 4 different algal strains comprising *Nannochloropsis occulata*, *Chlorella vulgaris*, *Spirulina* sp., and, *Porphyridium cruentum* and predicted the bio-crude oil yield in relation with biochemical composition of these microalgae. The study reported that the biocrude oil obtained was 5–25% weight of the lipids present in microalgae. Apart from lipids, non-oleaginous microalgae can also successfully be converted into bio-oil and other bio-based products. During HTL, it is preferable to utilize protein rich microalgae which results in short hydrocarbon chains in biocrude, thereby lighter oil is produced (Koley et al., 2018). Zhang et al. (2016) reported that combined *Spirulina* sp., and *Nannochloropsis* sp., with adequate protein content improvises the energy recovery during HTL. It is therefore essential to tailor the amount of carbohydrates and proteins in microalgae to improve the bio-crude oil quality. Smith et al. (2016) reported that the degradation temperature is influenced by the biochemical constituents of microalgae and the transition between hydrochar yield formed via HTC and bio-crude oil produced through HTL depends on the feedstock composition. At lower reaction temperature (250 °C), often the strain specific features have a prominent influence on the product yield, however, the effect of the algal physicochemical factors declines on increasing the process temperature beyond 375 °C (Barreiro et al., 2013b). The study has projected the need to maintain the process conditions at sub-optimal level to obtain higher yield of bio-crude oil.

4.2. Reaction temperature

Reaction temperature is the most critical factor that influences the hydrothermal processing and its subsequent product yield as it supplies the adequate amount of heat needed to modify the viscosity, density and dielectric properties of water to facilitate fragmentation of the algal biomass (Ji et al., 2017). Up to a temperature of 100 °C, lipids are fragmented into long chain fatty acids and glycerol, proteins are converted into amino-acids and, carbohydrates are assimilated into reducing and non-reducing sugars. As the temperature rises to 200 °C, deamination, decarboxylation and degradations of fatty acids, sugars and amino acid molecules occurs (Barreiro et al., 2013a). At around 250 °C temperature, hydrolysed products being hydrophilic reduces the bio-oil yield. With a further increase, up to the critical water temperature, the reduction of organic content in aqueous phase results in enhanced bio-oil yield. Study by Ji et al. (2017) reported that the bio-oil yield increases until a certain threshold temperature beyond which there is no appreciable change. Secondary cracking of bio-oil increases the gaseous fractions with further enhancement of hydrothermal reaction temperature beyond 350 °C (Tekin et al., 2014). Nevertheless, depending on the algal biomass characteristics, temperature of 270 °C–340 °C is often utilized to obtain the maximal bio-oil yield (Sharma et al., 2021). Temperature not only influences the bio-oil yield but also its subsequent fuel characteristic like the higher heating value (HHV) and the biochemical content. Maximum HHV of 36.99 MJ/kg (61% energy recovery) was obtained by Villaver et al. (2018) through HTL of *Spirulina platensis* carried at 350 °C for 45 min. The study reported maximum HHV to be achieved at highest temperature and reaction time. Increasing the HTL temperature from 250 °C to 350 °C has been reported to decline the nitrogen content in bio-oil from 3.8% to 1.6% (Jena et al., 2011). Hydrochar yield during HTC has also been reported to decline with an enhancement in temperature from 180 °C to 250 °C and with increasing retention time from 0.5 h to 4 h (Khoo et al., 2020). Gai et al. (2015) reported that the decrease in hydrochar yield is mainly attributed to the cyclic oxygenates decomposition from reducing sugars at 200 °C–210 °C and, that of nitrogenous and oxygen heterocyclic compounds from proteins at 240 °C–250 °C into bio-crude oil. Variation in fixed carbon and volatile matter of hydrochar as well as the changes in nitrogen content produced from raw and lipid extracted microalgae with extension of reaction temperature during HTC has been reported in a recent research study by Benavente et al. (2022) thereby, impacting its end application.

4.3. Operational pressure

Operational pressure is one of the essential factor as it maintains water as a single reaction medium in the sub critical/supercritical level, thereby facilitating the degradation of microalgal biomass. High pressure and temperature not only facilitate the transport of the wet slurry in a hydrothermal reactor but also facilitates the release of H^+ ions which thereby catalyses the liquefaction process (Elliott et al., 2015). Ji et al. (2017) reported that increasing the operational pressure during HTL of *Spirulina* sp., from 3.2 MPa to 9.7 MPa at 300 °C resulted in maximal biocrude oil and hydrochar yield, however further extension of pressure to 32.9 MPa at 350 °C temperature did not have any significant effect on product yield. Apart from quantitative yield, the physicochemical properties of bio-crude oil are also influenced by the operational pressure. Prapaiwatcharapan et al. (2015) reported that an increase in pressure to 20 MPa in sequential HTL results in increased C and N content as well as HHV of biocrude oil from *Coelastrum* sp. Masoumi et al. (2021a) reported maximum biocrude oil and hydrochar yield of 57.8% and 19.5% respectively, and 75% methanol at optimal temperature of 272 °C, 35 min residence time and 222 °C, 11.5 MPa pressure with 10 min residence time respectively from *Nannochloropsis gladitana*. In case of HTC, though temperature remains lower than other thermochemical processes, the pressure reached is significantly higher resulting in the release of gases in the system. Thus, maintenance of pressure is an essential criterion, which occupies majority of share of energy and economics during the hydrothermal treatment of algal biomass. Alvarez-Murillo et al. (2022) developed a theoretical frame-work to predict the pressure of HTC reactor as a function of water-carbon dioxide (H_2O-CO_2) system. Such models would aid in the easier design of hydrothermal reactor to obtain the desired product yield and physicochemical properties for specific application.

4.4. Catalysts

Catalysts are widely utilized during the hydrothermal treatment of algal biomass to derive products of appropriate yield and quality. During HTL, both heterogeneous (Pt/Al, Ni-Mo, Ni-Ra, Pt-C) (Ding et al., 2022) and homogenous (Na_2CO_3, K_2CO_3 and KOH) (Zhang et al., 2018; Chen et al., 2021) catalysts are commonly used to obtain better energy recovery, derive bio-crude oil with reduced oxygen, nitrogen and sulphur content, increased carbon/hydrogen ratio (C/H) and lower viscosity (Wang et al., 2018). On the other hand, catalysts are usually not required during HTC, as the medium remains acidic due to the presence of process water (Biller and Ross, 2016). Recent analysis by Muppaneni et al. (2017) reported higher bio-crude oil yield (21.23%–22.67%) during the HTL of *Cyanidioschyzon merolae* with the use of homogenous acid/alkali catalysts compared to the non-catalytic process (16.98%). It was observed that compared to alkali, acid catalyst showed lower yield, this might be attributed to carbohydrates decomposition into water-soluble phase and bio-oil polymerization into solid residues (Zhang et al., 2018). However, acid sites impregnated by the catalyst facilitates decomposition of macromolecules into smaller fragments improving the hydrothermal process efficacy (Liu et al., 2021). Homogenous base catalyst often increases the pH, inhibiting biomass monomers dehydration, facilitating water–gas shift reaction that generates H_2, which acts as a reducing agent improving the HHV and quality of bio-crude oil (Barreiro et al., 2013a). Apart from improving the bio-crude oil yield, homogenous catalysts also decrease the char/tar yield thus, are easy and economical to use but, it is difficult to recover the catalyst and their efficacy declines under harsh conditions. Heterogeneous catalysts function under harsh reaction conditions based on the principles of adsorption–desorption of reactants and increases the process efficiency. Xu et al. (2014) reported 49.87% and 34.02% bio-crude oil yield via HTL of *C. pyrenoidosa* with Ce-HZSM-5 and HZSM-5 respectively. The review by Mathimani and Mallick, (2019) provides a comprehensive summary of the bio-crude oil yield obtained with various homogeneous and heterogeneous catalysts during HTL.

Similar to HTL, use of specific metal catalysts i.e., Ruthenium (Ru) and Palladium (Pd) as well as homogenous catalysts like NaOH and KOH improves the gasification of tar/char, facilitates the formation of recalcitrant intermediate products during the hydrothermal processing of algal biomass thereby increasing the yield and selectivity of syngas (Guan et al., 2013; Shan et al., 2021). A recent study by Jiao et al. (2017) performed HTG of *S. platensis*, *C. pyrenoidosa*, *S. limacinum* and *Nannochloropsis* sp., at 430 °C for 1 h (batch reactor), reported an improvement in the yield of H_2 and CH_4 by 2–3 times and 3–9 times respectively with the use of different metal catalysts compared to the non-catalyzed reactions. The carbon monoxide (CO) content and the requirement of high process temperature during HTG could also be significantly avoided during the catalyst mediated gasification process (Xie et al., 2019).

4.5. Residence time

Residence time refers to the time needed to hold the algal biomass at a specific temperature and pressure inside the hydrothermal reactor (Benavente et al., 2022). Along with the operational temperature and pressure, residence time plays an essential deciding factor for the design economics of a hydrothermal reactor for microalgae (Wądrzyk et al., 2018). Residence time of algal biomass governs the extent of cracking, polymerization and re-polymerization of the algal biomass and decides the yield of solid, liquid or gaseous products during the hydrothermal reaction (Villaver et al., 2018). Shorter residence time results in higher bio-oil yield but longer the time more is the secondary cracking reactions yielding higher char and syngas (Cheng et al., 2017). Ji et al. (2017) analysed the effect on yield of bio-oil during the HTL of low lipid containing *Spirulina* sp. with varying residence time from 15 min to 45 min, at 300 °C, 50% vol. of solvent, 40/4 ml/g solvent: microalgae ratio. It was observed that the bio-oil yield increased from 15% to 60% with an increment in time from 15 min to 45 min. However, on further increase in holding time up to 75 min, only 46% yield was obtained. In contrast to the above-mentioned study, Barreiro et al. (2014) reported bio-oil yield of 60.3% from *N. gaditana* after 5 min reaction time, while 60% yield was obtained with *S. almeriensis* in 15 min hold-up time, keeping other reaction conditions for HTL constant. Thus, the study reported maximal hold-up time needed to achieve highest bio-oil yield is species specific. Masoumi et al. (2021a) investigated the HTL of *Nannochloropsis gaditana* in methanol–water system and reported that low temperature and time results in higher biocrude oil yield. Yield of 57.8% with energy recovery of 85.3% was obtained with temperature of 272 °C, reaction time of 35 min and 75% of methanol in water system. Similar to HTL, the impact of residence time on product yield is also evident in case of HTC and HTG reactions. Khoo et al. (2020) analysed the impact of reaction temperature and hold-up time on the hydrochar yield from high ash containing and low lipid containing *C. vulgaris*, predicting temperature influence to be more prominent compared to the hold-up time. 34% and 18% difference in the maximum hydrochar yield was evident with temperature (250 °C) and hold-up time (4 h) respectively by the authors in the above-mentioned study. Shan et al. (2021) utilized Ru supported activated carbon at 12 $mg_{(Ru/C)}\ ml^{1}_{(aq)}$ to boost supercritical water gasification at 600 °C for 1 h and obtained H_2 content of 50% and yield of 2.62 mmol g^{-1} with reduced total organic carbon and increased carbon gasification efficiency. Gasification yield and efficiency are maximum with longer hold up time, higher reaction temperature, and catalyst loading (Kumar et al., 2021; Tiong and Komiyama, 2022). Nevertheless, as evident in several eminent researches, an optimum residence time along with other operational conditions of hydrothermal processing influences the progress of reaction with respect to algal biochemical composition of microalgae.

5. Products of hydrothermal processing of algal biomass

5.1. Energy based products

Hydrothermal processing of wet algal biomass provides basically three products i). Hydrochar (solid product formed during HTC) ii). Bio-crude oil (liquid fuel formed during HTL) and, iii). Gaseous products as a result of HTG.

HTC often upgrades high moisture and low carbon content algal biomass into a high calorific value source that can be utilized as a solid fuel through a series of reactions involving dehydration, decarboxylation and demethylation that declines the oxygen/carbon (O/C) and hydrogen/carbon (H/C) ratios. Heilmann et al. (2010) were one of the first researchers who investigated the production and characterization of HTC derived hydrochar from algal monocultures. The study reported that in comparison to lignocellulosic feedstock, algal hydrochar have higher carbon content and calorific value similar to bituminous coal. A subsequent study by the same authors Heilmann et al. (2011), reported that fatty acids can be obtained from the hydrothermally derived char, and can act as the precursors for the production of biofuel. Marin-Batista et al. (2019) performed HTC of microalgal biomass at 210 °C, and produced algal hydrochar having 1.09 times higher carbon content and 1.10 times higher heating value than raw algal biomass. Park et al. (2018) reported that HTC reaction of algal biomass bears similarity with the coalification, where the carbon and energy recovery often increase, making it a suitable alternative as renewable fuel. Lipid extracted algal biomass undergoes devolatilization reactions resulting in decreased sulphur and ash content during the hydrothermal processing, thereby producing a cleaner source of renewable fuel (Lee et al., 2018). Liu et al. (2019) reported that deashing algal biomass based hydrochar have good combustion characteristics at high temperature, similar to medium calorific value coal and can be suitably be mixed with coal as an alternative renewable power source.

HTL of microalgae at low temperature and high pressure converts the biomass into a liquid energy based form called biocrude oil. The liquid biofuel obtained by upgrading the bio-crude oil finds economic value in the existing petroleum fuel product market. Microalgal slurry with 5% to 20% mass which are usually obtained by spending just 12% of the energy can easily be converted into the liquid-based energy carrier by HTL (Xu et al., 2011; Panahi et al., 2019). Under optimized conditions of 623 K, with an incubation time of 3 min to 14 min, 40–60% bio-crude oil yield can be obtained in a continuous flow reactor system. Jena et al. (2011) projected that 20% solid content in microalgae provided the highest biocrude oil yield during HTL. HTL utilizes not only lipids but also carbohydrates, proteins and, processes them into a fuel product that is similar to the crude product in petroleum biorefinery, thus provides much higher yield compared to the transesterification process (Panahi et al., 2019). However, studies by Tian et al. (2014) and Chen et al. (2017) reported that algae with higher lipids provides fuel of better quality, and the feedstock with high protein and carbohydrate is conducive to HTL. A recent study by Watson et al. (2021) proposed a strategy to combine the biological dark fermentation process with HTL, which improved the biocrude oil yield and energy conversion ratios by 10% and 61% respectively compared to the control process. The energy and the carbon content of biocrude oil was also enhanced by 40% and 10% respectively. Apart from feedstock composition, higher heating rates and lower residence time with harsh thermal processing conditions also improves the biocrude oil yield (Faeth et al., 2013; Wądrzyk et al., 2018). Utilization of catalysts (Hu et al., 2019) and organic co-solvents (Ji et al., 2017) has been shown to increase the yield of water insoluble products and decreases the viscosity of oil. Biocrude oil produced by HTL of algal biomass have high calorific value and low water content compared to other lignocellulosic biomass but has high viscosity, nitrogen and oxygen content that makes it inappropriate for direct use in fuel engines (Shakya et al., 2017). Microalgae derived biocrude oil obtained with a yield ranging from 36% to 64% weight and an energy recovery of 60% to 78%, typically has a calorific value of 25–37 MJ/kg with 5%–10%, 5%–18% and 4%–8% water, oxygen and nitrogen content respectively and viscosity of 40–67 cPa, total acidity of 25–110 mg KOH/g (Elliott et al., 2015; Shakya et al., 2017). Very often, higher oxygen content declines its miscibility with other fossil fuels, and results in lower thermal stability, making it prone to side reactions creating difficulty during storage and transportation. High water content might also delay the fuel ignition and decrease the calorific value (Lian et al., 2017). The physiochemical properties of biocrude oil can be modified or enhanced by tailoring the algal feedstock and altering the process conditions of HTL as mentioned in the previous sections. Upgrading the bio-crude oil involves a series of techniques as in i). Hydro-treating for reducing the viscosity, nitrogen and sulphur content; ii). Hydro-oxygenation to decrease the oxygen fraction; iii). Hydro-cracking and catalytic cracking for cetane number and hydrogen: carbon (H:C) ratio improvement respectively; iv). Esterification for decreasing acid number; v). Emulsification for phase separation prevention. The upgrading techniques have been detailed in the review by Panahi et al. (2019). Most of these upgrading steps are expensive due to costly catalysts or surfactants involved, thus there is a need to optimize the process conditions and also utilize durable and efficient cheaper catalyst/surfactants with good regenerative capacities. Also, detailed research on suitable methods to alleviate catalytic degradation and formation of triggering compounds during the upgradation steps are essential.

HTG at temperature greater than 374 °C (usually between 600 °C and 750 °C) and a pressure more than 22 MPa is often utilized to convert algal biomass into energy rich fuel gas comprising of hydrogen (H_2), apart from carbon dioxide (CO_2) and carbon monoxide (CO) (Patzelt et al., 2015). Several alkali hydroxides and carbonates (homogenous catalysts) and activated carbon, transition metals and oxides (heterogeneous catalysts) as mentioned by Norouzi et al. (2017) are often used to improve the process operating conditions like the carbon conversion ratio, providing requisite temperature and pressure for enhancing the product selectivity and quality in terms of composition and calorific value. The fuel gas produced via hydrothermal treatment, when water exists at supercritical temperature is much pure and does not get contaminated with char. Changes in reaction temperature, feedstock type and composition can influence the quality of fuel gas produced, thereby impacting its application.

5.2. By-products description and utilization

Apart from energy applications, the hydrothermal processing also generates by-products that finds use in diverse environmental applications like agriculture and environmental management especially adsorption. Along with being the alternative sources of bioenergy, hydrochar produced during HTC can also be used as an eco-friendly fertilizer. *Microcystis* sp., derived hydrochar treated with 1% citric acid, recovered 95% of phosphorus, and its subsequent utilization in pot experiments to grow wheat revealed that it could slowly release phosphorus, thereby increasing the nutrient utilization efficiency by 34% compared to chemical alternatives (Chu et al., 2021). HTC often breaks the macromolecular chains providing more labile forms of carbon and nitrogen pools to the soil microbiome. Chu et al. (2020) reported positive effects of *Chlorella* sp., derived hydrochar on rice grain yield, through increased nitrogen utilization. However, hydrochar might increase ammonia volatilization in soil thereby, negatively affecting the environment. Apart from agriculture, hydrochar with high oxygen containing functional groups, pore volume, and surface area can be used for adsorption of pollutants and heavy metals from wastewater. Saber et al. (2018) projected that hydrochar derived from *Nannochloropsis* sp., produced at 250 °C adsorb significant amount of copper at almost all solution pH, due to the presence of oxygen containing functional groups.

Aqueous phase extract formed as a by-product (rich in organic and inorganic nutrients) during HTC has been shown to be utilized as a growth medium for microalgae or microalgae-fungi co-cultivation. Chen et al. (2020) demonstrated that step-wise process to grow microalgae and fungi in 5% aqueous phase, could remove 32.91% total nitrogen and 95.30% total phosphorus, and the harvested biomass can later be utilized as a feedstock for renewable fuel. HTL also produces solid precipitate with recovered phosphorus and nitrogen that can act as the nutrient source for microalgae cultivation (Elliott et al., 2015).

5.3. Commercial status of the process and market portfolio of products

Hydrothermal processing of microalgae is regarded as an essential technique with significant potential for future commercialization. Several laboratory scale investigations involving different feedstock with various influencing reaction conditions, catalysts and reactors to improve the product quality and yield have been scaled up to commercial levels. Many of the pilot scale facilities of HTL have also been translated into field scale in the form of several companies like the Silva Green Fuel (Norway), the Altaca Energy (Turkey) and the Licella Pvt. Ltd. (Australia). These companies produce bio-crude oils that can be directly used as fuels or can be sold to the facilities where petroleum refining is being done. Additionally, several co-products are produced like electricity, hydrocarbon gases and green chemicals which can be traded for improving the process economics (Watanabe and Isdepsky, 2021). Study by Pearce et al. (2016) reported the market potential of bio-oil and bio-crude oil from microalgae cultivated using solar energy. Market value of bio-oil or bio-crude oil is similar to that of the petroleum crude fraction i.e. 550 USD per ton and 70 USD per barrel. Market report as of 2015 suggested that the bio-crude oil or biofuel from microalgae, would become more profitable with co-product exploration and the companies diversified their business towards value added products like nutraceuticals, aquaculture feed, agro based products like biostimulants and bio-fertilizers.

Apart from biocrude oil, hydrochar also has significant market potential and can be utilized as a replacement of peat in hydroponic growth mediums. Hydrochar can also act as porous medium to retain moisture and because of slow mineralization, can sequester large amount of CO_2 from the atmosphere, thereby generating carbon credits.

6. Sustainability challenges of hydrothermal processing of microalgae

Even-though hydrothermal technologies are promising enough to be utilized for the production of fuel in the form of solid product (Hydrochar), liquid (Biocrude oil) and other gaseous products (Fuel gas), it is essential to economically and environmentally assess the sustainability metrics of the process to understand its feasibility.

6.1. Techno-economic feasibility

Most research being limited to laboratory scale hydrothermal reactors, several technical issues as in the optimal reactor designs and operational conditions act as prominent technical hurdles during scale-up. Ruiz et al. (2020) highlighted that heat of reaction, process heat recovery, optimal residence time and waste product treatment are some of the technical hindrances witnessed during the scale-up of hydrothermal process during the multi-product biorefinery. Process optimization of operating conditions like temperature, hold-up time, feedstock quantity and composition increases the product yield and characteristics. Selection of appropriate algal strains with low nitrogen and sulphur content along with better environmental resilience will improve the process efficacy. The use of appropriate catalysts type and quantity also determines the quality of products during hydrothermal processing of microalgae. It is essential to understand the inherent mechanisms of reactions during hydrothermal processing of microalgae to control the operational conditions for enhancing the product yield and quality.

Undoubtedly, the intrinsic processing feature of hydrothermal technologies treating the wet biomass is regarded as an economically advantageous method where the wet feedstock can be processed into fuel and other bio-based products. Table 2 summarizes the techno-economics of hydrothermal processing of microalgae under different process conditions. Due to limited research on the uncertainties linked with the huge costs because of high temperature and pressure utilized during biomass processing, the field scale application of hydrothermal techniques is often less (Ou et al., 2015). Bennion et al. (2015) reported that the energetics of hydrothermal processing is mostly dominated by the heat energy required for achieving the requisite temperature and

Table 2
Techno-economic feasibility analysis for hydrothermal processing of microalgae.

Process approach	Software tools	Economic matrix	References
Feedstock: 2000 dry tonne per day defatted microalgae (*Scenedesmus* sp.) with initial 80% moisture content for hydrothermal processing with recycling of liquid/solid effluents	ChemCAD 6.5 software by Chemstations™; 30-year discounted cash-flow spreadsheet based ROI	CAPEX: 424 million US$ OPEX: 158 million US$/year MSPF: 679 $/m^3	Ou et al. (2015)
HTL of algae growin in tertiary treated municipal wastewater; hydroprocessing using hydrogen obtained through biogas reforming	Aspen Plus Economic analyser	CAPEX: 568 million US$ OPEX: 41 million US$/year MSPF: 4.3 US $/GGE	Ranganathan and Savithri, (2019)
HTL of algae treating 227 million Gallons/ day wastewater, bio-oil hydrotreating followed by co-product recovery and use	SuperPro Designer	CAPEX: 105 MM $ OPEX: 17.88 MM $/year MSPF: 6.62 $/Gallon	Juneja and Murthy, (2017)
Integrated HTL and concentrated solar power thermal processing of microalgae	Aspen Plus Economic analyser;Microsoft Excel model for equipment sizing and costing	CAPEX: 242K $ OPEX: 43K $/year MSPF: 1.23 $/kg	Pearce et al. (2016)
HTL of algal biomass (*C. sorokiniana*) and upgrading of bio-oil intermediates through hydrotreating (Catalytic HTG)	Aspen Plus; Microsoft Excel spreadsheet	CAPEX: 459 million US$ OPEX: 198 million US$ MSPF: 5.72 $/GGE	Gu et al. (2020)
Microalgae HTL to biocrude followed by its upgrading integrated with direct recycling (DR), catalytic hydrothermal gasification (CHG) and anaerobic digestion (AD)	Process simulations using Aspen plus with sequential modular approach; Aspen Process Economic analyser	TCI of 72.7 million US$, 119 million US$, 85.2 million US$ for HTL with DR, CHG and AD respectively having corresponding MSPF of 12.5 $/GGE, 13.8 $/GGE and 12.9 $/GGE	Zhu et al. (2019)

*Abbreviations: CAPEX -Capital Expenditure; MSPF – Minimum Selling Price of Fuel; OPEX – Operating Expenditure; TCI – Total Capital Investment; ROI: Return on Investment; GGE: Gasoline Gallon Equivalent.

pressure in a HTL reactor. The above energy requirements can be supplemented by integrating the HTL reactor with the solar power, thereby jeopardizing the heat energy requirements making it energetically and economically more favourable as highlighted in the study by Pearce et al. (2016). The authors reported that combining nutrient recycling and solar thermal power processing during HTL, can make the bio-oil production economically sustainable, with minimum price of 1.23 $/kg. Ou et al. (2015) performed techno-economic analysis for HTL of defatted algal biomass followed by hydro-processing of bio-crude considering total capital investment of 424 Million US$, resulting in a minimum fuel selling price (MFSP) of 2.57 $/gallon. The study also projected that the economic feasibility of the process is influenced by the hydrothermal conversion efficiency which ultimately determines the product yield. The economic analysis of hydro-processing to bio-crude oil using algae grown in wastewater from anaerobic digestate showed the process to be sensitive to the oil yield as well as the nutrient content of wastewater (Ranganathan and Savithri, 2019). One stage direct thermal processing produces bio-oil with high nitrogen content (6%) would involve higher manufacturing costs during further processing to remove impurities adding up to the total costs and energy burden. As an approach to alleviate the issues, Gu et al. (2020) described a sequential two-stage HTL at low temperature and pressure exploring the benefits of bio-oil and other co-products. The study described the two-stage HTL to have better returns on investments due to lower energy consumption and higher amount of fuel blend stock was produced compared to the single step process. Similar to the previous techno-economic studies, the above-mentioned research also emphasized that an increase in feedstock concentration, improvement in the yield and quality of bio-oil and co-products, use of recycled streams and appropriate fractionation techniques are expected to lower the production costs, thereby improving the overall process feasibility.

6.2. *Environmental impacts of hydrothermal processing*

Efforts to commercialize hydrothermal processing of microalgae into biofuel and value-added products requires improvement in process conversion technologies to subsidize the associated environmental impacts. Attributional life-cycle assessment of two thermochemical conversion processes i.e., pyrolysis and HTL showed that the net energy ratio (NER) and greenhouse gas emissions (GHG) were higher in case of the former process compared to the latter mainly due to feedstock drying requirements and co-product combustion for supplementing the energetics requirement (Bennion et al., 2015). Marangon et al. (2022) through gate-to-gate LCA of microalgal bio-oil production via hydrothermal processing showed marine eutrophication (due to high nitrogen content in aqueous waste) followed by climate change factor as the major environmental impacts. A comprehensive study carried out by Liu et al. (2013) compared the hydrothermal processing of microalgal biomass into biofuel and reported that HTL based algal fuel have lower GHGs than petroleum fuels with energy return on investment ranging between 1 and 3, lesser than the later. Table 3 shows the life-cycle impacts associated with the hydrothermal processing of algal biomass under different process conditions. As evident from the Table 3, several recent studies have assessed ecological metrics to quantify the overall impacts to provide a more comprehensive prediction linked with the process. It is also essential to focus and quantify the uncertainties linked with the parameters governing the product yield as well as the spatial–temporal factors that would impact the environmental predictions.

7. Circular bio-economy perspectives: Leading way into food-water-energy nexus

Utilization of algal biomass for hydrothermal processing makes it a viable bio-resource providing ample opportunities to establish and integrate the value and supply chain of products as highlighted previously for addressing the issues linked to energy-food-water nexus (Fig. 2).

From the bioenergy perspective, bio-crude oil from HTL of microalgae has gathered a lot of attention as a drop-in fuel with 25–30 MJ/kg energy that could be used in petrochemical biorefinery. However, bio-crude oil produced from HTL contains C13-C21 long chain fatty acids that results in higher viscosity and poor cold flow properties with heteroatoms of oxygen, nitrogen and sulphur thereby, hindering its direct use as fuel. Hydrotreating/processing to improvise the bio-oil properties

Table 3
Life-cycle impact analysis of hydrothermal processing of microalgae.

Process boundary/Approach	Software Tools/Functional Unit/Impact Assessment Methods	Environmental Impacts	Inferences	Reference
HTL reaction at petroleum refinery in wastewater treatment plant (WWTP) compared to conventional jet fuel	Well to wake (1 GJ of fuel) SimaPro 7.3.3 EPA TRACI 2.0	GHG Emissions: 35.2 kg CO_2 eq./GJ (HTL at WWTP)	55% reduction in GHG emissions with algal bio-jet fuel obtained from HTL at wastewater treatment plant compared to conventional jet fuel	Fortier et al. (2014)
Cultivation; HTL; hydrodeoxygenation with hydrochar processed via combustion (Method 1) or after chemical activation (Method 2) as by-product of HTL	Cradle to gate (1 kg biofuel/1 MJ of energy) Mass balance for LCA was done in Aspen Plus	GHG Emissions: 45.2 g CO_2 eq./ MJ (Method 1) 50 g CO_2 eq./ MJ (Method 2)	GHG emissions for petroleum fuel were 50% and 45% higher than the fuel from Method 1 and 2 respectively	Masoumi and Dalai, (2021)
Cultivation of microalgae, dewatering, thermochemical conversion, bio-oil stabilization, conversion into renewable diesel followed by its transport to pump Thermochemical conversion via HTL constitutes Method 1 and pyrolysis constitutes Method 2	Well to pump (1 MJ of renewable diesel) LCI data inventory: GREET 2013	NER: 1.23 GHG Emissions: −11.4 g CO_2 eq./ MJ	Higher environmental impacts with pyrolysis might be attributed to drying of biomass which was prevented during HTL	Bennion, (2014)
Cultivation, DAF, centrifugation, pre-treatment; HTL; nutrient recycle, and transport of biocrude oil to refinery	Stochastic life-cycle model in Microsoft Excel with Crystal Ball Plug-in with Monte Carlo simulation LCI Inventory from GREET	EROI: 1–3 GHG Emissions: ~160 – 311 kg/bbl	At pilot scale, the GHG emissions and energy use were higher than lab and industry full scale due to lower biocrude oil yield (20%)	Liu et al. (2013)
Microalgal cultivation, dewatering, lipid extraction, transesterification into biodiesel or subsequent HTL and upgrading into renewable diesel.	1 MJ of biofuel as functional unit LCI Inventory: GaBi and Ecoinvent database	Energy use: 0.1–1.7 MJ/ MJ GWP: −59–125 g CO_2 eq./MJ	Renewable diesel had lower GWP and energy consumption compared to biodiesel	Zhang and Kendall, (2019)

Abbreviations: HTL: Hydrothermal Liquefaction; DAF: Dissolved Air Floatation; EPA: Environmental Protection Agency; EROI: Energy Return on Investment; GREET: Greenhouse Gases, Regulated Emissions and Energy Use in Technologies; GWP: Global Warming Potential; GHG: Greenhouse Gas; LCI: Life-cycle Impact; NER: Net Energy Ratio; TRACI: Tools for the Reduction and Assessment of Chemical and other Environmental Impacts.

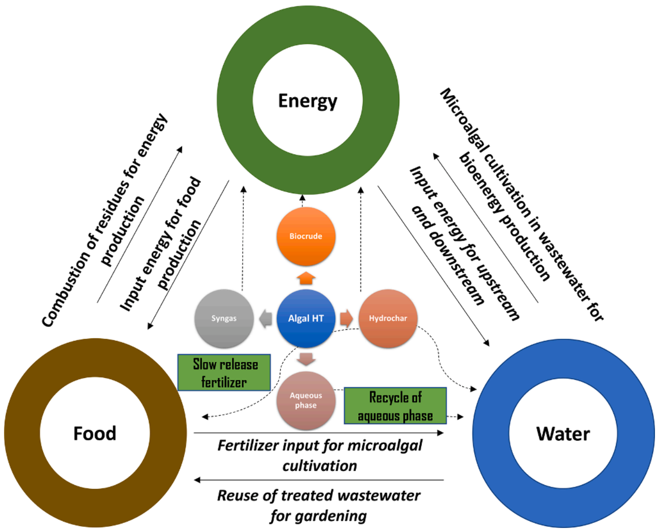

Fig. 2. Establishment of food-water-energy nexus with hydrothermal processing of microalgae.

adds up to the additional process costs. It is therefore essential to design a framework of HTL with appropriate operational parameters and catalysts to maintain adequate quality of biocrude oil. Another possible approach could be to co-integrate the HTL and gasification process together to increase the energy recovery and facilitate the use of hydrogen in bio-crude oil upgrading as suggested by Cherad et al. (2016). The authors demonstrated that gasification of aqueous phase produced from HTL of *C. vulgaris* to generate 30 mol H_2/kg, which was sufficient enough to treat the bio-crude oil produced during HTL. Apart from biocrude oil, syngas obtained via HTG of algal biomass also acts as a promising gaseous fuel. However, the requirements of high temperature and pressure often increases the overall process costs during HTG. The use of metal catalysts has been found to reduce the temperature requirements, energy consumption and also improvises the quality of gaseous products obtained. To further decline the cost requirements, the use of activated carbon as cheaper catalyst (Heidenreich et al., 2016), with lower solubility in supercritical water during gasification of algal biomass must be emphasized. Microalgal hydrochar also possess calorific value similar to bituminous coal and could be used as an alternative renewable solid fuel. However, it is essential to optimize the process conditions during the HTC and utilize appropriate feedstock characteristics to obtain hydrochar with desired fuel properties. In this regard, use of de-oiled algal biomass for the production of hydrochar suitable for combustion is considered as an essential strategy to integrate circular zero-waste bio-economy deriving value from waste resources. Coupling hydrothermal process with anaerobic digestion (AD) to increase the energy recovery as demonstrated by Nuchdang et al. (2018) and Marin-Batista et al. (2019) are considered essential strategy under the biorefinery based circular economy concept. Hydrothermal post-treatments of solid digestate from AD of *Scenedesmus* sp., have shown 4-fold increase in the biodegradability potential leading to an enhancement in yield from 66 L to 200 L methane/kg of volatile solids (Nuchdang et al., 2018). Similarly, the study by Marin-Batista et al. (2019) reported that co-combining HTC with AD could avoid refractory effects, resulting in better biodegradability, thereby recover 91% of the net energy during microalgal valorisation.

Algae as a third-generation feedstock serves the purpose of not only energy but also the domains lined to food and water nexus. Because of higher surface area and presence of specific functional groups, hydrochar can be used as a reservoir of nitrate and phosphate ions that can be utilized as soil conditioner and also for improvement in the plant growth and productivity. Insights of the strategy to use hydrothermally treated char in agriculture could be obtained from the review by Masoumi et al. (2021b). The solid precipitate produced during HTL can also be explored as nutrient rich source for animal feed as suggested in the review by Mathimani and Mallick, (2019). Cultivation of microalgae entrails huge water footprints, thus the recycle of the nutrient rich aqueous phase of hydrothermal reactor as a growth medium as proposed by Elliott et al. (2015) could bring down the freshwater requirements. A recent study by Chen et al. (2020) have discussed bio-remediation techniques to reduce the toxicity of aqueous phase during HTL using ion exchange resins bringing down the excessive nitrogen content making it suitable for algal cultivation. As an advanced approach to reduce the costs and fresh water footprints linked with algal cultivation, Aida et al. (2017) through hydrothermal processing of defatted *A. limacinum* at 200 °C – 250 °C, recovered 100% nitrogen and phosphorus into the water soluble fraction suitably effective for growing microalgae. Liquid by-products formed during algal HTC with residual nutrients can also be processed to recover sugars and volatile fatty acids (Broch et al., 2013) for industrial use. Hydrochar can also be functionalized to remove toxic metal ions via adsorption from waste/contaminated water, thereby provide avenues for basic water and wastewater treatment. For instance, Tsarpali et al. (2022) reported the use of hydrochar from residual algal biomass (after lipid extraction) for cumulative removal of Al^{3+}, Fe^{2+}, Cu^{2+}, Mn^{2+} and Pb^{2+} in the range of 75%–100%.

Circular bio-economy concept relies on the optimized interconnection of the input/output streams of substrates and products/by-products in a closed loop, thereby preventing wastage and facilitating complete valorisation of microalgae via hydrothermal processing. Detailed insights on the use of hydrothermal processing in batch/continuous mode, for pilot/industrial fractionation of biomass into platform chemicals for energy/food sectors have been comprehensively summarized by Ruiz et al. (2022). Though the study has been focussed on lignocellulosic biomass, the hydrothermal strategies based on biorefinery concept can be well extrapolated to algal biomass to establish a sustainable circular economy.

8. Research needs and future directions

In a nutshell, there have been extensive and well documented research linked with the hydrothermal processing of microalgae. However, several barriers still exist for its widespread deployment and commercialization. Though popular, the studies linked to hydrothermal processing of wet algal biomass grown in wastewater are limited (Bagchi et al., 2021). Thus, more experimentation linked with the utilization of microalgal strains growing in different wastewater sources subjective to different severity of hydrothermal processing and its subsequent impact on product yield must be emphasized. Further, owing to the huge demand of nutrient rich medium, the utilization of aqueous phase from hydrothermal treatment diluted/co-combined with industrial/domestic wastewater could also be proposed as a cost-effective approach during algal cultivation. System optimization of hydrothermal treatment needs to be focussed to design continuous reactors providing desirable quantitatively and qualitatively superior products. Since, the variation in the feedstock types as well as the critical operational conditions influences the product yield during the hydrothermal processing, it is imperative to understand the key mechanisms involved during the transformative conversion process from the perspectives concerning the type of algal strains involved, their growth conditions and inherent metabolite content.

Another challenge commonly being faced during commercialization of hydrothermal processing of microalgae is to design reactors that can process a large amount of biomass in a shorter time-period. Detailed insights on hydrothermal reactor operational modes and, instrumentation and control for obtaining multiple products in biorefinery can be referred from the critical review by Ruiz et al. (2020). A recent study by Johannsen et al. (2021) designed a pilot scale HTL reactor made up of polycarbonate coffer and inner protective steel additionally equipped with devices like thermocouples, heat exchangers and trim heaters for efficient energy control producing bio-oil in a timely way. To reduce the energy consumption linked with the hydrothermal reactors, alternative sources like solar energy, microwave and ultrasound apart from the superheated steam must also be explored. Also, since heat transfer plays an essential role in deciding the hydrothermal processing efficiency, studies linked with computational fluid dynamics simulations focussed on underlying reaction kinetics similar to Ranganathan and Savithri, (2018) which are presently limited needs to be focussed.

Compared to biochar, studies on application of hydrochar for remediating contaminated soil and water are limited. Activation of hydrochar, reaction kinetics during adsorption of pollutants must be focussed to expand its application in food-water nexus. With respect to agriculture, interaction of hydrochar with soil microbiota and mechanisms involved during mineralization, aiding soil conditioning needs to be studied in detail. Exploration of hydrochar as solid carbon fuel, super capacitors also needs attention, apart from its application for replacement to bituminous coal as also suggested by Padhye et al. (2022).

The following technical thematic areas must be focussed in future to achieve sustainable food-water-energy nexus via hydrothermal processing of microalgae.

1 Bioprospecting microalgal strains resistant to grow in toxic and high nitrogen containing aqueous phase from hydrothermal reactor
2 System optimization of hydrothermal process variables to achieve maximal product yield and desired quality
3 Utilization of cheaper and cost-effective heterogeneous catalyst with good process efficacy, stability and regenerative ability
4 Supply chain integration combining sequentially hydrothermal processes or integration with biochemical process deriving maximal energy recovery
5 System analysis in terms of environmental and economic feasibility of hydrothermal reactors under appropriate scale considering the spatial variables for obtaining reliable estimates during pilot/industrial applications

9. Conclusion

Microalgal biomass can be explored for a myriad of energy and value-added products through thermochemical processing. The state-of-art analysis through hybrid Sankey diagram clarified HTL to be the major focus theme, mainly for the exploration of biocrude oil. The review summarized in detail the key differences, mechanisms and the process factors for HTL/HTC and HTG to guide further research linked with the carbonization and gasification for exploring multiple co-products. It was also realized that enviro-techno-economic feasibility and market entry strategies are to be emphasized to promote commercialization. Process optimization, integration and supply chain management during thermochemical algal processing will facilitate establishment of food-water-energy nexus.

CRediT authorship contribution statement

Bunushree Behera: Conceptualization, Data curation, Writing – original draft, Writing – review & editing. **Mari Selvam S:** Conceptualization, Data curation, Writing – original draft. **Paramasivan Balasubramanian:** Conceptualization, Investigation, Funding acquisition, Writing – review & editing.

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.

Data availability

Data will be made available on request.

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