Green Chemistry

CRITICAL REVIEW

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Cite this: *Green Chem.*, 2017, **19**, 44

A review of thermochemical conversion of microalgal biomass for biofuels: chemistry and processes

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Renewable biomass sources are organic materials, in which solar energy is stored in bio-chemical bonds, and which commonly contain carbon, hydrogen, oxygen, and nitrogen constituents, along with traces of sulfur. Renewable biomass is now considered as a crucial energy resource, which is able to meet a range of energy requirements, including generating electricity and fueling vehicles. Among all the renewable energy sources, microalgal biomass is unique, since it profitably stores solar energy. It is one of the renewable sources of carbon that can be effectively converted into expedient solid, liquid, and gaseous biofuels through different conversion techniques. In this review, thermochemical conversion technologies involving microalgal biomass are highlighted, with emphasis on the background chemistry and chemical processes. Thermochemical conversion of microalgal biomass *via* pyrolysis, hydrothermal liquefaction, gasification, torrefaction, and direct combustion for bioenergy production from microalgal species is discussed, though there are limited literature sources available on these technologies. The unique features of hydrothermal gasification and supercritical gasification technologies are described, with the chemical reactions involved in these processes. The decomposition pathways of the main chemical components present in the microalgal biomass, such as carbohydrates and proteins, are well elucidated with the chemical pathways. The pros and cons of direct combustion are also spotlighted.

Received 16th July 2016,
Accepted 18th October 2016

DOI: 10.1039/c6gc01937d

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1. Introduction

Microalgal conversion technologies to produce biofuels are gaining significant attention due to their unique features, such as the abundance of biomass worldwide, as well as its high growth rate and CO_2 remediation.[1] Microalgal cellular components comprise carbohydrate polymers and proteins, which are all involved in thermochemical conversion for biofuel production technology.[2,3] Among thermochemical and other methods for biofuel production, technologies such as pyrolysis, hydrothermal liquefaction, gasification, torrefaction, and direct combustion, are propitious due to their higher yield and also the value added by product formation.[4,5] They attract major interest with respect to industrialization with low-lipid microalgal species.[6] During the last decade, mostly algal biodiesel conversion has been reviewed and also practiced for a long time; however, a recent trend has been following various new approaches to make the algal biofuels viable and applicable to large-scale operations. Very recently, thermochemical conversion has procured much attention due to its wide application and economic viability.[3–8] Algal biomass conversion to fuel in the form of liquid or gas is generally classified into two categories and is identified as biochemical (photo fermentation, dark fermentation, generally with the involvement of microbes) or thermochemical (torrefaction, liquefaction, pyrolysis, gasification, and direct combustion), involving catalysts and high temperature to produce char, oil, and gas.[2,3]

Information related to pyrolysis, hydrothermal liquefaction, gasification, torrefaction, and direct combustion is not widely available in the literature. Thus, this review/perspective focuses mainly on pyrolysis, hydrothermal liquefaction, gasification, torrefaction, and direct combustion technologies, with product decomposition at various stages. To the authors'

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knowledge, no research/review has been reported on the chemical pathways of decomposition of the protein and carbohydrate components, along with recent advances in the process. So, this would bring deeper knowledge to the field of applied chemistry regarding algal biofuel technologies.

2. Thermochemical conversion technologies

Microalgal biomass is a promising feedstock for biofuel production, which involves lipid extraction for the production of biodiesel *via* a transesterification process.[4] The microalgal residues obtained after conventional transesterification are mainly composed of proteins, carbohydrates, and a fraction of unutilized lipids, which can be employed to generate liquid and gaseous fuels, and biochar solids, depending on the temperature used.[4–6] This method of conversion is an alternative progression for low-lipid or post-extraction residues of high-lipid microalgal streams. It adopts thermal decomposition and chemical reformation of the organic structures into biofuels *via* pyrolysis, hydrothermal liquefaction (HTL), and gasification.[7]

This process is appropriate for both dry and wet microalgal biomass, even though it is principally considered more suitable for the processing of lignocellulosic materials of first and second-generation feedstocks than microalgal biomass.[8] The wet algal feedstock must undergo dewatering, followed by cost-intensive drying steps that comprise sedimentation, flocculation, dissolved-air flotation, filtration, and centrifugation. However, HTL is particularly suitable for the conversion of wet microalgae, because it is tolerant of the high moisture content of the algal feedstock, since higher quality and yield with respect to biofuel conversion is usually achieved with HTL at lower temperatures, with a longer residence time and much higher pressure.[9]

The thermochemical prolytic gaseous byproducts obtained are 75–83% N_2, 8.2–10.5% hydrocarbons (HC) of carbon C_1–C_4 (CH_4–C_4H_{10} and C_3H_4), 7.0–8.5% CO_2, 1.2–2.5% CO, and 0.37–0.73% H_2 in a nitrogen atmosphere. The TCL gaseous byproducts comprise 89% dominant N_2, 4–6% CO_2, 1.0–1.5% HC gases, 0.2–0.3% H_2, and an insignificant quantity of CO. The higher gaseous hydrocarbons consist of N-heterocycles, substituted furans, and substituted benzenes, such as toluene, styrene, xylene, and benzene, in addition to aliphatic C-chains, which are higher in the pyrolysis runs compared to the TCL runs.[9] High-performance liquid chromatography (HPLC) of the water-solubles of thermochemical conversion indicates the presence of 2.0–39.28 g L^{-1} formate, 3.36–16.16 g L^{-1} predominantly acetate, and a small quantity of propionate and ethanol. TCL water-soluble products were light yellow to brown in color and were characterized by a light smoky odor, while pyrolytic products were deep brown in color with a strong odor.[9]

The pyrolytic solid char obtained possesses higher energy values of 23.77–26.12 MJ kg^{-1} when compared to 10.98 MJ kg^{-1} for the solid char from TCL. Thus, the chemical energy of the original microalgal biomass was changed into valuable liquids and gaseous products by TCL, whereas in pyrolysis, most of these remain as unconverted solid char.[9] The pyrolysis performed at 350 °C (Pyro350) and 3.5 °C in 1 min produced more energy-dense char, with higher volatiles and lower ash contents, compared to Pyro500.[9]

2.1. Pyrolysis

Pyrolysis involves the thermochemical decomposition of organic structures into an energetically useful non-condensable mixture of gases, condensable liquids, and solid residues in the absence of an oxygen/trace-oxygen atmosphere[10] and in the presence/absence of a catalyst.[5] Commonly, three crucial stages are involved in this process, including the removal of moisture, decomposition of organic structures, and slow disintegration of residual solids. Agrawal and Chakraborty investigated the pyrolysis of *Chlorella vulgaris* and described the above stages.[11] Similar reports have been found for *Chlorella* sp., *Chlorella vulgaris*, *Nannochloropsis gaditana*, *Nannochloropsis* sp., *Potamogeton crispus*, and *Sargassum thunbergii*,[12–16] indicating that *Chlorella* sp. consisted primarily of water, CO_2, and H_2 at high temperatures and that *Nannochloropsis* sp. exhibited the biochemical decomposition of organic structures, in the order of carbohydrates, proteins, and lipids. The application of catalysts in the presence of Na_2CO_3 may influence the decomposition of carbohydrates and proteins only, due to the breakage of hydrogen bonds by Na^+ ions, which facilitates pyrolysis at low temperatures. Moreover, the pyrolytic investigation of *Tetraselmis chuii*, *Chlorella vulgaris*, *Chaetoceros muelleri*, *D. tertiolecta*, and *Synechococcus* reveals that they have different HHVs (higher heating values).[17]

Non-catalytic pyrolysis (direct pyrolysis) refers to the thermal degradation of organic structures and occurs moderately at 623–973 K in the absence of catalyst. The temperature and the heating rate have a noteworthy effect on the yields, and at high temperatures, the degradation is followed by the production of pyrolytic vapors that on downstream condensation yield a dark viscous bio-oil/pyrolysis oil and a nonvolatile solid biochar.[18] A slow pyrolysis process, namely, carbonization and conventional pyrolysis at heating rates of 0.1–1 K s^{-1} with residence times in min–hours, and fast pyrolysis *via* fast & flash pyrolysis at 1–200 K s^{-1} with a residence time of <0.5–0.5 s, have been conveniently observed.[19,20] Slow pyrolysis of a microalgal stream consequently yields biochar, CH_4, and CO_2 gaseous products. Peng *et al.*[21] found that the slow pyrolysis of *C. protothecoides* yielded bio-oil that exceeded about 40 wt%, and the yield of gaseous products increased with increasing temperature. The slow pyrolysis of *Spirulina* sp. yielded maximum biochar and bio-oil of <35 and <30 wt%, respectively, at an optimal temperature of about 773–823 K.[22] *Nannochloropsis* sp. indicated its main composition, which comprises long-chain carbonaceous structural units assisted by different terminal groups, with an oxygen content of 30.1 wt% and a HHV of 24.6 MJ kg^{-1}.[23]

Campanella *et al.*[24] pyrolytically studied the microalgal species *Scenedesmus* sp. and achieved a bio-oil yield of

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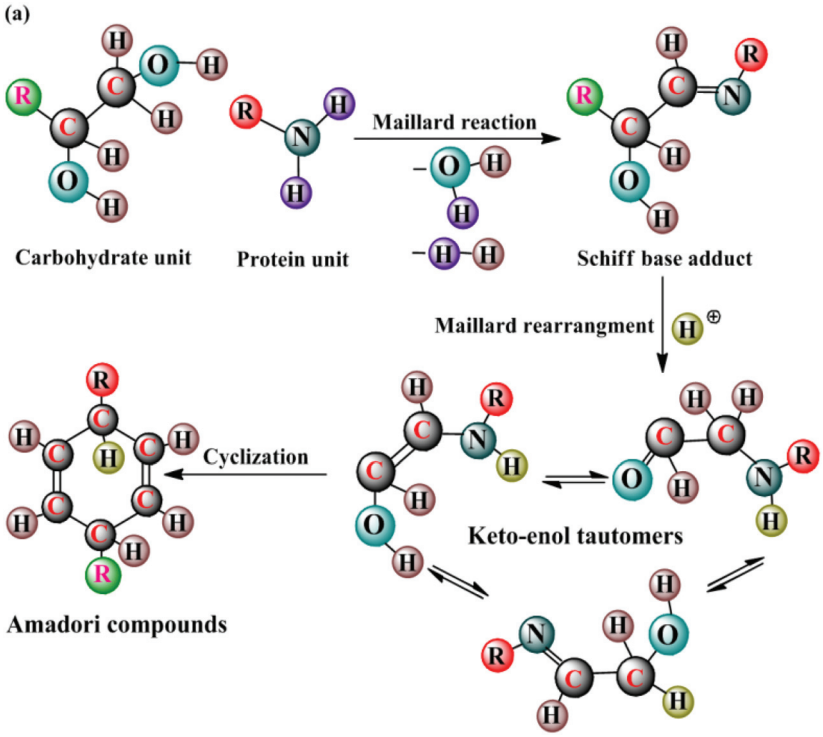


Fig. 1 Thermochemical conversion of microalgal carbohydrates and proteins involving Maillard reaction (modified ref. 52).

16–22 wt% with a HHV of about 19 MJ kg^{-1}. They found that, among the various pathways, *viz.* dehydration, deamination, direct methylation, decarboxylation, decarbonylation, cyclization, dimerization, and homolysis, there was a possibility of another path through Maillard's chemistry, which involved the thermochemical conversion of carbohydrates and proteins to yield Amadori compounds. The proposed mechanism is shown in Fig. 1.[24] The carbonyl group (–C═O) of the carbohydrate reacts with the amino group ($–NH_2$) of the amino acid to yield Schiff-base adducts. The unstable adduct undergoes Amadori rearrangement and forms keto–enol tautomers, which, on cyclization, yield liquid Amadori compounds, such as indole, phenol, and toluidine.

Fast pyrolysis is recommended, since the disadvantages of direct pyrolysis involve secondary cracking, condensation, and polymerization of the product, which decreases its HHV and high energy requirement. A fast pyrolytic investigation of the species *Scenedesmus* sp., *Chlorella protothecoides*, and *M. aeruginosa* showed that the bio-oil yields were 18–24 wt% with a HHV of about 29 MJ kg^{-1}.[25] Campanella and Harold[26] worked on fast pyrolysis and achieved 25–30 wt% of bio-oil with a HHV of 25 MJ kg^{-1} in a falling solid reactor with three dissimilar atmospheres *viz.* nitrogen, steam, and carbon dioxide. Harman-Ware *et al.*[27] showed that the weight ratio of bio-oil to char yielded from *Scenedesmus* sp. was within 3.76, *via* fast pyrolysis in a bench-scale fluidized bed, operated at 480 °C with a vapor residence time of 2 s, and the average total acid number for the bio-oil was 68 mg KOH g^{-1}, which was lower than that of a bio-oil obtained from pyrolysis of wood. Miao and Wu[28] examined the fast pyrolysis of heterotrophic *Chlorella protothecoides* microalgal feedstock and found that the bio-oil yield was about 57.9%, which was 3.4 times higher than that from autotrophic cells; they also found that heterotrophic microalgae might be better than autotrophic ones for fast pyrolysis. The bio-oil obtained was characterized by a much lower oxygen content, a higher heating value of 41 MJ kg^{-1}, a lower density of 0.92 kg L^{-1}, and a lower viscosity of 0.02 Pa s, compared to the corresponding values for bio-oils from autotrophic cells and wood. Table 1 shows a list of operating modes and conditions for microalgal pyrolysis, along with their bio-oil yield.

The microwave assisted pyrolysis (MAP) originally developed by Tech-in Ltd in Hainault, UK has advantages that include consistent internal heating of huge biomass particles, simplicity of control, and no necessity for agitation during the bio-oil production. Using a microwave power of 750 W, the *Chlorella* sp. yielded a maximum of 32 wt% of bio-oil, and using a power of 2250 W, bio-oil of about 74.9 wt% was observed with *Chlorella vulgaris* in the presence of activated charcoal as catalyst.[29] Since the bio-oils of direct pyrolysis are acidic and viscous, they must be upgraded through a hydrogenation process for the removal of excess oxygen and alkaline contents. Furthermore, the use of a catalyst in the pyrolysis process redirects chemical reactions, such as decarbonylation, dehydration, and aromatization, which results in *in situ* cost-effective upgradation of bio-oil.[30,31] Babich *et al.*[30] carried out

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Table 1 Operating modes and conditions of microalgae pyrolysis and bio-oil yield

Feedstock	Pyrolysis mode	Reactor	Operating conditions				Bio-oil yield (wt%)
			Temp. (°C)	Heating rate (°C min^{-1})	Sweep gas flow rate (mL min^{-1})	Duration (min)	
Chaetoceros muelleri	Slow	Fixed bed	500	10	100	20	33
Chlorella-like							41
Chlorella vulgaris							
Dunaliella tertiolecta							24
Tetraselmis chuii							43
Nannochloropsis sp.(res)			300–500		30	120	21–31
Synechococcus			500		100	20	38
Spirulina platensis			300–500	3.5–7.0	250	60	23–29
*C. prototheco*ides	Fast	Fluidized bed	500	36 000	6667		58
							18
C. vulgaris			400–700				58–72
C. vulgaris (res)			500				53
M. aeruginosa							24
Scenedesmus sp.			440		33 000		22
			480				55
Chlorella	Catalytic (Na_2CO_3)	Fixed bed	300–450	100–150		30	35–55
	Catalytic (ZSM-5)		400		250		29–36
Nannochloropsis sp.(res)			433–644		30	120	21–25
Chlorella sp.	Microwave		650–800	10	500	20	18–27
			450–550		300		21–36
Chlorella vulgaris						30	41–57
Nannochloropsis			500				41–59

Source ref. 108.

the catalytic pyrolysis of *Chlorella* species, with/without Na_2CO_3 as catalyst, and found that the catalyst promoted the gaseous yield, producing a bio-oil with low acidity and a high HHV. Campanella and Harold,[26] Wang and Brown,[32] Du *et al.*[33] and Hu *et al.*[34] investigated the bio-oil yield of *Chlorella* species in the presence of HZSM-5, Hβ, & HY molecular sieves and achieved high value-added aromatics of about 0.9–25.8 wt%, with a 30.1–19.5 wt% decrease in oxygen content and an improved HHV of about 24.4–32.2 MJ kg^{-1}, while there was no change with nitrogen compounds. This could be endorsed by the Brønsted acidity and precise pore structure of the zeolites. The proposed mechanism of catalytic pyrolysis includes deoxygenation and cracking of carbohydrates (1), decarboxylation, decarbonylation, and cracking of lipids (2), and deamination & cracking of proteins (3) for the bio-oil formation, which is shown in Fig. 2, and thus involves a total of three processes.[35–37] In the first process, the smaller organic moieties derived from carbohydrates of microalgal biomass residues, *viz*. alcohols, acids, aldehydes, and ketones, undergo deoxygenation and are then cracked into C_2–C_6 olefins; furthermore, these olefins experience a series of aromatization reactions to yield benzene, followed by alkylation and isomerization to produce other aromatics. In the second process, the triglycerides are thermally decomposed to heavy oxygenated hydrocarbons by decarboxylation coupled with decarbonylation, and these in turn are cracked into olefins, which are consequently converted into aromatics through a series of reactions, namely, oligomerization, cyclization, and aromatization. The third process involves the conversion of proteins to olefins and then to aromatics. In addition, the yields of different products from the catalytic pyrolysis of proteins at different temperatures are shown in Fig. 3.[38] The first and second processes of this proposed mechanism indicate the formation of toluene, styrene, and nitrogenated compounds, namely, amines, benzyl nitriles, and indole from phenylalanine and tryptophan, and the third process reveals the formation of phenol and cresols through a radical mechanism from the tyrosine protein within a temperature range of about 450–600 °C.

Nannochloropsis sp. yields bio-oil with a HHV of 24.6–32.7 MJ kg^{-1} in the presence of HZSM-5 (H–, Fe, Ni–, Cu–) catalyst over a range of temperatures, which was observed by Pan *et al.*[39] and the enhanced yield of organic fractions is due to Diels–Alder and condensation reactions. In the case of catalytic pyrolysis, the heteroatoms derived from the microalgal biochemical constituents can only be partially removed, and hence both these methods have their own advantages and disadvantages. Hence, to improve the quality of bio-oil, co-pyrolysis of microalgal streams with other feedstocks, such as solid wastes, coal, and polymeric materials, is given much consideration, and this does not require hydrogenation at high pressure. Moreover, the quality of the bio-oil involves the transfer of hydrogen from a co-feed of a higher H : C ratio, which effectively facilitates the deoxygenation process.[40,41] The literature indicates that the co-pyrolysis of microalgal species with municipal solid waste under N_2/O_2 & CO_2/O_2 atmospheres with a blending ratio of microalgae of 10–70 wt%, and with coal, decreases the yield of char-N & increases the volatile N, while

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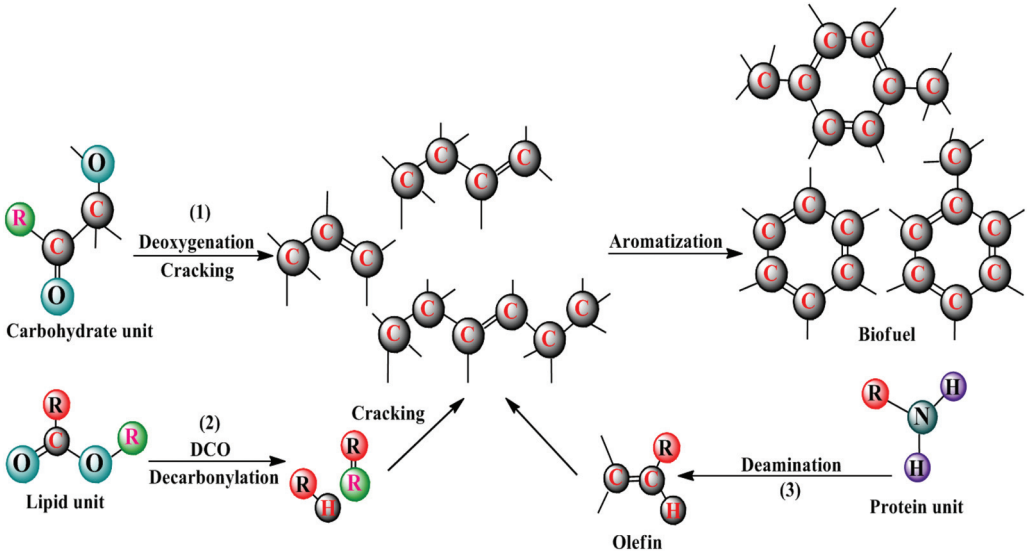


Fig. 2 Proposed mechanism of microalgal catalytic pyrolysis.

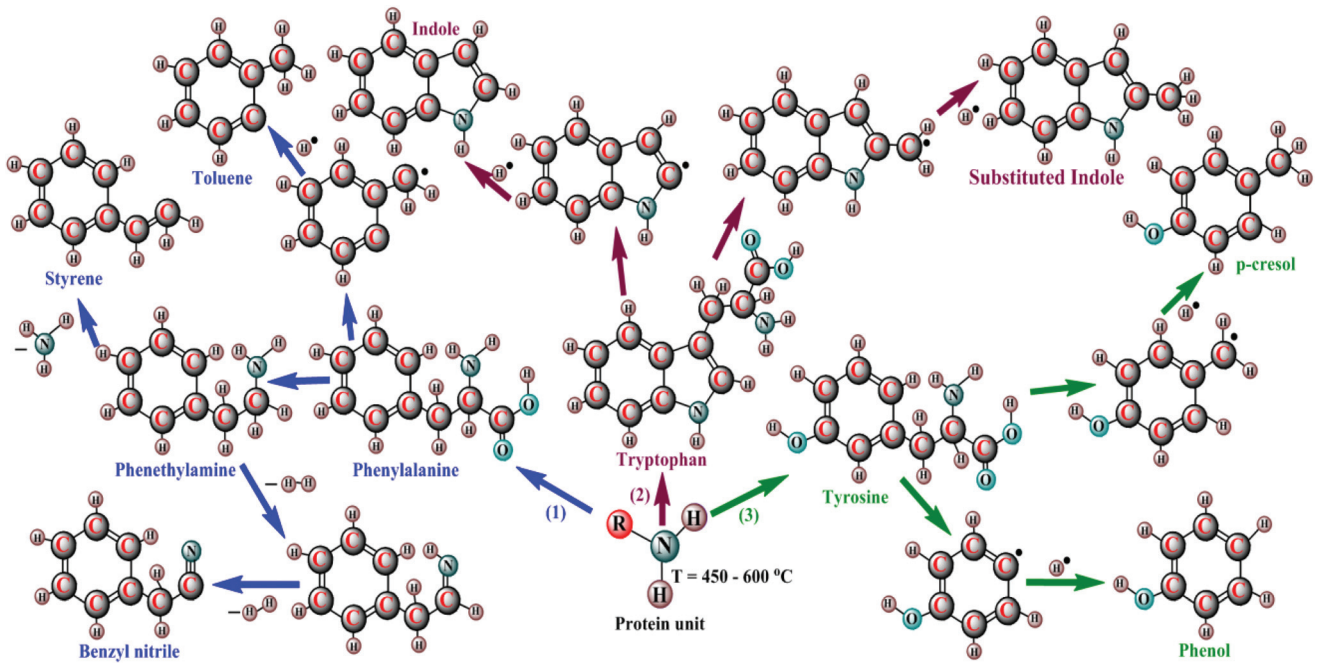


Fig. 3 Various by-products from microalgal protein pyrolysis.

the total yield of NH_3 & HCN decreases, and the formation of NH_3 is inversely proportional to the temperature.

2.2. Hydrothermal liquefaction

Hydrothermal liquefaction (HTL) is a promising option, since it does not need a cost-intensive dewatering and drying process for the microalgal stream. It was first described in the 1940s, followed by Shell *et al.* in the 1980s, with batch reactors.[42] It involves the thermochemical conversion of microalgae in a slurry of solvent and is carried out at moderate temperatures of about 280–623 °C and pressures of 10–25 MPa to keep the solvent in a liquid state. Moreover, it comprises water, as an eco-friendly and low-viscosity reaction medium, which can act as an acid/base catalyst embryo, as it has a high ionic product (K_w) *i.e.*, concentration of $[H_3O^+]$ & $[OH^-]$ ions, due to the self-dissociation and high solubility of organic compounds. The reaction depends on the temperature, retention time, and composition of microalgal feedstock. Moreover, the hydrogen bonding in water molecules is weakened on heating, and consequently there is a decrease in the dielectric constant

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and it becomes non-polar. For instance, when the water temperature rises from 25 °C to 260 °C, there is a decrease in the dielectric constant from 76.65–13.96; thereby, a simultaneous increase in K_w was observed from 10^{-14} to 10^{-11} at a temperature just below 250 °C, which all enhances the rate of acid/base catalysis in a water medium.[43] In this process, the bio-oil can be separated from the water phase easily with the addition of the organic solvents, *viz.* dichloro/trichloro methane, tetrahydrofuran, and *n*-hexane, following previously determined procedures.[44–47] This involves the direct conversion of lipids, including TAGs (triacylglycerides) into fatty acids, proteins into nitrogen heterocyclics, and carbohydrates, including polysaccharides and starch, into cyclic ketones and phenols; wet biomass is converted into a liquid bio-crude in the presence/absence of a catalyst in a water medium, which can sometimes act as a reactant under critical conditions, in which the temperature falls to around 280–370 °C and the pressure is maintained at approximately 10–20 MPa.[48] This is a multi-stage process (Fig. 4), which involves hydrolysis, depolymerization and repolymerization/self-condensation.[49,50] Hydrothermal liquefaction (HTL) is a substitute for pyrolysis and attracts much attention, as it does not need to expend energy to dewater and dry algae, as is required for other thermochemical conversions. HTL consumes a diversity of solvents, including water as the reaction medium. In addition, products such as bio-oils, water-soluble organic polar fractions, solid and gaseous residues, and a considerable fraction of oxygen from microalgal biomass, could be removed by means of dehydration/decarboxylation (DCO). In this process, carbohydrates are quickly converted into monosaccharides with a main product, glucose, which readily isomerizes into fructose, which in turn undergoes degradation and fragmentation to yield glycolaldehydes and glyceraldehydes. In addition, coke and some volatile products, such as H_2, CH_4, and CO, are formed. In the case of proteins, the C–N peptide linkage between the $-NH_2$ and –COOH structural groups hydrolyzes to yield amino acids, which in turn undergo DCO and deamination, producing HCs, $-NH_2$, –CHO, and –COOH functional groups. Lipid molecules are hydrolyzed to form stable free fatty acids (FFAs) and glycerol, which in turn forms water-soluble fractions. Partial degradation of FFAs yields long-chain HCs. The hydrolysates of carbohydrates react with protein to form nitrogen-based heterocyclics, following Maillard's path.[51]

Briefly, the mechanistic pathway of bio-oil production from microalgal residues under HTL conditions reveals that the macromolecules are hydrolyzed to produce molecular chips, which include fatty acids, amino acids, and monosaccharides. Specifically, amino acids produce HCs, amines, aldehydes, and acids by DCO followed by deamination. The formed unstable intermediates, on rearrangement, form larger compounds through condensation, cyclization, and polymerization. Many researchers studied[52–55] mechanistic pathways that warrant further research. Torri *et al.*[53] proposed a mechanism for the production of bio-oil, which is a mixture of a large number of compounds, from peptides to long-chain macromolecular HCs, from *Desmodesmus* sp., and this comprises the pathways shown in Fig. 5. In the first step, microalgal lipids, algaenans, and some hydrophobic protein fractions, are retained in the organic solvent portion by means of solvent extraction of microalgal cellular constituents at moderately low temperatures of about 473–523 K. The cellular mass undergoes thermal degradation at temperatures below 523 K, whereby the hydrophobic proteins and carbohydrates are converted into their hydrophilic form. There is then a possibility for protein–carbohydrate–lipid interactions *via* several pathways. The second step includes the formation of diketopiperazines (DKP) by peptide depolymerization, and derivatives of amino acids &

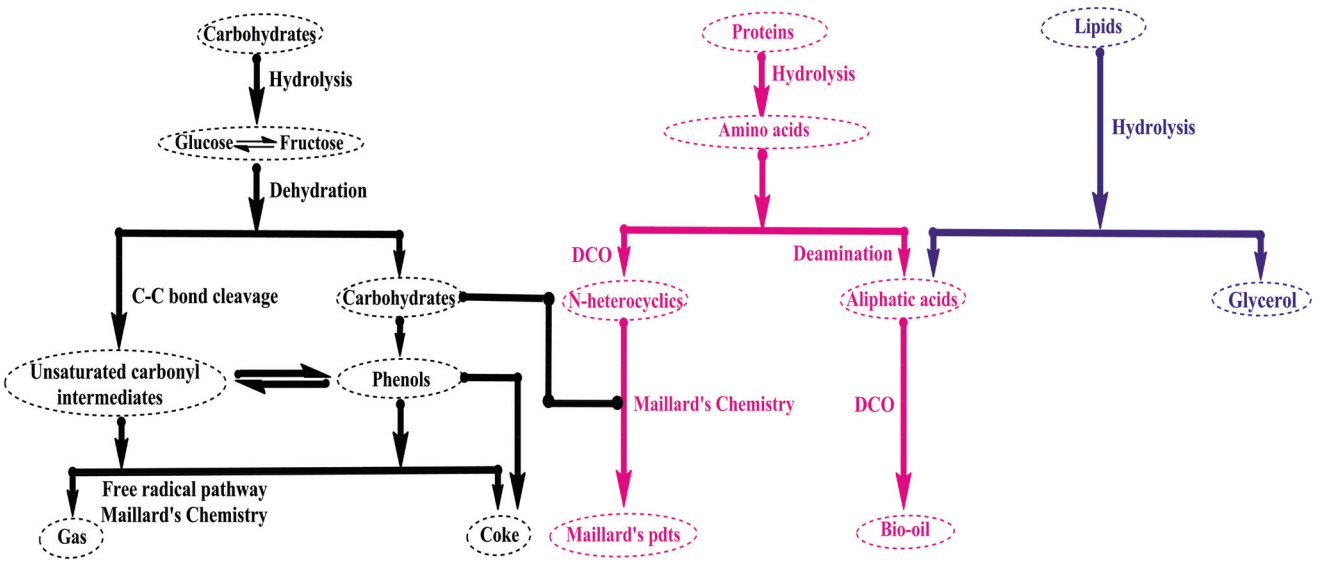


Fig. 4 General proposed pathway of hydrothermal liquefaction (modified ref. 52 and 53).

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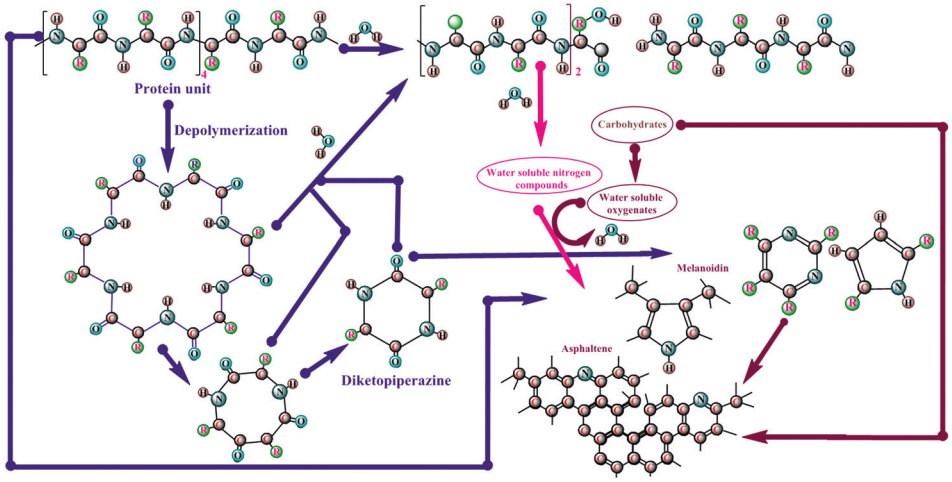


Fig. 5 Proposed mechanism for the production of bio-oil by HTL process from microalgal biomass (modified ref. 52 and 53).

carbohydrates (furans) and asphaltene-like structures as a result of breakdown of proteins and cellular constituents at about 573–648 K. In addition, proteins and carbohydrates may break into small fragments (–NH_2 and –CHO functionalities), even at 473 K, yielding melanoid and asphaltene-like structures. Protein degradation increases the bio-oil yield, while protein–carbohydrate-derived components amplify the nitrogen content of bio-oil. Thermal fragmentation of protein–carbohydrates yield pyrolysis-like products, *viz.* amino acid side chains/2-methyl cyclopentenone, and some smaller Maillard products, such as pyrroles, in the third step.

Zhang *et al.*[54] proposed a mechanical pathway for bio-oil production from microalgae under HTL conditions (Fig. 6). In the first step, the breakdown of lipids, proteins, and carbohydrates to their corresponding monomers *via* hydrolysis, *viz.* fatty acids, amino acids, glucose, fructose, xylose and phenols; in turn these monomers undergo decomposition into various intermediates. The second and third steps involve a series of reactions, in which monomers and intermediates are formed. Amines/ammonia and their corresponding keto acids are formed by amino acids on DCO (2) and deamination (3), respectively. Fatty and amino acids also form amines/ammonia by a DCO (2) mechanism. The keto and fatty acids undergo a DCO process (2) to form ketones, and the fatty acids are converted into aliphatic HCs through DCO (2). The fatty acids may experience esterification (4) and acylation (5) to yield fatty esters and amides, respectively, in the fourth and fifth steps. In the sixth step, monomers and amino acids react together *via* Maillard's chemistry (6) to form a nitrogenous compound, melanoidin. The seventh step involves decomposition (7) of monosaccharides to furfurals and smaller carboxylic acids. On polymerization (8), phenols and furfural derivatives form solid products. The esters are more stable, suppressing DCO as a result; there is thus a decrease in the formation of volatile products.

Chen *et al.*[55] worked with sub/supercritical ethanol co-solvent–water as a weak acidic reaction medium for *D. tertiolecta* species to produce bio-oil under acid-catalyzed HTL conditions, and proposed a mechanical pathway (Fig. 7). This pathway involves the conversion mechanism for lipids, proteins, and carbohydrates. First, the proteins form long-chain amino acids on acidic hydrolysis; in turn, these form liquefied products *via* cracking, condensation, DCO, and deamination. Secondly, the carbohydrates form monosaccharides on dehydration, a part of which, on simultaneous dehydration and alcoholysis, yield glucose anhydride. Another part yields liquid products on protonation. Then, the lipid molecules, under weakly acidic conditions, form acid and glycerol on hydrolysis. *Via* alcoholysis and ammonolysis reaction paths, the formed acid yields ester and amide, respectively. The NH_3 released from acid-catalyzed decomposition of proteins can be utilized for ammonolysis. The formed amide undergoes ethanolysis in the presence of a high ethanolic concentration to yield esters.

From Table 2, the HTL of a variety of microalgal species like *B. braunii*, *D. tertiolecta*, *D. salina*, *C. vulgaris*, *N. oculata*, *S. platensis*, and *Spirulina* yields more (5–30 wt%) than the initial lipid constituents. The study on *B. braunii* reinforces[56] that the gaseous products mainly include CH_4 and CO_2, which is further supported by Gutierrez *et al.*[57] Gutierrez *et al.* obtained 37 wt% of bio-oil with a HHV of 36 MJ kg^{-1} from *D. tertiolecta*. From low-lipid microalgal sources like *Spirulina*[58] and *Desmodesmus* sp.[59] it is possible to achieve bio-oil yields of 78.3 and 49 wt%, respectively, with HHVs of 22–36 MJ kg^{-1}. Yu *et al.*[46] obtained a low nitrogen and oxygen content bio-oil yield of 65.4 wt% and a 35.4–38.5 MJ kg^{-1} HHV with *C. Pyrenoidosa* at 553–573 K within 30–120 min. Zou *et al.*[60] obtained a bio-oil yield of 36.9 wt% and a HHV of 26.6 MJ kg^{-1} with *D. tertiolecta* feed and a water ratio of 1 : 10 at 633 K within a time period of 30 min. They ascertained that this bio-oil composition included hexadecanoic acid, palmitamide, and FAMEs with molecular formula $CH_{1.38}O_{0.43}N_{0.07}$. Brown *et al.*[47] and Faeth *et al.*[61] obtained the highest bio-oil yields of 43 wt% and 66 wt%, respectively, with

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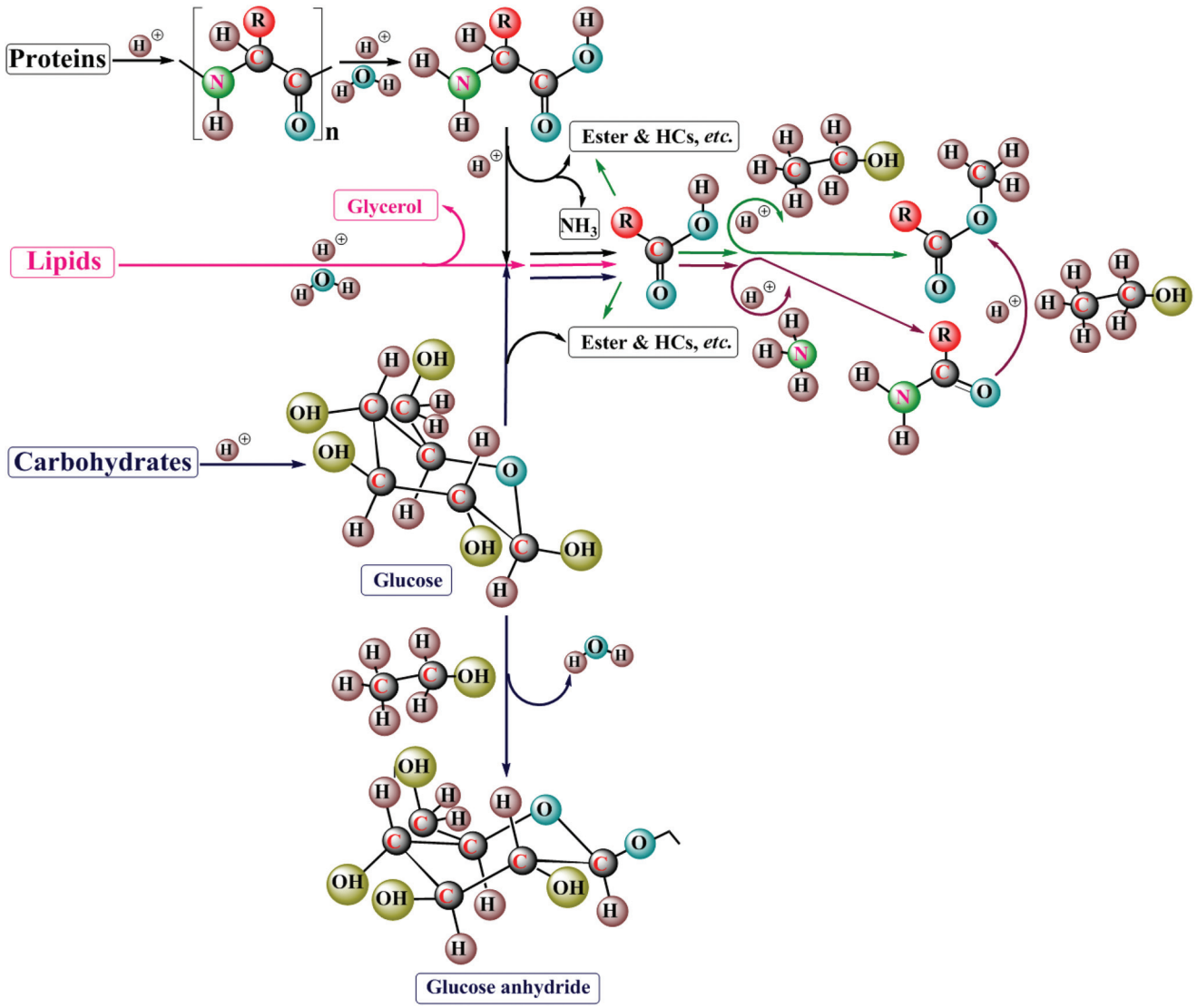


Fig. 6 A mechanistic pathway of microalgal biomass for bio-oil production under HTL conditions (modified ref. 52 and 54).

Nannochloropsis sp. at 623 K, using a subcritical water medium at 573–873 K within 1 minute.

Amongst the small bench scale studies, Jena *et al.*[62] conducted a comparatively large-scale study on *S. platensis* (20 wt%) in a 1.8 L batch reactor at 623 K for 60 min, and obtained a yield of bio-oil ≈40 wt% with a HHV of 39.9 MJ kg^{-1}. Moreover, Jazrawi *et al.*[63] developed and Elliott *et al.*[64] followed a continuous flow, pilot scale HTL for *Chlorella* and *Spirulina* species and accomplished 41.7 wt% bio-oil yields at 623 K for 3 min and at a moderate pressure of 20 MPa in the case of the *Chlorella* species. Based on the experimental data, the highest 66 wt% bio-oil yield was achieved at reaction temperatures of 573–873 K within 1 minute for *Nannochloropsis* sp.[61] The high heteroatomic profile of bio-oils will probably lead to upgrading requirements before their application. Thus, the overall bio-oil yield depends on the cellular carbohydrate and protein profiles of the microalgal species. It also depends on the kinetics of depolymerization and the methods adopted under the HTL experimental conditions. Moreover, the bio-oil yield of different microalgal species depends on the optimal reaction parameters, higher heating values (HHV) and product distributions.[47] Furthermore, both the carbon and water contents effectively determine the HHV.

An improvement in the quality of bio-oil can be achieved either by homogeneous or heterogeneous catalysis. The other methods involve the use of co-solvents/co-liquefaction for microalgal HTL. The majority of studies highlight non-catalytic and homogeneous catalytic HTL; only a few used heterogeneous catalysis (Table 2).[52] The homogeneous catalyzed HTL employs alkali salts to improve gasification and the water gas shift reaction to increase the bio-oil yield; these raise the pH, inhibiting the dehydration of biomass monomers, so that the reaction involves deoxygenation and dehydration instead of DCO in the case of acid catalysis; as a result there is simple

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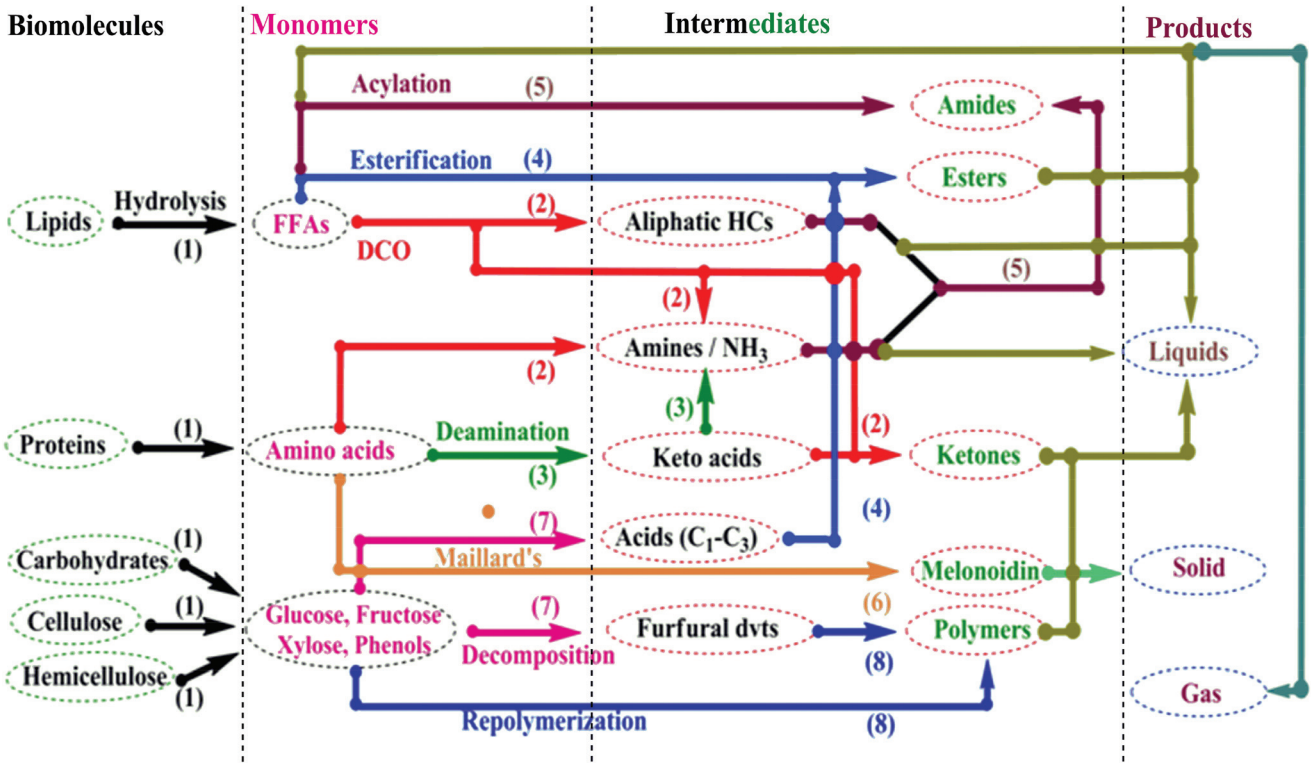


Fig. 7 A thermochemical conversion mechanism for microalgal biomass (modified ref. 52 and 55).

polymerization of char and tar. Dote *et al.*[65] carried out homogeneous Na_2CO_3 base-catalyzed HIL for *B. braunii* and *D. tertiolecta* and observed a bio-oil yield of 28–32 wt%, with a decrease in oxygen content from 24.2 to 19.7 wt%[56] at 573–613 K. Similar results[56,66–68] were observed for *B. braunii* and *D. tertiolecta* with 5% Na_2CO_3, and the bio-oil yield followed the order, lipids > proteins > carbohydrates. In certain cases, a catalyst like FeS does not improve the yield, but alters the distribution of products, such as ethyl hexadecanoate.[52] Ross *et al.*[68] reported the effect of an alkaline catalyst that induced saponification in the case of high-lipid microalgal species. They carried out HTL with KOH and Na_2CO_3, as well as CH_3COOH and HCOOH mixtures, as catalysts for *Chlorella* and *Spirulina* species, and found an enhanced bio-oil yield, which followed the order, Na_2CO_3 > CH_3COOH > KOH > HCOOH. In addition, they suggested that the alkaline catalysts were suitable for HTL of high-carbohydrate-content species, and acids were appropriate for high-lipid microalgal species. Jena *et al.*[69] used alkaline-earth $[Ca_3(PO_4)_2]$ and transition-metal (NiO) catalysts for the microalga *S. platensis* and compared the bio-oil yield with that obtained using Na_2CO_3, revealing that there was an increase in the bio-oil yield to 51.6 wt%, which was 29.2 wt% higher than that obtained under non-catalytic conditions. The alkaline-earth and transition-metal catalysts increased the yield of gaseous products and decreased the bio-oil production. Zhou *et al.*[70] carried out HTL using 0.3–2.4 wt% sulphuric acid–glycol as catalyst at 393–473 K for *D. tertiolecta* and observed a 45.0 wt% bio-oil yield, mainly composed of FAMEs and alkanes of C_{17}–C_{20} carbon chains at 443 K in 33 min. Due to cost-intensive recovery for homogeneous catalysts, the use of heterogeneous catalysts is alternatively considered, since their separation in the active state is approached simply by filtration, and they are used even for low-temperature water gasification, which is essential, as the oxygen is removed in this process.[71]

Duan and Savage[72] liquefied *Nannochloropsis* sp. in the presence of six heterogeneous catalysts, *viz.* Pd/C, Pt/C, Ru/C, Ni/SiO_2–Al_2O_3, $CoMo/\gamma$-Al_2O_3 (sulfided), and zeolites. Among these, zeolites are the most widely used catalysts. Their acidity is associated with the Si/Al ratio, demonstrating high acidity with a low ratio. A possible mechanism of cleavage of the O–H bond for dehydration of hydroxyl-containing carbohydrates on aluminosilicate zeolite is given in Scheme 1.[18]

The most important reactions involved in Scheme 1 are cracking and dehydration. Adsorption of the oxy-carbohydrate occurs on an acid site of aluminosilicate zeolite. This is followed by bimolecular monomeric dehydration, which yields hydroxyl-substituted olefin (olefin-ol).[18] Olefin-ol, on aromatization and dehydroxylation, yields bio-oil. With oxide and transition metal catalysts, the acidity of the zeolite affects the reactivity and yields, with high acidity leading to a higher affinity towards the formation of carbon linkages and water. Pore blockage from depolymerization of carbohydrates and deamination of proteins causes deactivation of the catalyst. Zeolites form aromatics at atmospheric pressure without a requirement for H_2. The final product generally has a low heating value,

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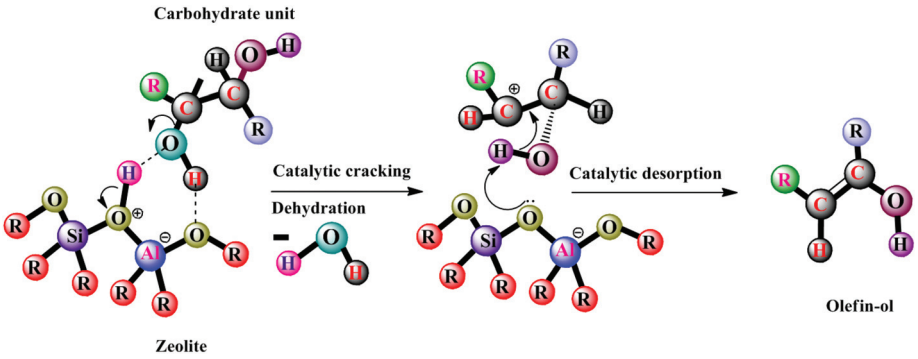
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Table 2 Survey on non-catalytic/catalytic hydrothermal liquefaction

Hydrothermal liquefaction	Catalysts employed	Microalgal feedstock	Reaction medium	Conditions		Max. bio-oil yield (wt%)	Max. HHV (MJ kg^{-1})
				Temperature (K)	Holding Time (min)		
Noncatalytic Liquefaction (Direct liquefaction)	—	*Chlorella pyrenoidosa*	Water	573	30	31.0	35.8
				553	120	39.4	35.4
			Ethanol	443–643	5–120	64.6	38.9
		Desmodesmus sp.	Water	448–723	5–60	49.0	36.0
		Dunaliella tertiolecta		633	30	36.9	26.6
		Nannochloropsis salina		493–648	30	46.0	38.1
		Nannochloropsis sp.		473–773	60	43.0	39.0
				873	1.0	66.0	37.0
		Scenedesmus		573	30	45.0	35.5
				553	120	39.4	35.4
		Spirulina		573	30	32.6	34.7
			Ethanol	623	-	35.4–45.3	32.6
			Water	448–723	5–60	38.0	35.2
				573	30	31.0	35.8
			Ethanol	653	20	54.0	38.3
			Methanol			55.1	39.8
			1,4-Dioxane			56.6	36.8
			Water	573	30	32.6	34.7
		Spirulina platensis		623	60	39.9	39.9
				623		41.0	34.6
Homogenous catalysis	Na_2CO_3	*Botryococcus braunii*		473–613		64.0	—
	HZSM-5/RANEY® Ni	*Chlorella pyrenoidosa*	Ethanol	473–573	30	71.3	36.2
	Na_2CO_3	*Chlorella vulgaris*		573 and 623		35.8	37.1
			Water	573 and 613	30 and 60	27.3	37.9
	HCOOH			623		27.0	33.2
	H_2SO_4	*Dunaliella tertiolecta*	Ethylene glycol	443	33	45.0	28.4
	Na_2CO_3		Water			43.8	36.0
						25.8	30.7
	Na_2CO_3	*Enteromorpha prolifera*		493–593	5 and 60	23.0	30.0
		Microcystis viridis		573 and 613	30 and 60	33.0	
	HCOOH	*Nannochloropsis oculata*		573 and 623	60	34.3	34.3
				623		26.0	39.6
		Porphyridium cruentum		573 and 623		20.0	36.3
				623		27.1	
	H_2SO_4	*Sargassum polycystum*	Ethylene glycol	443	15	87.7	—
	KOH	*Spirulina*	Water	573 and 623		20.0	39.9
	Na_2CO_3			623	60	29.0	36.8
	$FeSO_4$		Ethanol	633		46.0	37.1
	HCOOH		Water	623	60	29.0	35.1
	$Ca_3(PO_4)_2$/NiO	Spirulina platensis		573–623	30–60	34.5	38.4
Heterogeneous catalysis	$Co/Mo/Al_2O_3$	*Chlorella vulgaris*		623	60	38.7	39.1
	RANEY® Ni	*Dunaliella salina*		473	60	72	30.1
	$Ni/Al/Al_2O_3$	*Nannochloropsis oculata*				30.0	38.2
	$Pt/Al/Al_2O_3$					38.9	
	Pd/C; Pt/C; Ru/C; Ni/SiO_2-Al_2O_3;$CoMo/\gamma$-Al_2O_3/Zeolite	*Nannochloropsis* sp.				57.0	38.0
	$Fe(CO)_5$-S	*Spirulina*		573 and 613	30 and 60	78.3	33.0

Source ref. 26,31–34,39 and 52.

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Scheme 1 Proposed catalytic HTL pathway of carbohydrates [modified ref. 18].

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which is due to its low H/C and high O/C ratios. The formed olefins and aromatics increase with increasing H/C_{eff} ratios, suggesting that the hydrogenation of the feedstocks before the upgradation process with zeolites increases this ratio to 1.2.

The metals used play a key role in decreasing the O/C ratio, lowering the viscosity and lightening the colour, due to the promoted catalytic deoxygenation. An increase in the bio-oil yield of about 57.0 wt% was observed with a Pd/C catalyst. Ni/SiO_2–Al_2O_3 is used for desulphurization.[52] The literature revealed that NiO was used as a catalyst for both single (*Spirulina*) and mixed algal culture (open ponds with waste water)[73] at temperatures of 573–623 K with 40.0 wt% bio-oil and a HHV of 39.0 MJ kg^{-1}. The study[52] also established that the bio-oil yield of *C. vulgaris* and *N. oculata* increased to some extent up to 10% using Ni/Co/Mo/Pt–Al_2O_3 heterogeneous catalysts. For a low-lipid microalgae, on HTL with RANEY® Ni/H_2 and HZSM-5 catalysts, only hydrogen played a vital role in the quality and bio-oil yield, and the catalysts had no effect.[54] The liquefaction reactions of *Spirulina* in 1-methylnaphthalene, with a smaller proportion of water in CO and $Fe(CO)_5$, provided a conversion efficiency larger than 98.0 wt% with bio-oil, and gas and water yields were up to 83.0 wt%.[59] The catalytic conversion yields bio-oil and gas composed of hydrocarbons and H_2/CH_4, respectively. Metal-based catalysts specifically occupy an imperative function. The recovery of the deactivated catalyst is the only inconvenience of heterogeneous catalysis.

Furthermore, water, as a single-solvent reaction medium, has some drawbacks in the HTL process, since a large portion of organic structures reside in the aqueous medium and the conversion is low; *i.e.* only 40% C and 35% of the feedstock were converted to bio-oil.[55] Moreover, the high working temperatures (523–623 K) and pressures (10–20 MPa) consequently resulted in high O and N contents of the bio-oil, which decreased the HHV and storage stability.[74] To overcome such shortcomings, organic solvents, such as 2-propanol, ethanol, and methanol, have been investigated as co-solvents, since they possess low dielectric constants to dissolve weak/non-polar reaction intermediates, leading to a higher yield of bio-oil, and they need only moderate operating circumstances.[75] For example, the hydrophobic hydration of methanol–water mixtures under supercritical conditions is now attracting research in the field of chemical engineering.[76,77] The literature[78] showed that the low-lipid microalga *C. pyrenoidosa*, on HTL under sub/super-critical alcohol–water, yielded 71.3 wt% at 513 K with a HHV of 36.2 MJ kg^{-1} at 573 K by a deoxygenation process. Similar results were found for *D. tertiolecta*,[75] since the sub/super-critical water presented ionic, polar non-ionic, and free radicals, and the role of alcohol as a hydrogen donor favored the production of bio-oil,[79,80] which could be investigated by the isotopic tracer method.[55] However, the *C. pyrenoidosa* species, with ethanol as a single reaction medium, yielded 9.8–84.6 wt% with a decrease in solid residue of 60.1–11.9 wt% and a HHV of 27.7–36.5 MJ kg^{-1} at temperatures of 443–623 K, which was due to solvent polarity. The principal components of bio-oils are FAMEs and FAEEs when ethanol and methanol are used as solvents, respectively,[52] while hexadecanenitrile is the chief ingredient with the solvent 1,4-dioxan.

Currently, co-liquefaction of microalgae and coal has become a considerable attraction, since it reduces the consumption of hydrogen and the requirement for milder operations, compared to the direct liquefaction of coal. Moreover, the literature[25] contained similar studies on *Chlorella*, *Spirulina*, and *Littorale*, with *Australian Yallourn* brown coal and *Illinois* no. 6 coal with pressurized hydrogen in 1-methylnaphthalene at 623–673 K in 60 min, using catalysts such as $Fe_{1-x}S$, $Fe(CO)_5$, and $Ru_3(CO)_{12}$. Under optimal conditions, *D. tertiolecta* and coal exhibit a synergistic effect, which not only improves bio-oil conversion (70.6 wt%) efficiently, but also improves the quantity (40.3 wt%) and quality of the bio-oil.[81] In this case, microalgae can act as hydrogen donors, due to their high hydrogen content. In addition, the co-processing of microalgal biomass with waste polymer increases both the quantity and quality of the bio-oil production with a HHV of about 40 MJ kg^{-1}, as this possesses high C and H contents. The literature[82] revealed that co-liquefaction of *Spirulina* species and HDPE (high density polythene) with a 4/6 feed ratio in sub/super critical ethanol–water mixtures at 613 K yielded 44.8 wt% of aliphatic HC-dominant bio-oil with a HHV of 48.4 MJ kg^{-1}. This was due to the high C and H contents and low O content. Here, microalgae could act as hydrogen receivers as they possessed a lower hydrogen content than the

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Table 3 Comparison of pyrolysis and HTL processes of microalgae

Parameters	Hydrothermal liquefaction	Slow pyrolysis
Nature of feedstock	Suitable for wet feedstock (80%). Removal of moisture is done by means of bio-flocculation, dissolved air filtration & centrifugation	Suitable for dried feedstock by means of thermal methods
Reaction temperature (K)	623	623–773
Pressure (MPa)	5–20	atm. Press.
Conversion (wt%)	93.0	60.0–72.0
Bio-oil yield (wt%)	40.7	23.8–28.5
HHV (MJ kg^{-1})	34.2	29.3–33.6
Energy recovery from the original algae (%)	67.9	33.9–46.7
Energy consumption ratio	0.70	2.11–1.56
Thermal stability	High	Low
Storage stability	High	Low
Upgradation of bio-oil	Easy approach	Hard approach
Presence of Inorganic elements	High	Low
Cyclic oxygenates (wt%)	08–12	16–24
Low-boiling compounds (wt%)	45–54	62–66
Mean bio-oil mol wt (Da)	700–1330	280–360

Source ref. 52.

polymer. Table 3 shows a comparision of pyrolysis and HTL processes with microalgal species.[9]

2.3. Gasification

Hydrothermal gasification is the gasification of carbonaceous components in a stream of supercritical water at temperatures above 374 °C and pressures above 22.1 MPa to yield CH_4. Under these experimental conditions, water possesses properties of both the gaseous and liquid states, and the viscosity and diffusivity of water are comparable to those of gases. Hydrothermal gasification is an eco-friendly conversion of microalgal biomass into biofuels, which involves the partial oxidation of microalgal biomass in steam at high temperatures, yielding a mixture of combustible gases of low calorific values (≈ 4–6 MJ kg^{-1}) in a gasifier. The product gas constitutes CH_4, CO_2, and N_2 and can be burned directly to produce energy to run diesel/gas turbine engines.[83] The general reaction pathway is shown in Fig. 8. Hydrothermal gasification does not involve drying of biomass, even that with a high water content.[5,84] It can be carried out at dissimilar temperatures and pressures/in the presence of a catalyst. Hydrothermal gasification can be non-catalytic at high temperatures (>500 °C), catalytic under sub-critical conditions (225–265 °C & 2.9–5.6 MPa)[85] and low-temperature catalytic under supercritical conditions (≈ 500 °C).[86] Gasification involves three main reaction pathways (Fig. 9).[87] The endothermic decomposition steps of the biomass (CH_aO_b) include (Scheme 2) the formation of H_2 and CO, followed by a water–gas shift exothermic reaction; this produces further H_2 and CO_2. This step is continued by means of exothermic methanation by the previously formed CO and CO_2 to yield water and CH_4.

Supercritical water gasification (SCWG) is an alternative to both conventional gasification and anaerobic digestion pathways for wet biomass with/without catalysts under batch/continuous conditions into biofuels. Gassner *et al.*[88] and van der Meijden *et al.*[89] compared both conventional gasification and SCWG, and determined their energy efficiencies. Understanding the gasification path is somewhat challenging due to the complex structures of biomass. Moreover, the decomposition of microalgal cellular monomers was established by Kabyemela *et al.*[90] and Matsumura *et al.*[91]

The mechanism reveals that (Fig. 9) the carbohydrate in the form of glucose/xylose isomerizes under ionic conditions to form fructose. On decomposition at temperatures of 300–400 °C, it yields acids and furfurals as intermediates under free-radical conditions.[92] The smaller organic acid moieties formed then undergo decomposition by means of dehydration and decarboxylation to produce gaseous products at temperatures of 450–650 °C.[93,94] The furfurals undergo polymerization under subcritical conditions into the char form. On gasification, amino acids undergo decomposition by means of hydrolysis in sub- and supercritical water at temperatures of around 250–265 °C.[95] The amino acids can be converted into amino compounds and acid intermediates with the release of NH_3 gas (Fig. 10). The acid intermediates on decomposition produce smaller intermediates and gases. The presence of a solid, black product is observed, in addition to liquids and gases at 500 °C.[96–99] Surveys of the mechanisms are thus given in Fig. 8–10. A comparison of the thermochemical conversion of microalgal biomass with biofuel yield is given in Table 4. An investigation of methanol production from *Spirulina* at temperatures of around 850–1000 °C shows that at 1000 °C, a high methanol yield can be obtained.[100] Fig. 11 depicts the existing integration between algal cultivation and hydrothermal gasification processes.[101]

2.4. Torrefaction

The aforementioned thermochemical conversion processes of microalgal biomass may be cost-intensive, and offer low efficiency due to some inherent characteristics of this biomass, which remarkably include low carbon content and

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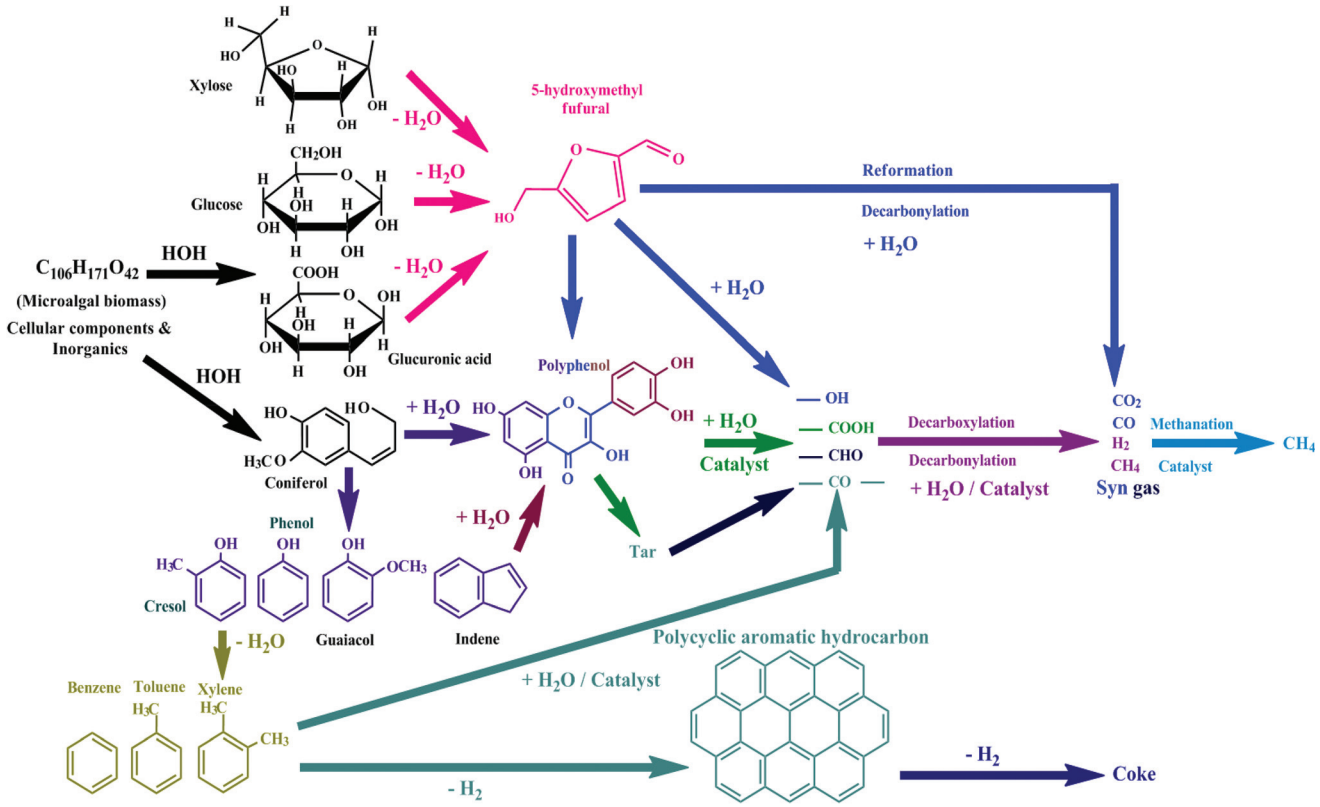


Fig. 8 General reaction pathway of hydrothermal gasification (source ref. 84–99).

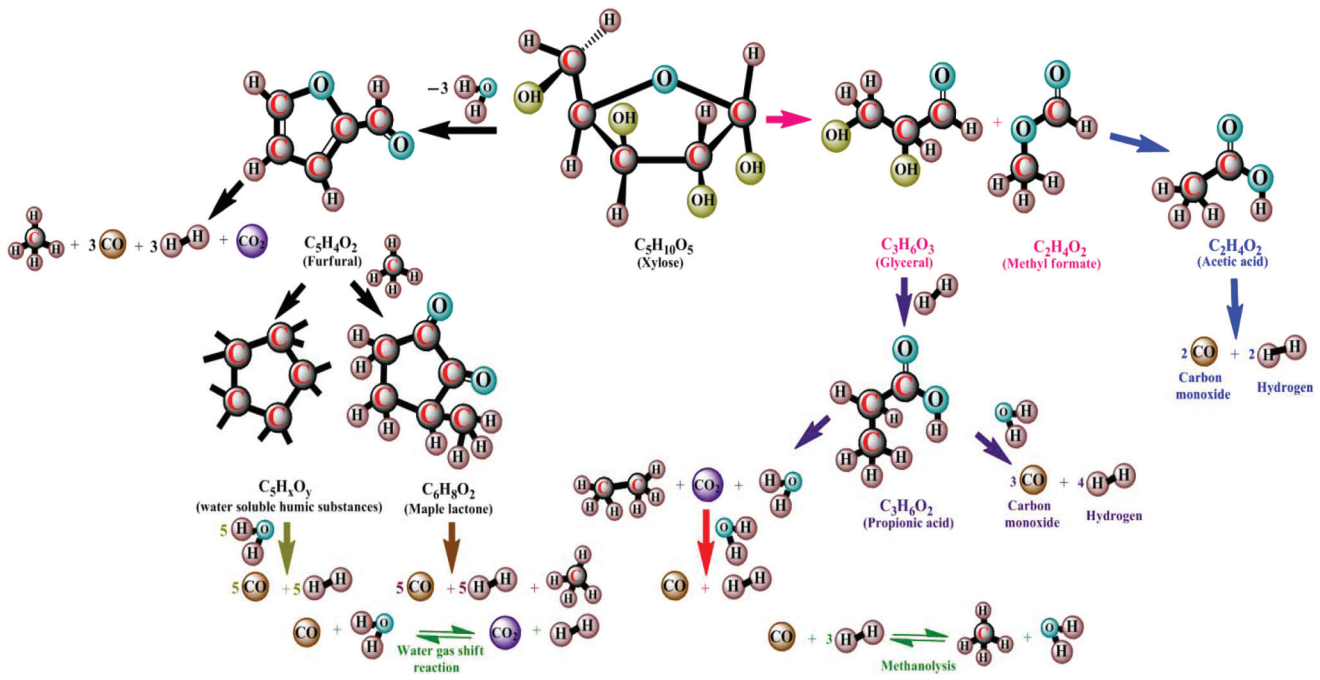


Fig. 9 Carbohydrate decomposition mechanism in hydrothermal gasification (modified ref. 84–99).

high water content. These drawbacks dramatically reduce the HHV and consequently the volumetric energy density of microalgal biomass.[102] In addition, the presence of a high water content increases the operating cost for dewatering or drying prior to further conversions, such as pyrolysis, gasification, and combustion. The high water content in microalgae also

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(i) $CH_aO_b \xrightarrow[(1-b)H_2O]{\text{Decomposition}} CO + [(1-b)+(a/2)]H_2$ $\Delta H^o_{(glucose)} = +608$ kJ / M

(ii) $CO + H_2O \rightleftharpoons H_2 + CO_2$ (Water gas shift reaction) $\Delta H^o = -41$ kJ / M

(iii) $CO + 3H_2 \rightleftharpoons CH_4 + H_2O$ (Methanation) $\Delta H^o = -211$ kJ / M

$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$ (Methanation) $\Delta H^o = -223$ kJ / M

Scheme 2 The endothermic decomposition steps of biomass.

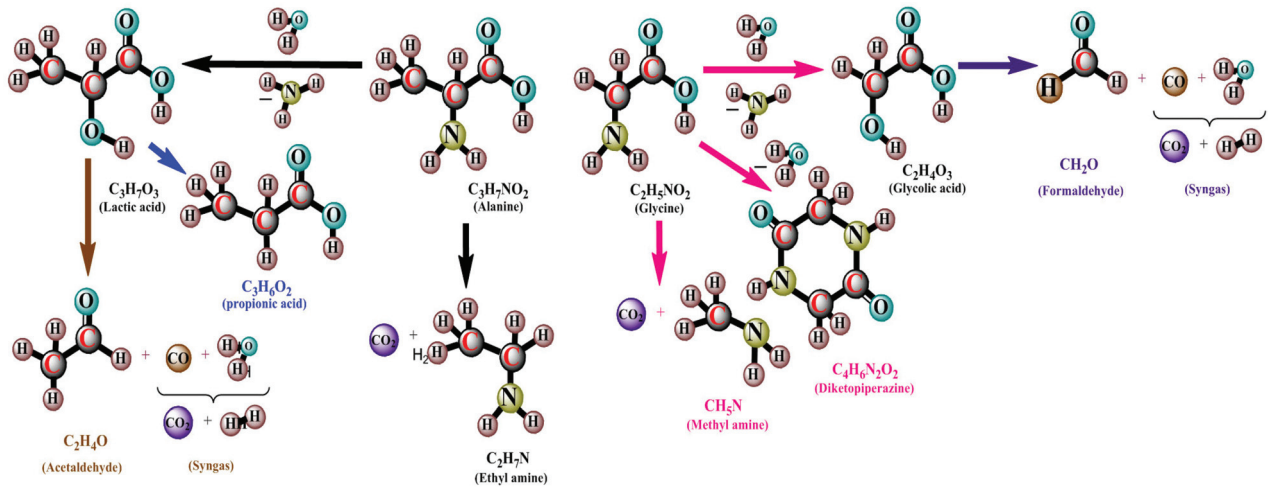


Fig. 10 Protein decomposition mechanism in hydrothermal gasification (modified ref. 84–100).

decreases the overall conversion efficiency due to energy lost in the form of latent heat to vaporize water during these processes.[102,103]

Recently, torrefaction has been recognized as an effective method to upgrade biomass into more energy-dense and hydrophobic solid fuels, which can effectively overcome the aforementioned drawbacks when microalgal biomass is thermochemically converted.[104] In recent years, a large number of torrefaction studies and reviews have focused on lignocellulosic biomass materials, but only a few studies employed microalgae or their residues as feedstocks.[102–108] Nevertheless, it is worthy to have an overview of the torrefaction process of microalgal biomass, because the composition of lignocellulosic biomass is significantly different from that of microalgal biomass, which may show different behaviors during the torrefaction process and have different effects on the biochar products. Torrefaction is defined as a thermal pretreatment process of biomass in an oxygen-free atmosphere over a temperature range of 200–300 °C. Within this range, this can be classified into three different severities: light (200–235 °C), mild (235–275 °C), and severe (275–300 °C) torrefaction.[3]

A study by Wu *et al.*[102] showed that an increase in the torrefaction temperature and residence time of *Spirulina platensis* increased the carbon, ash, and fixed carbon contents, as well as the HHV and hardgrove grindability index (HGI). The HHV of a microalga torrefied at 300 °C for 30 min increased from 20.46 to 25.92 MJ kg^{-1}, and the upgraded biomass was consequently more suitable for partial replacement of the coal employed in industry. The torrefaction kinetics for the thermogravimetric analysis (TGA) indicated that the activation energy of *Scenedesmus obliquus* CNW-N under isothermal torrefaction was 57.52 kJ M^{-1}, whereas it was in the range 40.14–88.41 kJ M^{-1} for non-isothermal torrefaction, as demonstrated by Chen *et al.*[103] A comparative study between isothermal and non-isothermal torrefaction revealed that the latter gave more severe pretreatment of microalgae than the former at the same mean temperature. According to the study by Chen *et al.*[3] torrefaction of microalgae involves two main stages: (1) dehydration (below 200 °C) and (2) depolymerization, decarbonization, and cracking due to the thermal decomposition of proteins and carbohydrates (above 200 °C). Furthermore, recent TGA and Fourier transform infrared (FTIR) spectra[108] clearly suggested that carbohydrate is first destroyed with increasing torrefaction severity, followed by protein consumption.

Similar to lignocellulosic biomass, the most important torrefaction parameter is temperature, followed by the residence time. On the other hand, the main indicators for torrefaction include solid yield and enhancement (or energy densification)

Table 4 Thermochemical conversion of microalgal biomass with biofuel yield

			Yield (% dry wt)					
			Solid			Liquid bio-oil		
Species	Scale	Conversion methods and Conditions	Charcoal	Content	HHV (MJ kg $^{-1}$)	Properties/Elemental composition	Gaseous	Ref.
Chlorogloeopsis fritschii	Lab-scale	Hydrothermal liquefaction, 300 °C and 350 °C (accompanied with nutrient recycling of aqueous phase)	~10.0	38.6		O (19.0), C (66.5), H (07.2), N (06.8)	~13.0	38, 49 and 52
Chlorella protothecoides		Fast pyrolysis, heterotrophic, at 500 °C, 0.101 MPa, heating rate of 600 °C s^{-1}, a sweep gas (N_2) flow rate of 0.4 m^3 h^{-1}, a vapor residence time 2–3 s.	11.2	57.2	41.0	An average of low oxygen content O (11.2), C (76.2), H (11.6), a density of 0.92 kg l^{-1}, viscosity of 0.02 Pa s (at 40 °C)	32.0	16, 20, 38 and 52
		Fast pyrolysis, phototrophic, at 500 °C, 0.101 MPa, heating rate of 600 °C s^{-1}, a sweep gas (N_2) flow rate of 0.4 m^3 h^{-1}, a vapor residence time 2–3 s.	53.8	16.6	30	O (19.4), C (62.1), H (08.8). A density of 1.06 kg l^{-1}, viscosity of 0.10 Pa s (at 40 °C)	32.0	45, 52, 53 and 61
		Fast pyrolysis, at 775 °C, 0.101 MPa, a heating rate of 10 K s^{-1}	08.4	55.3	39.7	—	36.3	16 and 31
Chlorella pyrenoidosa		Non-catalytic hydropyrolysis, temperature 310 °C, time 60 min and H_2 pressure 3 MPa (a stainless steel batch)	12.3	53.2	37.3	Low oxygen content, O (7.6), C (72.9), H (9.8), N (9.7)	18.5	31, 38, 61, 68 and 108
Chlorella sp.		Fast pyrolysis, non catalytic and catalytic using Na_2CO_3 catalyst, at 300–450 °C (fixed-bed reactor)	48 & 55 at 300 °C	55 & 40.5 at 450 °C	27 & 33 at 400 °C & 450 °C	Low oxygen content (33.2), lower acidity, higher aromatics	23 & 34 at 400 °C	16, 52, 75 and 100
	Pilot-scale	Microwave-assisted pyrolysis, catalyst, power of 500, 750, 1000 and 1250 W, (462–627 °C), 20 min	~25.0 at 750 W	28.6 at 750 W	30.7 at 750 W	O (16.5), C (65.4), H (7.84), N (10.3) a density of 0.98 kg L^{-1} (at 30 °C), a viscosity of 61.2 cSt at 750 W	27.0 at 750 W	45, 53, 61, 68 and 100
Chlorella vulgaris	Lab scale	Catalytic pyrolysis using H+ZSM-5 catalyst, at 500 °C (fixed-bed)	25.7	52.7	18.6	O (24.8), C (51.4), H (10.4), N (12.4), high hydrocarbons (~25%)	21.6	20, 31, 38 and 49
		Hydrothermal liquefaction, 350 °C, ~200 bar in either pure distilled water, or 1 M base Na_2CO_3 or 1 M of the organic acid HCOOH (batch reactor)	~03.0	~39.0	337.1	O (14.8), C (73.6), H (10.7), N (5.9)	~28.0	16, 20, 31, 38, 45, 49, 52, 53 and 68
		Microwave-assisted pyrolysis, power of 750, 1500 and 2250 W	~90 Solid residues	35.8 at 1000 W	—	—	52.4 at 2250 W	49 and 52
	Reactor		~08.0	46.6	37.5	O (09.3), C (75.9), H (09.0), N (05.3)	~12.0	52 and 53
Microcystis aeruginosa	Lab scale	Fast pyrolysis, phototrophic, 500 °C, 0.101 MPa, a heating rate of 600 °C min^{-1} at residence time of 2–3 s (in fluid bed reactor)	~21.0	24.0	29.0	O (21), C (62.1), H (08.2), A density of 1.06 kg l^{-1}, viscosity of 0.10 Pa s	~54.0	31, 38, 61, 68 and 100
Nannochloropsis oculata			07.0	~37.0	39.0	O (18.9), C (74.7), H (10.6), N (4.3)	~48.0	52, 61 and 68

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Table 4 *(Contd.)*

			Yield (% dry wt)					
			Solid			Liquid bio-oil		
Species	Scale	Conversion methods and Conditions	Charcoal	Content	HHV (MJ kg $^{-1}$)	Properties/Elemental composition	Gaseous	Ref.
Porphyridium cruentum			~10.0	~27.0	36.3	O (13.3), C (72.8), H (09.1), N (05.7)	~15.0	20 and 100
		Fast pyrolysis, at 500–900 °C, heated by using a SK2-4-13 tube furnace (quartz tube reactor)	30 at 500 °C	91.09 (at 900 °C)	Syngas (heating based on energy consumption at 900 °C s 1.3391 (ppmv kJ) L^{-1} kW^{-1} h^{-1})	—	Syngas H_2 emission rate 50.75 ppmv s^{-1} at 900 °C, CO 102 ppmv s^{-1} at 800 °C	16, 20, 31, 38, 45, 49, 52, 53 and 100
Scenedesmus dimorphus	Pressure reactors		~18.0	27.1	33.6	O (12.6), C (73.0), H (08.2), N (05.7)	~08.0	20 and 52
Scenedesmus sp.	Bench scale	Fast pyrolysis, 480 °C and 100 kPa with a 2 s vapor residence time and 2 hours' total run time (isothermal spouted bed/dynamic)	Oil/char 3.76	55.0	18.4	An average of O (27.6), C (51.9), H (9.0), N (8.6)	—	52 and 100
Raw *Scenedesmus* biomass	Lab scale	Slow pyrolysis at 450 °C, reaction time of 2 h	30.0	31.0	35.0–37.0	O (10.5), C (72.6), H (9.0), N (6.5)	12.0	16, 20, 31 and 38
Raw *Scenedesmus* biomass		Hydrothermal liquefaction (HTL) at 300 °C, pressure ranging from 10 to 12 MPa	07.0	45.0	33.0–40.0	O (8.1), C (73.9), H (9.3), N (7.9)	30.0	52, 75 and 100
Defatted *Scenedesmus*	Triplicate		06.0	36.0		O (8.2), C (72.6), H (8.9), N (10.0)	41.0	52, 75 and 100
	Lab scale		33.0	24.0		O (10.5), C (72.2), H (8.9), N (7.8)	21.0	52, 75 and 100
Spirulina biomass			30.0	24.0		O (9.2), C (72.2), H (9.1), N (8.1)	15.0	49 and 52
	Batch		11.0	31.0		O (9.2), C (71.2), H (9.0), N (9.2)	35.0	45, 49 and 52
Spirulina platensis	Lab-scale	Pyrolysis at 500 °C, 60 min, heating rate 7 °C min^{-1} (batch reactor)	25.6	29.0	33.62	O (6.81), C (74.7), H (10.8), N (7.13)	28.0	38, 45, 49, 52 and 68
		Pyrolysis at 350 °C, 60 min, heating rate 3.5 °C min^{-1}	39.7	23.0	29.3	O (11.3), C (67.5), H (9.82), N (10.7)	19.2	52
		Thermochemical liquefaction (TCL), at 350 °C, 60 min, heating rate 3.5 °C min^{-1}, 2 MPa	05.7–07.0	39.9–41.0	34.21	O (10.1), C (73.7), H (8.90), N (6.30), TCL bio-oil better in quality and stability compared to pyrolysis oil	22.0–23.2	38, 45, 49, 52 and 68
	Batch		~02.0	35.5	36.1	O (11.5), C (72.7), H (08.8), N (06.3)	~05.0	52
Spirulina sp.			~07.0	~27.0	36.8	O (10.9), C (75.4), H (10.8), N (07.0)	~32.0	49 and 52
Blue-green algae blooms	Lab-scale	Pyrolysis, at 500 °C, particle size below 0.25 mm and sweep gas flow rate of 100 mL min^{-1} (fixed bed reactor)	25.0	55.0	31.9	O (14.5), C (67.6), H (8.95), N (7.75), high level of long-chain alkanes	20.0	38, 45, 49, 52 and 100

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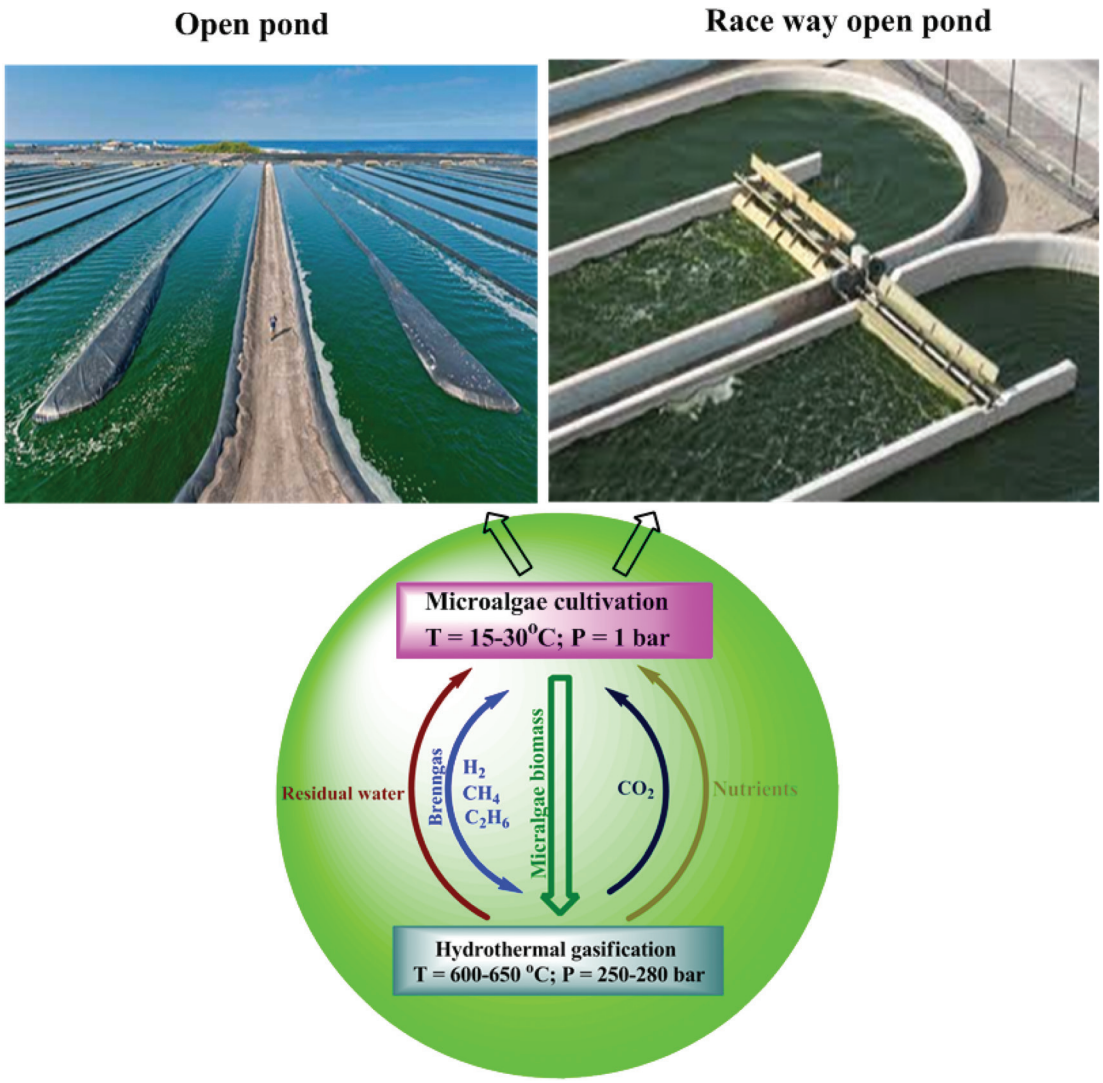


Fig. 11 Integration between algal cultivation and hydrothermal gasification process (modified ref. 101).

factors, which reveal the mass ratio of the remaining solid to its parent biomass, as well as the energy densification in the solid, respectively. Based on these two indicators, the energy yield of torrefaction can be obtained.[106] Some microalgae contain high contents of lipids, which are valuable oil sources for biodiesel production. It can be seen in the literature that most torrefaction studies focus on the utilization of the residues from microalgae, which undergo oil-extraction to produce solid fuels. Table 5 summarizes the results from the torrefaction studies of microalgae and microalgal residues, showing the two most important indicators of the solid yield and the enhancement factor. The table reveals that the solid yield and the enhancement factor after a microalgal biomass torrefaction (for 30 min) are 51–95% and 1.03–1.46, respectively. However, the solid yield may drop to 40% if the residence time is as long as 60 min. Higher torrefaction temperatures and longer durations increase the fuel quality of torrefied products, but severe conditions consume more energy and lead to a lower energy yield.[106,107] Consequently, process optimization becomes important in selecting the optimal operating conditions in terms of fuel quality and energy consumption.

3. Biochemical characterization of microalgae

Microalgae are considered as a suitable feedstock for third-generation renewable biofuels, owing to three plentiful major biochemical components, *viz.* lipids, carbohydrates, and proteins (Table 6). Solid, liquid and combustible gaseous biofuels can be obtained efficiently from microalgae through torrefaction, liquefaction, and gasification thermochemical conversion technologies, respectively; these can replace fossil fuels and stop the atmospheric greenhouse effect.[3] Compared to lignocellulosic biomass, functional groups with primary elemental constituents, such as C, H, O, and N, of microalgae also com-

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Table 5 Outcome of the torrefaction studies of microalgae and microalgal residues

Microalgal species	Torrefaction condition	Solid yield (%)	Enhancement factor	Ref.
Spirulina platensis	200 °C – 30 min	90	1.07	98
	250 °C – 30 min	76	1.07	
	300 °C – 30 min	62	1.27	
Spirulina platensis residue	200 °C – 30 min	96	1.05	98
	250 °C – 30 min	91	1.06	
	300 °C – 30 min	72	1.18	
Chlorella vulgaris ESP-31 residue	200 °C – 60 min	74	1.14	101
	225 °C – 60 min	68	1.17	
	250 °C – 60 min	54	1.34	
	275 °C – 60 min	45	1.43	
	300 °C – 60 min	40	1.48	
Chlamydomonas sp. JSC4 residue	200 °C – 30 min	94	1.06	102
	225 °C – 30 min	91	1.08	
	250 °C – 30 min	82	1.15	
	275 °C – 30 min	68	1.38	
	300 °C – 30 min	51	1.46	
Chlorella vulgaris ESP-31 residue	200 °C – 30 min	95	1.03	103
	225 °C – 30 min	89	1.08	
	250 °C – 30 min	84	1.11	
	275 °C – 30 min	61	1.30	
	300 °C – 30 min	57	1.36	

Table 6 Biochemical composition and higher heating values of microalgae

	Elemental analysis (wt%)					Composition (dry-ash-free, wt%)				
Microalgae biomass	C	H	N	O	S	Protein	Lipid	Carbohydrate	Others[a]	HHV (MJ kg^{-1})
Chlorella	50.20	7.25	09.30	33.20						21.20
Chlorella vulgaris[b]	45.80	5.60	04.60	38.70		29.00	49.50	19.70	01.80	18.40
Chlorella vulgaris[c]	53.80	7.72	01.10	37.00		06.00	43.00	51.00	0.000	24.00
Chlorella vulgaris	42.51	6.77	06.64	27.95		41.51	15.67	20.99	21.83	16.80
Chlorella vulgaris	43.90	6.20	06.70	43.30		54.90	15.50		29.60	18.00
Chlorella vulgaris residue	45.04	6.88	09.79	29.42		61.24	05.71	20.34	12.71	19.44
Chlorella sorokiniana CY1 residue						18.81	09.90	35.67	35.62	20.24
Chlamydomonas sp. JSC4 residue						12.18	06.85	35.70	45.27	17.41
Chlamydomonas reinhardtii (wild)	52.00	7.40	10.70	29.80		47.40	18.10		34.50	23.00
Chlamydomonas reinhardtii CW15+	50.20	7.30	11.10	31.40		45.70	22.40		31.90	22.00
Dunaliella tertiolecta	39.00	5.37	01.99	53.20	0.62	61.32	02.87	21.69	14.12	14.24
Hapalosiphon sp.	47.94	7.44	06.45	37.58	0.58					14.75
Nannochloropsis oculata	39.90	5.50	06.20			39.00	20.00	17.00	24.00	16.80
Nannochloropsis oceanica	50.06	7.46	07.54	34.47	0.47	19.10	24.80	22.70	33.40	21.46
Nannochloropsis oceanica residue	45.24	6.55	11.07	36.58	0.56					18.17
Spirulina platensis	46.16	7.14	10.56	35.44	0.74	48.36	13.30	30.21	08.13	20.52
Spirulina platensis	45.70	7.71	11.26	25.69	0.75					20.46
Scenedesmus obliquus CNW-N	37.37	5.80	06.82	50.02		30.38	04.66	13.41	51.55	16.10

[a] By difference, others (%) = 100 − protein − lipid − carbohydrate. [b] The standard nutrients condition. [c] The nutrients starvation condition. Source ref. 3 and 108.

pensate for the potentiality towards the production of high value-added chemicals. The conventional microalgae-to-biodiesel technology necessitates high-lipid strains, which tend to have lower biomass productivity when compared to low-lipid microalgal strains, and thereby such strains need an alternative conversion strategy. Lipids that comprise saturated and polyunsaturated fatty acids with typically 14–20 carbon units, proteins, and carbohydrates consisting of D-glucopyranose units linked *via* β- and/or α-glycosidic bonds, make up 7–23, 6–52, and 5–23 wt%, respectively, of the weight of microalgae for high-quality biofuel yields.[3]

The foremost challenge in the thermochemical conversion is to synthesize the preferred products with an adequate yield and purity, since most of the heteroatoms, such as O, N, and S, from the microalgal biomass are detached, and most of the C and H atoms remain in the residue; consequently, the residual constituents are transformed into liquid fuel. So, the thermochemically produced microalgal bio-oils are characteristically similar to those from some lignocellulosic biomass, except for the existence of a smaller amount of some derivatives of aromatic compounds, due to the absence of lignin moieties. Microalgal bio-oils consist of a number of

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N-compounds, which were produced *via* degradation of proteins.[3,5,6]

4. Direct combustion

Incineration of microalgal biomass in the presence of air at high temperatures (>800 °C) converts the chemical energy into hot gases for heating boilers, furnaces, and steam turbines, ranging from small-scale to large-scale (100–300 MW).[5,108–110] Its main disadvantage is the necessity for standardized pre-treatment processes, such as sun/drum/vacuum/freeze drying, grinding, centrifugation, and settling, so it is cost-intensive. These methods are proficient in reducing the moisture content up to ≈2% and adding ≈0.5–1$ kg^{-1} to the cost processing of microalgal biomass. It is employed mostly for microalgal biomass with less than 50% of moisture.[111,112] Moreover, its biofuel conversion efficiency is more favourable than that of coal and the efficiency can be improved if combusted along with coal.[5] Only limited surveys are available on the investigation of combustion of microalgal biomass, and this requires further improvement.[5,83]

The literature[62–67] showed that the hypothetical molecular structural formula of microalgal biomass is $C_{106}H_{171}O_{42}N_{16}P$, which can be simply represented as $C_5H_8O_2$, which is based on the mass fraction and elemental analytical report. $C_5H_8O_2$ is stoichiometrically similar to acetylacetone algal biomass surrogate, so the combustion reaction, neglecting the ash content, can be given as

$$C_5H_8O_2 + 6.5O_2 \rightarrow 5CO_2 + 4H_2O - 2510\ kJ\ M^{-1}$$

Moreover, it is unfeasible to burn the biomass directly in an internal combustion engine; the machinery for power production could be a Rankine engine by means of a forced convection industrial boiler. A basic model of this structure has been extended in Aspen plus™ to achieve the mass and energy flow that is essential for 1 kW continuous generation, and it would demand an area ≈20 × 20 m to output 1 kW of electricity continuously at a cost of about ≈0.95 kW h^{-1}. This is four times the cost of modern diesel production in off-grid regions.[112] Besides, the pumping of algae from a separator to a drier, along with algal solid treatment and feeding into a combustor, have not yet been automated for power production design, and so this would still necessitate noteworthy engineering input.

5. Economic feasibility

Currently, more than a few countries are promoting biofuel programs,[4] since the first-generation biofuels are on the commercialization scale, second-generation biofuels are moving towards the market, and third-generation biofuels are still at the laboratory scale. It is predictable that they will all achieve improvement in the direction of the industrial scale within the next few decades. The degree of the marketplace decides the diverse techniques intended for the production of bio-fuels *via* thermochemical conversion of microalgal biomass, which can be coupled with discrete steps in the sequence of research, development, and innovation. At this juncture, the differences among biofuels need to be well recognized by means of analytical tools, such as energy balance and GHG emissions, considering the life cycle analysis in addition to the resource demand, job generation, and the availability of necessary technologies.[4]

The commercialization of biofuels necessitates advanced laboratory-scale processes to yield productivities that approach the theoretically probable and scale them up without losing the concern. Since algae are cultivated in water, they require dewatering and energy-intensive drying before pyrolysis. The water used in the pyrolysis process is a source of hydrogen, and all the way through reforming of pyrolytic products is one of the cost-effective approaches.[3] Bio-oil refineries should be situated in close proximity to the areas producing the algal biomass, and then the stabilized bio-oil could be transported to the refineries for conversion in the direction of transportation of the liquids, which creates a trade-off between transportation costs and economies-of-scale, which can be paid for by larger pyrolysis processes.[3]

Since the energy-intensive drying process is not essential, HTL is a desired conversion procedure and is particularly appropriate for producing biofuel from wet microalgal feedstock in its early stages. By comparision, the HTL biofuel is more energy-intensive, as the removal of oxygen from the algal feedstock involves a decarboxylation pathway. However, there are some advantages in the HTL process with respect to microalgal biofuel production; this is cost-competitive and so financial assistance from the Government is essential. In the case of microalgal hydrothermal gasification, there are some economically feasible basic necessities required, which comprise energy for pumping the aqueous streams, heating the reaction system to maintain its temperature at the preferred levels, and recycling of the gasification products, such as residual water, salts, and CO_2, which are the nutrients for algal cultivation.

The low moisture content of torrefied microalgal biomass leads to cost-effective transportation and easy packaging, along with better quality of the torrefied biofuels. Even though, these days, a number of cost-effective torrefaction technologies are available, further research is obligatory, particularly on the reaction kinetics for designing large-scale reactors. There are limited data on the feasibility of combustion of microalgae biomass and so this necessitates further research and development; however, the overall combustion efficiency may be enhanced if it is combusted along with coal.[83] In our view, with sufficient progress towards conversion technologies, the microalgal biomass could potentially be an economically workable alternative for chemical energy storage.

6. Perspectives and concluding remarks

Recently, the production of renewable biofuels from microalgal species has received substantial attention, essentially contri-

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buting to the fast growth rate of microalgae, high efficiency photosynthesis and CO_2 capture, and negligible competition with food crops. Moreover, microalgae-based biofuels play an significant role in energy shortages, global warming, and climatic changes. Though there is remarkable potentiality in this field, the commercial large-scale production of microalgae-based biofuels is still in the early stages. This consequently requires sustained intensive research to step up the realistic utilization of microalgae as a promising energy feedstock and the enhancement in bio-oil production, with proficient energy-efficiency of the technologies. The thermochemical conversion technologies for microalgal feedstock are still in the early stages and the concluding remarks comprise the following significant essentials.

To date, the technologies available for the cultivation, harvesting, and biofuel conversion techniques for microalgae cannot achieve cost-effective microalgal biofuel production.[113,114] Even though the growth rate of microalgal biomass is fast, and the cultivation circumstances probably incorporate flue gas as a carbon source, the drying operation consumes a great deal of energy compared to other plants. Microalgal biomass productivity, land area, and water requirement are key issues throughout the cultivation and harvesting. Microalgae have the ability to absorb CO_2 for their growth from cement and coal-fired power plants, and to biosorb heavy metals from industrial effluents. For their growth, about 81 g dry algae m^{-2} per a day needs 25% of essential energy towards bio-oil production, with a land area requirement of 6.2 million acres, 8.466×10^8 m^3 saline water, and 7.914×10^9 m^3 fresh water.[115,116] Moreover, microalgal strains with an elevated growth rate and intense energy are vital when considering genetic engineering approaches to such species. One potential cost-effective method of diminishing the microalgal production and processing the energy cost is to merge the algal cultivation with current wastewater treatment methods.

Co-processing of microalgae with waste polymers as a hydrogen source is cost-effective, in thermochemical pyrolytic techniques. Catalysts play a critical role in the production of bio-oils from microalgae by HTL techniques. Furthermore, this technique has been focused on homogeneous/heterogeneous catalysis and on non-precious-metal-based catalysts to afford major progress toward the achievement of an essential improvement in bio-oils production. An understanding of the mechanistic pathways of algal thermochemical conversions is more significant in improving the conversion procedure and conducting experiments, particularly those involving catalytic desorption. A kinetics approach is tremendously useful in microalgal conversion techniques to design pilot-scale reactors. The special effects of a variety of microalgal feedstock constituents with working parameters that facilitate a good yield and quality of bio-oils are further examined to determine the optimal processing circumstances, as such microalgal species could be used as feedstocks under suitable reaction conditions. Direct energy conversion of microalgae *via* gasification and direct combustion is a propitious technology, compared to other photosynthetic conversion technologies. However, the major temperature regime involved in the process should be considered critically, along with the production of some other byproducts that would make the process economical and within the bounds of possibility.

Moreover, the consideration of the chemical composition of bio-oil is obligatory in the estimation/optimization/upgradation of the thermochemical conversion techniques, and accordingly the bio-crude characterization of the liquid products has been limited to GC-MS and micro-elemental analytical techniques. Other analytical methods are spectral studies, which can be performed with a superior quantity of samples, affording more comprehensive information concerning the composition profile of all the products.

Thus, microalgal feedstocks proficiently construct renewable bio-fuels and attract research attention due to their fast growth rate, tolerancy level towards greenhouse gases, and heavy-metal biosorption from industrial effluents and waste water sources. Moreover, many studies showed that employing thermochemical techniques is related to the oil upgrading process.

Acknowledgements

This work was supported in part by the Korea Research Fellowship Program through the National Research Foundation of Korea (NRF), funded by the Ministry of Science, ICT and Future Planning (Grant No: 2016H1D3A1908953). The financial assistance to one of the authors (GK) from Ton Duc Thang University, Vietnam is gratefully acknowledged. This research also received funding in part from the Ministry of Science and Technology under grant numbers MOST 102-2221-E-006-288-MY3 and 105-3113-E-042A-001, Taiwan, R.O.C. The authors would like to acknowledge Erciyes University, Kayseri, Turkey for the financial support under FOA-2015-5817 and FOA-2015-5790 projects (BAP, Bilimsel Araştırma Projeleri).

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