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Review

Thermochemical conversion of microalgal biomass into biofuels: A review

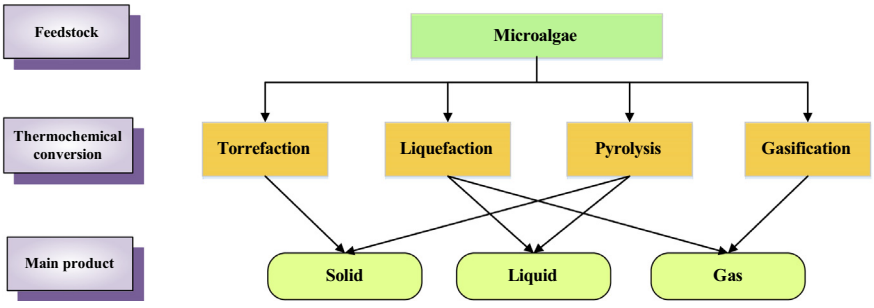
Wei-Hsin Chen [a,*], Bo-Jhih Lin [a], Ming-Yueh Huang [a], Jo-Shu Chang [b,c,d]

[a] Department of Aeronautics and Astronautics, National Cheng Kung University, Tainan 701, Taiwan, ROC
[b] Department of Chemical Engineering, National Cheng Kung University, Tainan 701, Taiwan, ROC
[c] Center for Bioscience and Biotechnology, National Cheng Kung University, Tainan 701, Taiwan, ROC
[d] Research Center for Energy Technology and Strategy, National Cheng Kung University, Tainan 701, Taiwan, ROC

HIGHLIGHTS

- Thermochemical conversion technologies using microalgae as feedstocks are reviewed.
- The progress of torrefaction for solid biofuels is introduced.
- Liquefaction and pyrolysis techniques for producing bio-oils are illustrated.
- Gasification routes to produce combustible gases are outlined.
- Detailed conversion processes and their outcome are addressed.

GRAPHICAL ABSTRACT



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ABSTRACT

Following first-generation and second-generation biofuels produced from food and non-food crops, respectively, algal biomass has become an important feedstock for the production of third-generation biofuels. Microalgal biomass is characterized by rapid growth and high carbon fixing efficiency when they grow. On account of potential of mass production and greenhouse gas uptake, microalgae are promising feedstocks for biofuels development. Thermochemical conversion is an effective process for biofuel production from biomass. The technology mainly includes torrefaction, liquefaction, pyrolysis, and gasification. Through these conversion technologies, solid, liquid, and gaseous biofuels are produced from microalgae for heat and power generation. The liquid bio-oils can further be upgraded for chemicals, while the synthesis gas can be synthesized into liquid fuels. This paper aims to provide a state-of-the-art review of the thermochemical conversion technologies of microalgal biomass into fuels. Detailed conversion processes and their outcome are also addressed.

1. Introduction

Since the Industrial Revolution occurred in eighteenth century, fossil fuels have become the most important energy resources. However, mass consumption of fossil fuels has caused serious environmental problems such as air pollution, deteriorative atmospheric greenhouse effect, and global warming. To abate these problems, the development of renewable energy has received a great deal of attention over the past decades. Biomass energy or bioenergy is currently the fourth largest primary energy source in the world (Wu et al., 2012), biomass is thus a potential substitute to fossil fuels. When plants grow, all carbon in the biomass comes from the atmosphere, and it is liberated into the environment as the plants are burned. On account of having a zero net carbon footprint in the aforementioned cycle, biomass is considered

* Corresponding author. Tel.: +886 6 2004456; fax: +886 6 2389940.
E-mail address: weihsinchen@gmail.com (W.-H. Chen).

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as a carbon–neutral fuel. First-generation biofuels produced from food crops, such as sucrose- and starch-derived bioethanol, have been extensively consumed (Naik et al., 2010). Second-generation biofuels from non-food crops, such as lignocellulosic bioethanol, have been developed to avoid food shortage problems (Chen et al., 2010). Biofuels, such as biodiesel, bioethanol, and biobutanol, produced from macroalgae and microalgae are termed third-generation biofuels (Chen et al., 2011).

Microalgae are characterized by their rapid growth and high carbon fixing efficiency (Chen et al., 2014a); accordingly, carbon capture and storage are achieved while they grow and are harvested. Microalgae have numerous commercial applications; they can enrich the nutritional value of food, serve as animal feed, and be incorporated into cosmetic products (Spolaore et al., 2006). From the aspect of biofuels, microalgae can be consumed in the forms of solid, liquid, and gas phases. The bioenergy development from microalgae can be categorized into: (1) direct combustion, (2) torrefaction, (3) chemical conversion, (4) biochemical conversion, and (5) thermochemical conversion. Heat is the main product from direct combustion, whereas biofuels can be obtained from the other conversions.

For solid biofuels, energy stored in microalgae can be released and employed through burning or co-firing. Unlike lignocellulosic biomass in which the main constituents are made up of cellulose, hemicellulose, and lignin, microalgae are composed of proteins, carbohydrates, lipids, and others such as ashes and acids (Chen et al., 2014a). Lignin is only contained in red algae (Martone et al., 2009) and certain green algae such as *Coleochaete* species (Sørensen et al., 2011). The contents of protein, carbohydrate, lipid, and others in some microalgae are given in Table 1. Lipids accumulated in some microalgae cells are high, and hence can be extracted and converted into biodiesel by means of transesterification, which belongs to chemical conversion. Bioethanol and biobutanol can be produced from microalgae fermentation, while methane and hydrogen can be produced through the anaerobic digestion of microalgae (Spolaore et al., 2006). Both fermentation and anaerobic digestion pertain to biochemical conversion. Thermochemical conversion consists of torrefaction (Chen et al., 2014b), liquefaction (Barreiro et al., 2013), pyrolysis (Akhtar and Saidina Amin, 2012), and gasification (Amin, 2009). The operating conditions (temperature, pressure, and duration) and main products of torrefaction, liquefaction, pyrolysis, and gasification are given in Fig. 1.

Compared to chemical and biochemical methods, the thermochemical method gives a simpler route to produce biofuels. In chemical conversion, biomass needs to be separated or purified; transesterification needs an installation for methanol recycle, and the disposal process is complex because of soap formation (Huang et al., 2010). In biochemical conversion such as fermenta-

Table 1
A list of elemental and composition analyses as well as higher heating values of microalgae.

Materials	Elemental analysis (wt%)					Composition (dry-ash-free, wt%)				HHV (MJ kg^{-1})	References
	C	H	N	O	S	Protein	Lipid	Carbohydrate	Others[c]		
Chlorella	50.20	7.25	9.30	33.2						21.20	Babich et al. (2011)
Chlorella vulgaris[a]	45.80	5.60	4.60	38.70		29.00	49.50	19.70	1.8	18.40	Xu et al. (2011)
Chlorella vulgaris[b]	53.8	7.72	1.1	37.0		6.00	43.00	51.00	0	24.00	Xu et al. (2011)
Chlorella vulgaris	42.51	6.77	6.64	27.95		41.51	15.67	20.99	21.83	16.80	Wang et al. (2013)
Chlorella vulgaris	43.90	6.20	6.70	43.30		54.90	15.50		29.6	18.00	Kebelmann et al. (2013)
Chlorella vulgaris residue	45.04	6.88	9.79	29.42		61.24	5.71	20.34	12.71	19.44	Wang et al. (2013)
Chlorella sorokiniana CY1 residue						18.81	9.9	35.67	35.62	20.24	Chen et al. (2014b)
Chlamydomonas sp. JSC4 residue						12.18	6.85	35.7	45.27	17.41	Chen et al. (2014b)
Chlamydomonas reinhardtii (wild)	52.00	7.40	10.70	29.80		47.40	18.10		34.5	23.00	Kebelmann et al. (2013)
Chlamydomonas reinhardtii CW15+	50.20	7.30	11.10	31.40		45.70	22.40		31.9	22.00	Kebelmann et al. (2013)
Dunaliella tertiolecta	39.00	5.37	1.99	53.2	0.62	61.32	2.87	21.69	14.12	14.24	Zou et al. (2010)
Hapalosiphon sp.	47.94	7.44	6.45	37.58	0.58					14.75[d]	Liu et al. (2012)
Nannocloropsis oculata	39.90	5.50	6.20			39.00	20.00	17.00	24	16.80	Du et al. (2012)
Nannochloropsis oceanica	50.06	7.46	7.54	34.47	0.47	19.1	24.8	22.7	33.4	21.46	Cheng et al. (2014)
Nannochloropsis oceanica residue	45.24	6.55	11.07	36.58	0.56					18.17	Cheng et al. (2014)
Spirulinaplatensis	46.16	7.14	10.56	35.44	0.74	48.36	13.30	30.21	8.13	20.52	Jena and Das (2011)
Spirulinaplatensis	45.70	7.71	11.26	25.69	0.75					20.46	Wu et al. (2012)
Scenedesmus obliquus CNW-N	37.37	5.80	6.82	50.02		30.38	4.66	13.41	51.55	16.10	Chen et al. (2014a)

[a] The standard nutrients condition.
[b] The nutrients starvation condition.
[c] By difference, others (%) = 100 − protein − lipid − carbohydrate.
[d] Lower heating value.

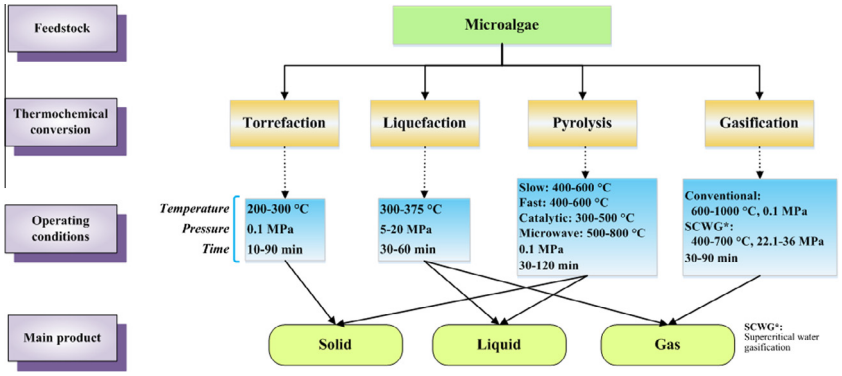

Fig. 1. A schematic of thermochemical conversion of microalgae.

tion, several days are usually required to produce biofuels (Nahak et al., 2011). In contrast, thermochemical conversion usually needs no chemicals addition, and can convert a variety of biomass feedstocks and utilize the entire biomass feedstock. The period for producing biofuels using the thermochemical method is short. Consequently, thermochemical conversion is one of the most crucial conversion methods for biofuels from microalgae.

Solid, liquid, and gas biofuels can be produced through thermochemical conversion processes. The properties of microalgae can be improved via torrefaction for the utilization as solid fuels. The prime product of liquefaction is bio-oils. Bio-oils and biochar can be produced from microalgae pyrolysis. Syngas (i.e., a gas mixture of hydrogen and carbon monoxide) and methane are produced from microalgae gasification. Some review papers relating to microalgae pyrolysis and liquefaction have been reported (Akhtar and Saidina Amin, 2012; Barreiro et al., 2013; Bridgwater, 2012; Mohan et al., 2006). Though conventional and supercritical water gasification of microalgae was introduced in a few papers (Amin, 2009; Bridgwater, 2012), attention was mainly paid to the behavior of oil extraction, and detailed information concerning operating conditions as well as product distributions and characteristics was absent. Up to now, the review of microalgae torrefaction has not been introduced yet. For these reasons, this review is intended to provide a comprehensive overview of recent development in the thermochemical conversion using microalgae as feedstocks. The potentials of solid, liquid, and gas biofuels produced from microalgae and the details of operating conditions will be addressed.

2. Torrefaction

2.1. Calorific values of microalgae

Combustion is the most direct route to utilize microalgae as fuels. The higher heating value (HHV) or gross calorific value of a fuel is a crucial indicator to reveal its application in industry. Typically, the HHV of lignocellulosic biomass is in the range of 15–20 MJ kg^{-1} (Parikh et al., 2005), which is significantly lower than that of coal, ranging from 25 to 35 MJ kg^{-1} (Du et al., 2010). The HHVs of microalgae are between 14 and 24 MJ kg^{-1} (Table 1), which are close to that of lignocellulosic biomass but lower than that of coal. This can be explained by relatively low carbon content in microalgae in which the weight percentage of elemental carbon is between approximately 37 and 53 wt% (Table 1). Though microalgae can be burned directly, their energy densities are relatively low when compared to coals. They are inappropriate to be utilized in industry. Instead, microalgae can be co-fired with coals for power generation, which may lead to lower greenhouse gas emissions and air pollution (Kadam, 2002).

2.2. Principle and classification of torrefaction

To overcome the disadvantage of low calorific values of microalgae, they can be upgraded through a thermochemical conversion process called torrefaction. In this process, microalgae are thermally degradated in an inert or nitrogen environment at one atmosphere and temperature range of 200–300 °C for several minutes to several hours. This process resembles pyrolysis which usually occurs between 350 and 650 °C. Because of lower operating temperatures of torrefaction compared to pyrolysis, it has also been called mild pyrolysis (Chen and Kuo, 2010). The pyrolytic process of microalgae in a thermogravimetric analysis (TGA) at temperatures of 25–800 °C could be divided into four stages (Chen et al., 2014a): (1) dehydration (25–200 °C); (2) depolymerization, decarbonization, and cracking due to the thermal decomposition of proteins and carbohydrates (200–430 °C); (3) lipid thermal degradation (430–530 °C); and (4) continuous and slow weight loss of carbonaceous matters (530–800 °C). Accordingly, microalgae are dehydrated during torrefaction, and proteins and carbohydrates in the materials are thermally decomposed in part, thereby achieving partial carbonization. Torrefaction temperature and duration are two important factors affecting the pretreatment performance, and the impact of the former on biomass is more than that of the latter. In light of the reaction temperature of microalgae, the torrefaction extent can be classified into light, mild, and severe torrefaction, and their temperature ranges are approximately 200–235, 235–275, and 275–300 °C, respectively (Chen et al., 2014a). This classification resembles the torrefaction of lignocellulosic biomass (Chen and Kuo, 2011). The higher the torrefaction severity, the higher the carbonization extent is.

2.3. Torrefaction characterization

Because relatively more carbon is retained in torrefied microalgae, their HHVs become higher when compared to their parent materials. The study by Wu et al. (2012) revealed that the carbon content, ash content, fixed carbon content, HHV, and Hardgrove grindability index (HGI) in *Spirulina platensis* increased with increasing temperature and residence time. The HHV of the microalga torrefied at 300 °C for 30 min increased from 20.46 to 25.92 MJ kg^{-1}. The upgraded biomass is thus more suitable to partially replace coals employed in industry. Considering torrefaction kinetics, the TGA of Chen et al. (2014a) indicated that the activation energy of *Scenedesmus obliquus* CNW-N under isothermal torrefaction was 57.52 kJ mol^{-1}, whereas it was in the range of 40.14–88.41 kJ mol^{-1} for non-isothermal torrefaction. A comparison between isothermal and non-isothermal torrefaction reflected that the latter gave more severe pretreatment on the microalgae than the former under the same average temperature.

The utilization of microalgae residues is also a potential topic for developing solid fuels. The analysis of Wu et al. (2012) indicated that the HGI of torrefied microalgal residue exceeded that of sub-bituminous coal when the torrefaction temperature was up to 250 °C. Chen et al. (2014b) conducted a torrefaction severity index (TSI) to indicate the thermal degradation degrees of *Chlamydomonas* sp. JSC4 and *Chlorella sorokiniana* CY1 due to torrefaction. The sharp curvature along severe torrefaction in the initial pretreatment period was exhibited, revealing that microalgae upgraded at high temperatures with short durations were more effective than that at low temperatures with long durations.

Raw lignocellulosic biomass is characterized by hygroscopic nature, high moisture content, large volume, low density, low calorific value, and low grindability (Lu et al., 2013), but these properties can be improved greatly by torrefaction (Rousset et al., 2011; Peng et al., 2012). This results in easier storage and delivery as well as higher utilization efficiency of torrefied biomass than its parent biomass.

3. Liquefaction

3.1. Principle of liquefaction

Liquefaction, also termed thermochemical liquefaction or hydrothermal liquefaction (HTL), is a thermal process to convert wet microalgal biomass into liquid fuel where hot compressed or sub-critical water is employed. In general, liquefaction is operated at temperatures of 300–350 °C (Table 2) and pressures of 5–20 MPa, while microalgal mass fraction is 5–50% in the slurry feed (Suali and Sarbatly, 2012; Barreiro et al., 2013). Pressures are high to keep water in the liquid phase and the reaction temperature is normally held for 5–60 min. Catalysts could be used to aid in

Table 2
A list of operating conditions of microalgae liquefaction as well as bio-oil yield and HHV.

Feedstock	Operating conditions			Elemental analysis (wt%)					Bio-oil yield (wt%)	HHV (MJ kg^{-1})	References
	Temperature (°C)	Duration (min)	Catalyst (wt%)	C	H	N	O	S			
Chlorella vulgaris	300	60		75.9	9.0	5.3	9.3[b]	0.4	46.6	37.5	Biller et al. (2012)
Chlorella vulgaris	350	60		70.7	8.6	5.9	14.8[b]	0	36	35.1	Biller and Ross (2011)
Dunaliella tertiolecta	300	60	Na_2CO_3 (5%)	74.4	9.4	6.8	9.4		42	37.0	Minowa et al. (1995)
Dunaliella tertiolecta cake	360	50	Na_2CO_3 (5%)						25.8	30.74	Zou et al. (2010)
Desmodesmus sp.	375	5		74.5	8.6	6.3	10.5		49.4	35.4	Garcia Alba et al. (2012)
Microcystis viridis	340	30	Na_2CO_3 (5%)	63.3	7.6	7.1	19.7	2.3	33	31	Yang et al. (2004)
Nannochloropsis	350	60		68.1	8.8	4.1	18.9[b]	0	35	34.5	Biller and Ross (2011)
Nannochloropsis sp.	350	60		76	10.3	3.9	9.0	0.89	43	39.0	Brown et al. (2010)
Porphyridium	350	60	Na_2CO_3[a]	46.1	5.6	3.2	13.3[b]	0.2	27.1	22.8	Biller and Ross (2011)
Scenedesmus dimorphous	350	60		73	8.2	5.7	12.6[b]	0.5	27.1	33.6	Biller et al. (2012)
Spirulina	350	60		73.3	9.2	7	10.4	0	29	36.8	Biller and Ross (2011)
Spirulina platensis	300	60		72.7	8.8	6.3	11.5[b]	0.6	35.5	36.1	Biller et al. (2012)
Spirulina platensis	350	60		73.73	8.9	6.3	10.17[b]	0.9	39.9	35.27	Jena et al. (2011)

[a] With Na_2CO_3 (1 mol L^{-1}).
[b] By difference.

liquefaction reactions. The operating conditions of microalgae liquefaction in some studies are summarized in Table 2. Microalgae have high water content (80–90 wt%). Because of wet feedstocks utilized in liquefaction, there is no need to dry feedstocks in this technology and it is particularly suitable for high moisture feedstocks (Jena and Das, 2011). Microalgae are excellent feedstocks for liquefaction since their sizes are small; this enhances rapid thermal transfer up to the required processing temperature (Lam and Lee, 2012).

The critical temperature and pressure of water are 374 °C and 22.1 MPa, respectively. When water approaches its critical point, there are significant changes in its properties such as solubility, density, dielectric constant, and reactivity, and hot compressed water becomes a highly reactive medium (Jena et al., 2011). Water at sub-critical conditions becomes an effective solvent but is significantly less corrosive than other chemical solvents. When microalgae are in hot compressed water, lipids, proteins, and carbohydrates in the materials will undergo hydrolysis (or depolymerization) and repolymerization, thereby transforming the biomass into bio-oil (or biocrude), gas, and solid compounds. The entire liquefaction process in hot compressed water is the reaction competition between hydrolysis and repolymerization (Barreiro et al., 2013). At the early liquefaction stage, hydrolysis is the dominant mechanism and microalgae are depolymerized into small compounds. Thereafter, the highly reactive small compounds polymerize and form bio-oil, gas, and solid compounds.

3.2. Products of liquefaction

Liquefaction can provide a higher amount of oil product relative to other methods. Bio-oils are the main products; gaseous, aqueous, and solid bi-products are also obtained from the conversion (Yang et al., 2004). For the separation procedure, after a liquefaction reaction is finished in an autoclave, it is cooled down to room temperature and the produced gas is emitted or collected for analysis. The reaction mixture is treated by a solvent such as chloroform (Garcia Alba et al., 2012) or dichloromethane (Biller and Ross, 2011). Then, the bio-oil contained in the mixture is extracted and recovered by evaporating the solvent. The aqueous phase and insoluble solid residue are separated by filtration. A schematic of liquefaction products and separation procedure is show in Fig. 2.

3.2.1. Bio-oil

Bio-oils are a dark, viscous, and energy-dense liquid. Bio-oil yields from a number of microalgae were 5–25 wt% higher than the lipid content in the biomass (Biller and Ross, 2011), suggesting that bio-oils are produced not only from lipids in microalgae but also from proteins and carbohydrates. The bio-oil yield depends on biochemical composition, and the yields from the substituents are ranked as: lipids > proteins > carbohydrates. The major constituents of bio-oil comprise phenol and its alkylated derivatives, heterocyclic N-containing compounds, long-chain fatty acids, alkanes and alkenes, and derivatives of phytol and cholesterol (Brown et al., 2010). Proteins produce large amounts of nitrogen heterocycles, pyrroles, and indoles; carbohydrates produce cyclic ketones as well as phenols, while lipids are converted to fatty acids (Biller and Ross, 2011).

The physical and chemical properties of bio-oil appear to depend strongly on feedstock and operating conditions. The bio-oil yield and HHV are typically in the ranges of 30–65 wt% and 30–50 MJ kg^{-1} (Table 2), and the HHV is comparable to that of petroleum fuel oil (around 43 MJ kg^{-1}) (Brown et al., 2010). Consequently, bio-oils from liquefaction can be used as fuels to be burned. Compared to raw microalgae, bio-oils have significantly lower elemental O. For example, the weight percentages of elemental O in *Dunaliella tertiolecta* and its bio-oil from liquefaction (360 °C, 50 min) are 53.02 and 25.08 wt%, respectively (Shuping et al., 2010). Compared to petroleum crude oil, however, bio-oils have higher O content. By virtue of partial bio-oils generated from proteins in microalgae, high content of N is contained in bio-oils, ranging from 5 to 9 wt%. The S content in bio-oils is usually less than 1 wt% (Brown et al., 2010), which is relatively lower than the sulfur content in some fossil fuels in that it is normally in the range of 0.05–5.0% (Jena and Das, 2011).

3.2.2. Gaseous, aqueous, and solid bi-products

The gas products of liquefaction include CO_2, H_2, CH_4, N_2, C_2H_4, C_2H_6, and so forth (Brown et al., 2010). CO_2 is the most abundant gas; the concentrations of H_2 and CH_4 may be high (Brown et al., 2010), whereas the concentrations of C_2H_4 and C_2H_6 are low. Very little CO could be detected in the product gas, suggesting that the generated CO is consumed, perhaps in the water gas shift and/or methanation reactions (Brown et al., 2010). The low amount of CO also indicates that deoxygenation occurs mainly via decarboxylation rather than by decarbonylation (Garcia Alba et al., 2012). The CH_4 concentration is higher at higher liquefaction temperatures, perhaps resulting from the intensified methanation reaction (Yang et al., 2004).

The aqueous phase is rich in nutrients such as nitrogen (e.g., NH_4^+) and phosphorous (e.g., PO_4^{3-}), metallic cations such as Ca^{2+},

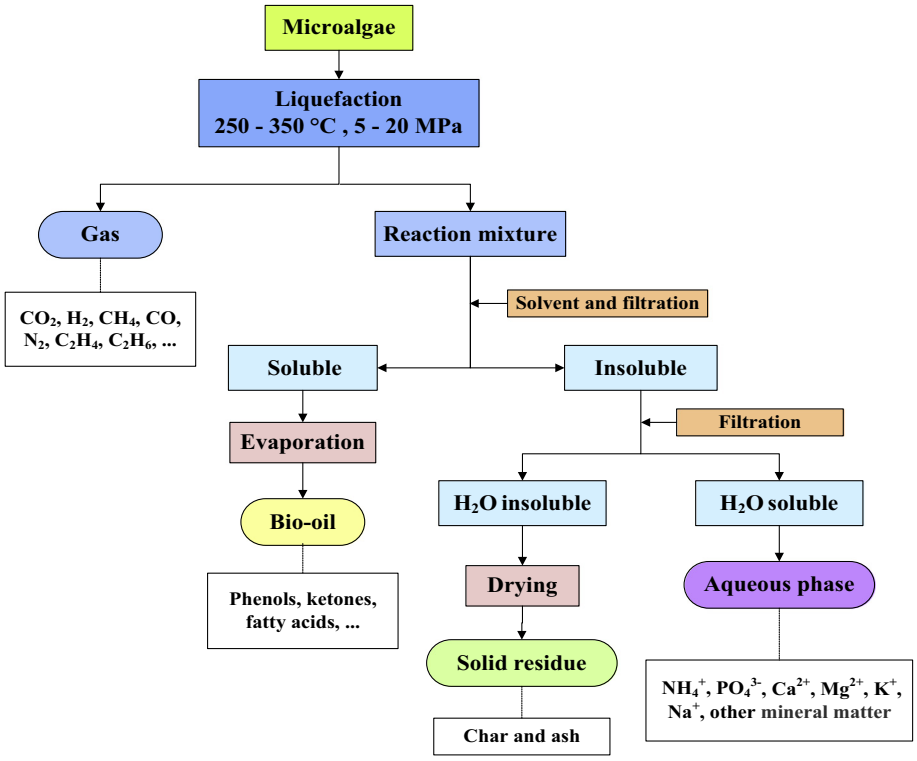

Fig. 2. A schematic of microalgae liquefaction.

Mg^{2+}, K^{+}, Na^{+}, and other mineral matter (Barreiro et al., 2013). Therefore, the aqueous phase can potentially be recycled for microalgae cultivation (Biller et al., 2012). High contents of organic C are also retained in the aqueous phase; this may be suitable for carbon source of heterotrophic strains. However, the large amount of organic C in the aqueous phase represents the reduction in carbon efficiency and bio-oil yield. Low-concentration glucose can be found at the liquefaction temperature of 200 °C; however, it was not presented at higher temperatures.

The solid bi-products from liquefaction contain ash and char. The weight percentages of C, H, N, and S in the solid residues from the liquefaction of *S. platensis* at 350 °C with holding times of 0–120 min were in the ranges of 8.81–11.82 wt%, 1.4–1.81 wt%, 1.32–1.41 wt%, and 0.61–0.71 wt%, respectively (Jena et al., 2011). After *Microcystis viridis* underwent liquefaction, the weight of residual solid was less than 5 wt% of the original microalga, and the elemental analysis of the residual solid indicated that its energy yield ranged from 0.8% to 5.2% (Yang et al., 2004). These evidences suggest that the energy content in the solid residues was low. Nevertheless, the some nutrients may be retained in the solid residues, making them as potential soil amendments (Barreiro et al., 2013).

3.3. Influence of operating conditions

The microalgae conversion is a function of operating conditions. The important variables affecting liquefaction performance include reaction temperature, holding time, feedstock load, and the presence of catalysts.

3.3.1. Temperature

Temperature plays a pivotal role in determining liquefaction performance. At subcritical conditions, an increase in reaction temperature tends to increase the bio-oil yield (Jena et al., 2011). The main constituents in bio-oil are derived mostly from the liquefaction of lipids and algaenans when microalgae ares treated at lower temperatures (<250 °C), whereas higher temperatures (300–375 °C) promote the conversions of carbohydrates and proteins (Barreiro et al., 2013). Increasing temperature decreases O and H contents in bio-oils, but increases C content and HHV (Brown et al., 2010; Garcia Alba et al., 2012). As a consequence, the H/C and O/C ratios of bio-oil decrease with increasing temperature (Brown et al., 2010). The N content in bio-oil increases with temperature, likely due to the more protein conversion at high temperatures (Garcia Alba et al., 2012). The gas yield and the mole fractions of hydrocarbons (CH_4 and C_2) in the product gas increase as the temperature increases (Brown et al., 2010; Jena et al., 2011), but the mole fractions of CO_2 and N_2 decrease. On account of higher conversions of organics into liquid and gas products at higher temperatures, there is a drop in solid residues yield when the temperature increases (Jena et al., 2011). A higher temperature also results in a decrease in the yield of water solubles, revealing the conversions of intermediate water soluble products into gases and bio-oils.

3.3.2. Holding time

The holding time is defined as the duration of the temperature maintained for liquefaction, disregarding the transient heating and cooling periods. The holding time is generally controlled within 60 min (Barreiro et al., 2013), but sometimes is as long as 120 min. The study of Jena et al. (2011) revealed that the bio-oil yield at 350 °C increased with increasing holding time until 60 min, but decreased with further increasing the time. This decrease was likely attributed to the conversion of lighter hydrocarbon compounds in the bio-oil into gaseous products. Therefore, there might exist an optimal holding time for maximizing bio-oil yield at a certain temperature. On the contrary, the gas yield increased when the holding time increased from 60 to 120 min. They found that there was no significant change in solids residue yield, but the yield of water-solubles decreased as the holding time increased from 0 to 120 min. Consequently, the reaction temperature and holding time should be simultaneously considered in

liquefaction. Normally, a higher temperature accompanied by a shorter holding time may get a higher bio-oil yield. For example, in the study of Garcia Alba et al. (2012), a maximum bio-oil yield of 49.4 wt% was exhibited from the liquefaction of *Desmodesmus* sp. at 375 °C for 5 min. On the other hand, at the liquefaction temperatures of 200 and 300 °C, the longer the holding time, the higher the bio-oil yield, revealing that there might exist an optimal combination of temperature and holding time for maximizing bio-oil yield.

3.3.3. Feedstock load

The mass fraction of microalgal biomass in a slurry is also a factor affecting liquefaction performance, but its influence is not as significant as the reaction temperature and holding time except at low mass fractions. For example, the bio-oil yield from the liquefaction of *S. platensis* increased from 32.5 to 39.9 wt% when the solid load increased from 10 to 20 wt% (Jena et al., 2011). However, the yield remained more or less constant when the solid load increased from 20 to 50 wt%. The yield of water solubles dropped from 44.6 to 30.9 wt% for the solid load increasing from 10 to 50 wt%. For the solid loads of 10–50 wt%, the gases and solid residues yields were not markedly affected by the load in that they were in the ranges of 18.0–19.4 wt% and 5.4–7.0 wt%, respectively.

3.3.4. Catalysts

Both alkali salts and metals can be employed as catalysts in the liquefaction technology, and they are called homogenous and heterogeneous catalysts, respectively. Sodium carbonate (Na_2CO_3) is the most commonly used homogenous catalyst for microalgae liquefaction. The liquefaction of *M. viridis* with Na_2CO_3 addition (5 wt%) and 30 min holding time significantly enhanced bio-oil yield (Yang et al., 2004). Similar results were observed for the conversion of carbohydrates into bio-oil using Na_2CO_3 as a catalyst (Biller and Ross, 2011); however, proteins and lipids were converted to bio-oil most efficiently without the use of catalysts. The addition of Na_2CO_3 may increase (Biller and Ross, 2011) or decrease (Yang et al., 2004) the residual solid, perhaps due to different feedstocks adopted.

As a whole, the addition of heterogeneous catalysts in the slurry is able to increase the bio-oil yield and HHV and reduce its O content. The presence of Co/Mo/Al_2O_3, Pt/Al_2O_3, and Ni/Al_2O_3 catalysts during the liquefaction of *Chlorella vulgaris* and *Nannochloropsis occulta* appeared to reduce O content in bio-oil and increase its HHV, resulting from the de-oxygenation reaction by the catalysts (Biller et al., 2011). The liquefaction of *Nannochloropsis* sp. at 350 °C in the presence of six different catalysts of Pd/C, Pt/C, Ru/C, Ni/SiO_2-Al_2O_3, CoMo/γ-Al_2O_3, and zeolite and in the absence of H_2 addition showed that all the catalysts led to higher bio-oil yields, but the elemental composition and HHV of the bio-oils were insensitive to the catalysts (Duan and Savage, 2011). The bio-oil properties were insensitive to the catalysts might be due to the equivalent extent of de-oxygenation or hydrodeoxygenation reactions by the catalysts during liquefaction.

4. Pyrolysis

4.1. Principle of pyrolysis

In pyrolysis, microalgae are heated and thermally decomposed in the absence of oxygen or air; the pressure in the reactor is normally one atmosphere and the temperature is usually between 400 and 600 °C. The reaction temperature may be as high as 800 °C when microwave pyrolysis is performed, and as low as 300 °C when catalytic pyrolysis is carried out. Microalgae are feasible feedstocks for pyrolysis because bio-oils produced from microalgae are more stable than those from lignocellulosic biomass (Suali and Sarbatly, 2012). The major products from pyrolysis are made up of bio-oils, chars, and non-condensable gases, and their relative amounts depend on operating conditions, microalgae properties, and reaction type. Chars are the major product from the thermal decomposition of microalgae at lower pyrolysis temperatures (Akhtar and Saidina Amin, 2012). Moderate temperatures of 400–550 °C with short residence times (2–3s) favor liquid production. The gas product increases when the pyrolysis temperature goes up.

Bio-oils from the pyrolysis of lignocellulosic biomass are complex, unstable, and viscous; they contain solids and chemically dissolved water, and have high O content (Brennan and Owende, 2010). The bio-oils contain hundreds of chemical compounds, including aldehydes, cresols, and acids. Therefore, upgrading bio-oils through hydrogenation and cracking is required to facilitate their utilization (Liang, 2013; Harman-Ware et al., 2013; Brennan and Owende, 2010; Bridgwater, 2012; Mohan et al., 2006). In contrast, bio-oils produced from microalgae pyrolysis contain different types and amounts of compounds such as linear hydrocarbons and nitrogenous species, resulting from the pyrolysis of lipids and proteins, respectively (Harman-Ware et al., 2013). Kim et al. (2014) compared the bio-oil produced from the pyrolysis of microalga *Scenedesmus* sp. to that from Jatropha seedshell cake, and concluded that the former was characterized by higher H/C and O/C molar ratios due to compositional difference. The pyrolytic oils of microalgae showed high yield of fatty oxygenates and nitrogenous compounds due to high contents of lipids and proteins. The bio-oils were also featured by high concentrations of aliphatic compounds, fatty acid alkyl ester, alcohols, and nitriles. These differences from lignocellulosic biomass may lead to improved properties in the resulting bio-oils from microalgae, such as HHV and reduced tar formation.

4.2. Classification of pyrolysis

Depending on the heating rate, the presence of catalysts, and/or heating route, microalgae pyrolysis can be categorized into four modes: (1) slow pyrolysis, (2) fast pyrolysis, (3) catalytic pyrolysis, and (4) microwave pyrolysis. Two different types of reactor with one the fixed-bed reactor and the other the fluidized-bed reactor are frequently employed. Fixed-bed reactors have been widely used in slow, catalytic, and microwave pyrolyses; fluidized-bed reactors are commonly used for fast pyrolysis. The combination of pyrolysis modes and reactors is given in Fig. 3, while a number of studies concerning pyrolysis operations and bio-oil yields are tabulated in Table 3.

4.2.1. Slow pyrolysis

According to the heating rate, microalgae pyrolysis can be divided into slow and fast pyrolyses. Slow pyrolysis is characterized by a low heating rate (5–10 °C min^{-1}) and a long residence time of hot vapor (10–30 s), whereas fast pyrolysis is featured by a high heating rate (10–600 °C s^{-1}) and a short residence time of hot vapor (1–3 s) (Liang, 2013; Suali and Sarbatly, 2012; Miao et al., 2004; Demirbas, 2006). Due to the low heating rate, the reaction rate of microalgae in slow pyrolysis is slow. In contrast to fast pyrolysis, a longer residence time of hot vapor in slow pyrolysis results in larger portions of char and non-condensable gas in the products. For example, Jena and Das (2011) studied the slow pyrolysis of *S. platensis* and found that bio-oil and solid residue yields were in the ranges of 23–29 wt% and 28–40 wt%, respectively. The bio-oil yield from the slow pyrolysis of microalgae typically ranges from 23 to 43 wt%; the HHV and pH value of the bio-oil are between 24 and 34 MJ kg^{-1} as well as 9 and 10, respectively (Grierson et al., 2009; Jena and Das, 2011). Grierson et al. (2009) examined the properties of bio-oil derived from the slow pyrolysis

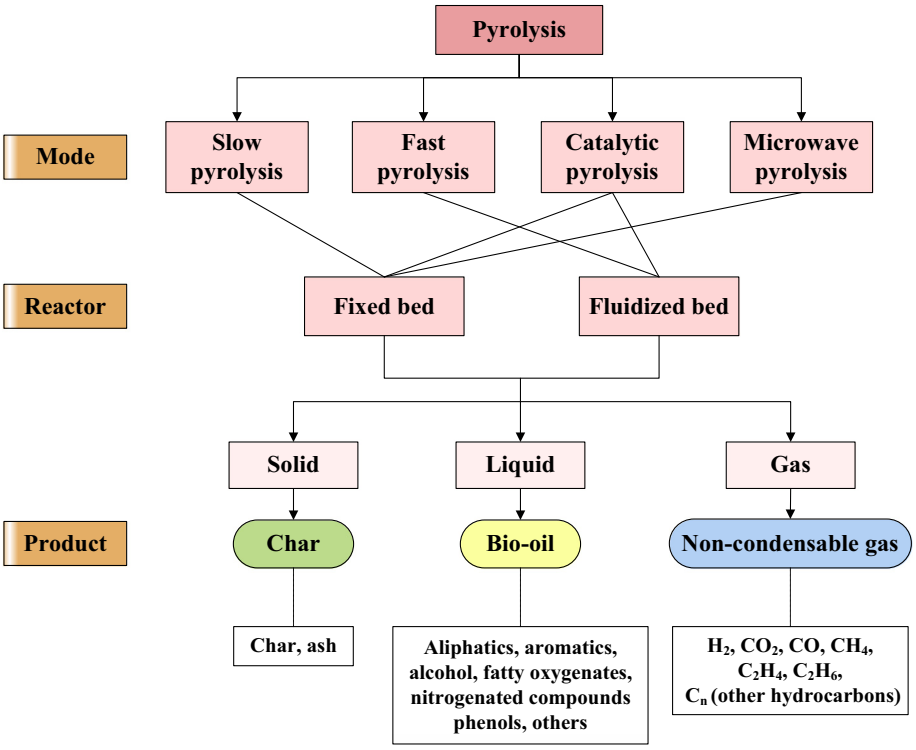

Fig. 3. A schematic of microalgae pyrolysis.

of *Tetraselmis chui* and found that the components in the bio-oil had fatty acids, alkanes, alkenes, amides, aldehydes, terpenes, pyrrolidinines, phytol, and phenols. The HHV of produced char from slow pyrolysis is between around 14 and 26 MJ kg^{-1} (Grierson et al., 2009; Jena and Das, 2011). In the produced non-condensable gas, the main gaseous species include CO_2, H_2, CH_4, C_2H_4, and C_2H_6, and the calorific value of the product gas is between 1.2 and 4.8 MJ kg^{-1} (Grierson et al., 2009). In view of low calorific value of the non-condensable gas, its application in industry is limited. In light of the aforementioned literature, the heating values of the products are ranked as: bio-oil > char > non-condensable gas. The reaction temperature is also an important factor in affecting the performance of slow pyrolysis. The study of Demirbas (2006) revealed that the bio-oil yield from the slow pyrolysis of microalgae increased with temperature until approximately 500 °C. Thereafter, the yield decreased when the temperature was further increased.

4.2.2. Fast pyrolysis

Slow pyrolysis is usually operated in a discontinuous process, resulting in viscous bio-oil products. The longer residence time of hot vapor means more energy input required. Fast pyrolysis is carried out at a high heating rate accompanied by a short residence time of hot vapor to achieve a higher reaction rate and a higher bio-oil yield. Therefore, fast pyrolysis has received more attention lately for bio-oil production. The yield and HHV of bio-oil from the fast pyrolysis of microalgae are in the ranges of 18–72 wt% (Kim et al., 2014; Belotti et al., 2014; Miao and Wu, 2004; Miao et al., 2004) and 24–41 MJ kg^{-1} (Wang et al., 2013; Miao and Wu, 2004; Miao et al., 2004), respectively.

Miao et al. (2004) pointed out that the bio-oils from the fast pyrolysis of microalgae have higher calorific values and lower O contents when compared to the bio-oils from wood. The lower O content makes the microalgae derived bio-oils have better storage stability than the wood derived bio-oils. Harman-Ware et al. (2013) examined the bio-oil from the fast pyrolysis of *Scenedesmus* sp. in a bench-scale spouted (fluidized) bed operated at 480 °C with the vapor residence time of 2 s, and showed that the weight ratio of bio-oil and char was 3.76, and the average total acid number (68 mg KOH g^{-1}) of the bio-oil was lower than the bio-oil produced from wood pyrolysis. For microalgae as feedstocks of fast pyrolysis, the study of Miao and Wu (2004) illustrated that the bio-oil yield (57.9%) from heterotrophic *Chlorella protothecoides* cells was 3.4 times higher than that from autotrophic cells, and the bio-oil was characterized by a much lower O content, a higher heating value (41 MJ kg^{-1}), a lower density (0.92 kg l^{-1}), and lower viscosity (0.02 Pa s) compared to those of bio-oils from autotrophic cells and wood. Accordingly, heterotrophic microalgae might be better than autotrophic ones as feedstocks for fast pyrolysis.

4.2.3. Catalytic pyrolysis

Microalgal biomass pyrolyzed in the presence of catalyst is termed catalytic pyrolysis. Catalytic pyrolysis is usually operated at temperatures of 300–600 °C and catalyst-to-biomass mass ratios of 0.2–5 (Pan et al., 2010; Babich et al., 2011; Du et al., 2013). The yield and HHV of bio-oil produced from catalytic pyrolysis are approximately in the ranges of 20–33 MJ kg^{-1} and 19–40 wt% (Babich et al., 2011; Pan et al., 2010). The oxygen content in microalgae derived bio-oils is still high, the oils thus need to be improved to enhance their stability, prevent polymerization and condensation reactions, and increase energy density (Liang, 2013). Recent studies have suggested that catalytic pyrolysis is an appropriate method to improve the bio-oils produced from microalgae pyrolysis; that is, higher oil yields with less oxygenic compounds can be achieved in catalytic pyrolysis (Suali and Sarbatly, 2012). For example, the study of Pan et al. (2010) indicated that the bio-oil from the catalytic pyrolysis of *Nannochloropsis* sp. residue had a lower O content (19.5 wt%) and a higher heating value

Table 3
A list of operating modes and conditions of microalgae pyrolysis and bio-oil yield.

Feedstock	Pyrolysis mode	Reactor	Operating condition				Bio-oil yield (wt%)	References
			Temp. (°C)	Heating rate (°C min^{-1})	Sweep gas flow rate (mL min^{-1})	Duration (min)		
Chaetocerous muelleri	Slow	Fixed bed	500	10	100	20	33	Grierson et al. (2009)
Chlorella like	Slow	Fixed bed	500	10	100	20	41	Grierson et al. (2009)
Chlorella vulgaris	Slow	Fixed bed	500	10	100	20	41	Grierson et al. (2009)
Dunaliella tertiolecta	Slow	Fixed bed	500	10	100	20	24	Grierson et al. (2009)
Tetraselmis chui	Slow	Fixed bed	500	10	100	20	43	Grierson et al. (2009)
Nannochloropsis sp.(res)	Slow	Fixed bed	300–500	10	30	120	21–31	Pan et al. (2010)
Synechococcus	Slow	Fixed bed	500	10	100	20	38	Grierson et al. (2009)
Spirulina platensis	Slow	Fixed bed	350–500	3.5–7	250	60	23–29	Jena and Das (2011)
C. prototthecoides	Fast	Fluidized bed	500	36,000	6667		58	Miao and Wu (2004)
C. prototthecoides	Fast	Fluidized bed	500	36,000	6667		18	Miao et al. (2004)
C. vulgaris	Fast		400–700				58–72	Belotti et al. (2014)
C. vulgaris (res)	Fast	Fluidized bed	500				53	Wang et al. (2013)
M. aeruginosa	Fast	Fluidized bed	500	36,000	6667		24	Miao et al. (2004)
Scenedesmus sp.	Fast	Fluidized bed	440		33,000		22	Kim et al. (2014)
Scenedesmus sp.	Fast	Fluidized bed	480				55	Harman-Ware et al. (2013)
Chlorella	Catalytic (Na_2CO_3)	Fixed bed	300–450	100–150		30	35–55	Babich et al. (2011)
Chlorella	Catalytic (ZSM-5) [a]		500		250		29–36	Campanella and Harold (2012)
Nannochloropsis sp.(res)	Catalytic (HZSM-5)	Fixed bed	400	10	30	120	21–25	Pan et al. (2010)
Chlorella sp.	Microwave [b]	Fixed bed	433–644		500	20	18–27	Du et al. (2011)
Chlorella sp.	Microwave [c]	Fixed bed	650–800		300	20	21–36	Hu et al. (2012)
Chlorella vulgaris	Microwave	Fixed bed	450–550			30	41–57	Borges et al. (2014)
Nannochloropsis	Microwave	Fixed bed	450–550			30	41–59	Borges et al. (2014)

[a] Four exchanged ZSM-5 catalysts (H-, Fe-, Cu-, and Ni-ZSM-5).
[b] Microwave reactor power: 500, 750, 1000, 1250 W.
[c] Microwave reactor power: 1500, 2250 W.

(32.7 MJ kg^{-1}) than that from the direct pyrolysis of the residue which had an O content of 30.1 wt% and a heating value of 24.6 MJ kg^{-1}. Du et al. (2013) used HZSM-5 as a catalyst and found that an increase in catalyst-to-biomass ratio from 1:1 to 5:1 significantly improved the aromatic yields. Another advantage of catalytic pyrolysis is that catalysts used for pyrolysis can be recycled to the reactor (Babich et al., 2011).

The common catalysts used for microalgae pyrolysis include Na_2CO_3 and ZSM-5-based zeolites such as H-ZSM-5, Fe-ZSM-5 Cu-ZSM-5 and Ni-ZSM-5. Babich et al. (2011) investigated the pyrolysis of *Chlorella* in the presence/absence of Na_2CO_3, and found that the gas yield from the catalytic pyrolysis increased when compared with the non-catalytic pyrolysis at the same temperature, whereas the liquid yield decreased. It was also discovered that an energy recovery of bio-oil of approximately 40% could be achieved under catalytic pyrolysis using Na_2CO_3. Campanella and Harold (2012) investigated the non-catalytic and catalytic pyrolyses of microalgae where five different catalysts of ZSM-5, H-ZSM-5, Fe-ZSM-5, Cu-ZSM-5, and Ni-ZSM-5 were used in the catalytic pyrolysis. The bio-oil yield from the catalytic pyrolysis of *Chlorella* sp. was 43–51 wt%. A comparison of four exchanged ZSM-5 catalysts (i.e., H-, Fe-, Cu-, and Ni-ZSM-5) indicated that the HZSM-5 provided the largest enhancement of the bio-oil yield and composition among the catalysts. HZSM-5 increased the yield of the hydrocarbon fraction in the organic phase from 21 wt% to 43 wt% and exhibited the least coking (1.3 wt%), whereas Fe-ZSM-5 produced the most coke (2.2 wt%). In summary, the bio-oil from catalytic pyrolysis had a higher heating value, higher aromatics, and lower acidity, implying that better quality bio-oil could be produced from catalytic pyrolysis.

4.2.4. Microwave pyrolysis

Microalgae pyrolysis performed with microwave-assisted heating is spoken of as microwave pyrolysis. Microwave-assisted heating has been widely used in industrial processes. However, only a few studies of microalgae pyrolysis with microwave-assisted heating have been reported (Du et al., 2011; Hu et al., 2012; Borges et al., 2014). Microwave pyrolysis is usually operated at temperatures of 500–800 °C, supplied powers of 500–2250 W, and absorber contents of 5–30 wt%. The yield and HHV of produced bio-oils from microwave pyrolysis are in the ranges of 18–59 wt% and 30–42 MJ kg^{-1}, respectively.

When materials certain dielectrics such as Fe_3O_4, CuO, water, and fat are in a microwave environment, they are heated through a process named dielectric heating (Chen and Lin, 2010). The advantages of microwave pyrolysis over traditional heating routes include rapid heating, uniform internal heating of feedstock, instantaneous response for rapid start-up and shut down, no need for agitation via fluidization, and hence fewer particles (ashes) in the produced bio-oil (Du et al., 2011; Borges et al., 2014). In a microwave pyrolysis system, microwave absorbers such as activated carbon, chars, SiC, metallic oxides, ionic liquids, and sulfuric acid are usually blended with microalgae to improve bio-oil yield or quality (Salema and Ani, 2012).

Du et al. (2011) studied the pyrolysis of *Chlorella* sp. in a microwave oven using char as a microwave absorber. The maximum bio-oil yield of 28.6 wt% was obtained at the microwave power of 750 W. The bio-oil was characterized by low O content with aliphatic and aromatic hydrocarbons, and the non-condensable gas comprised H_2, CO, CO_2, and gaseous hydrocarbons. Hu et al. (2012) studied the microwave pyrolysis of *C. vulgaris* under various microwave powers (i.e., 750, 1500, and 2250 W), catalysts (i.e., activated carbon, CaO, SiC, and solid residue), and catalyst contents (5, 10, 20, and 30 wt%). The maximum bio-oil yield (39 wt%) and gas yield (52 wt%) developed at the powers of 1500 and 2250 W, respectively, where the temperatures were 650 and 800 °C, respectively. The higher the microwave power, the higher the maximum temperature rising rate and pyrolysis temperature. A high microwave power and catalyst would enhance gas production. Activated carbon was the best catalyst among the tested materials, and its optimal content was 5 wt% where the maximum bio-fuel yield was 87.47 wt%. Borges et al. (2014) examined the microwave pyrolyses of *Chlorella* sp. and *Nannochloropsis* sp. in the presences of SiC and HZSM-5, and the effects of temperature and catalyst-to-biomass mass ratio on the liquid products were analyzed. For *Chlorella* sp., the maximum bio-oil yield of 57 wt% was exhibited at 550 °C without addition of the catalyst (HZSM-5). For *Nannochloropsis* sp., the maximum bio-oil yield of 59 wt% was obtained at 500 °C along with the catalyst-to-biomass mass ratio of 0.5. The catalyst HZSM-5 tended to produce water in the bio-oil and reduced its HHV. Nevertheless, the catalyst also reduced the number of species in the bio-oil, implying that the bio-oil quality was improved. The elemental analysis and HHV of bio-oils from microalgae pyrolysis are given in Table 4.

Table 4
A list of elemental analysis and HHV of bio-oils from microalgae pyrolysis.

Feedstock	Pyrolysis mode	Elemental analysis (wt%)					HHV (MJ kg^{-1})	References
		C	H	N	O	S		
Spirulina platensis	Slow[a]	67.52	9.82	10.71	11.34	0.45	29.30	Jena and Das (2011)
Spirulina platensis	Slow[b]	74.66	10.57	7.13	6.81	0.81	33.62	Jena and Das (2011)
C. prototheocoides[c]	Fast	76.22	11.61	0.93	11.24		41	Miao and Wu (2004)
C. prototheocoides[d]	Fast	62.07	8.76	9.83	19.43		30	Miao and Wu (2004)
C. vulgaris	Fast	59.5	4.6	8.0	24.9		27.9	Belotti et al. (2014)
C. vulgaris (res)	Fast	51.4	8.34	12.8	27.46		24.57	Wang et al. (2013)
M. aeruginosa	Fast	60.99	8.23	9.83	10.95		29	Miao et al. (2004)
Scenedesmus sp.	Fast	62.6	8.77	8.8	22.5	<0.1	29.6	Kim et al. (2014)
Nannochloropsis sp.(res)	Catalytic (HZSM-5)	65.21	9.83	5.43	19.53		32. 2[g]	Pan et al. (2010)
Chlorella sp.	Microwave	65.4	7.84	10.28	16.48[f]		30.7[g]	Du et al. (2011)
Chlorella sp.	Microwave	65.70	9.34	8.34	15.78		32.37[g]	Borges et al. (2014)
Chlorella sp.	Microwave[e]	59.27	7.75	9.46	23.52		32.37[g]	Borges et al. (2014))
Nannochloropsis	Microwave	81.64	8.20	5.24	4.90		42.00[g]	Borges et al. (2014)
Nannochloropsis	Microwave[e]	59.75	6.75	16.34	17.16		27.15[g]	Borges et al. (2014)

[a] Pyrolysis at 350 °C.
[b] Pyrolysis at 500 °C.
[c] Autotrophic *C. prototheocoides*.
[d] Heterotrophic *C. prototheocoides*.
[e] With HZSM-5.
[f] By difference.
[g] HHV (MJ kg^{-1}) = $(3.55C^2 - 232C - 2230H + 51.2C \times H + 131\,N + 20{,}600) \times 10^{-3}$ (Pan et al., 2010; Du et al., 2011; Borges et al., 2014).

A comparison between Table 2 and Table 4 suggests that the carbon content and HHV of bio-oil from HTL are usually higher than those from pyrolysis. The study of Jena and Das (2011) indicated that the viscosity of bio-oil from the HTL of *S. platensis* at 350 °C was higher than that from the pyrolysis of the microalga at the same temperature. Moreover, the bio-oil color from the former was black, while it was reddish from the latter. In other words, the bio-oil color from the HTL of *S. platensis* was darker than that from the pyrolysis of the microalga.

5. Gasification

5.1. Principle of gasification

In gasification, carbonaceous materials in microalgae are converted into H_2, CO, CH_4, and other combustible gases in an environment of insufficient oxidizer. Seeing that the nature of microalgae is different from that of lignocellulosic biomass, the gasification technology of microalgae can be partitioned into two branches: (1) conventional gasification and (2) supercritical water gasification (SCWG), as shown in Fig. 4. The conventional gasification of biomass has been commercialized, but has a lower thermal efficiency, especially for wet biomass (Haiduc et al., 2009). SCWG has a higher thermal efficiency, but the commercial techniques are still under developed.

5.2. Conventional gasification

In conventional gasification, dry microalgae react with oxidizer, such as air, oxygen, and water or steam, in a partial oxidation environment at temperature range of 800–1000 °C and pressure range of 1–10 bar (Khoo et al., 2013). In the entire reaction process, microalgae undergo several different reactions in a gasifier, including dehydration or drying, devolatilization or pyrolysis, combustion or oxidation, and gasification or reduction; the homogeneous water gas shift and methanation reactions as well as heterogeneous water gas and Boudouard reactions are also involved (Yang et al., 2004).

Up to now, only a few studies were reported concerning conventional gasification or co-gasification of microalgae with coal. In the study of Hirano et al. (1998), *Spirulina* was continuously supplied as a water-slurry (0.25 g min^{-1}) into a reactor and partially oxidized by O_2 (0.39 ml min^{-1}) where the temperature was between 850 and 1000 °C. The main gaseous species in the product gas were H_2, CO, CO_2, and CH_4; small amounts of C_2H_4, N_2, and O_2 were also detected, but hydrocarbons such as C_2H_6, C_3H_6, and C_3H_8 were not detected. The H_2 concentration increased with increasing temperature, whereas the CO, CO_2, and CH_4 concentrations decreased. The carbon conversion of the microalga increased from 93% at 850 °C to nearly 100% at 1000 °C. Khoo et al. (2013) carried out the gasification of *Nannochloropsis* sp. in a fixed-bed reactor at 850 °C. Their results suggested that the weight percentages of char, bio-oil, and gas were 58.18, 13.74, and 28.08 wt%, respectively, and their HHVs were 17.5, 34.1, and 32.9 MJ kg^{-1}, respectively. Sanchez-Silva et al. (2013) performed the gasification of *Nannochloropsis gaditana* using a thermogravimetric analyzer where steam was used an oxidizer. The main gas species during gasification were CO_2, CO, and H_2, indicating that oxidation reactions, water gas, and water gas shift reactions were predominant. An increases of water in the feed gas enhanced H_2 production and decreased CH_4 yield, indicating that water gas, water gas shift, and methane reforming reactions were intensified. On the other hand, CO and CO_2 emissions kept constant.

Yang et al. (2013) investigated the co-gasification of torrefied microalga (*S. platensis*) pellet and woody biomass (*Eucalyptus globulus*) pellet in a 30 kW bubbling fluidized bed reactor. When the mass ratio of the torrefied microalgal pellet increased, H_2, and CH_4 contents first decreased and then increased slightly, but CO and the lower heating value (LHV) of the product gas showed the contrary tendency. The high ash content in the microalgal pellet caused sintering and agglomeration during gasification which dominated the gasification products. This rendered different gasification phenomena from the woody biomass pellet. Alghurabie et al. (2013) performed the gasification of *Tetraselmis* sp. and co-gasification with a low-rank coal in a spouted, fluidized bed reactor at temperatures of 830–880 °C. The gasification of the microalga alone failed, due to the ash agglomeration and defluidization phenomena in the reactor. The co-gasification of *Tetraselmis* sp. (10 wt%) and the coal (90 wt%) had a trend to decrease H_2 and CO_2 with increasing temperature but increase CO. It follows that microalgae can be mixed with coal for co-gasification. However,

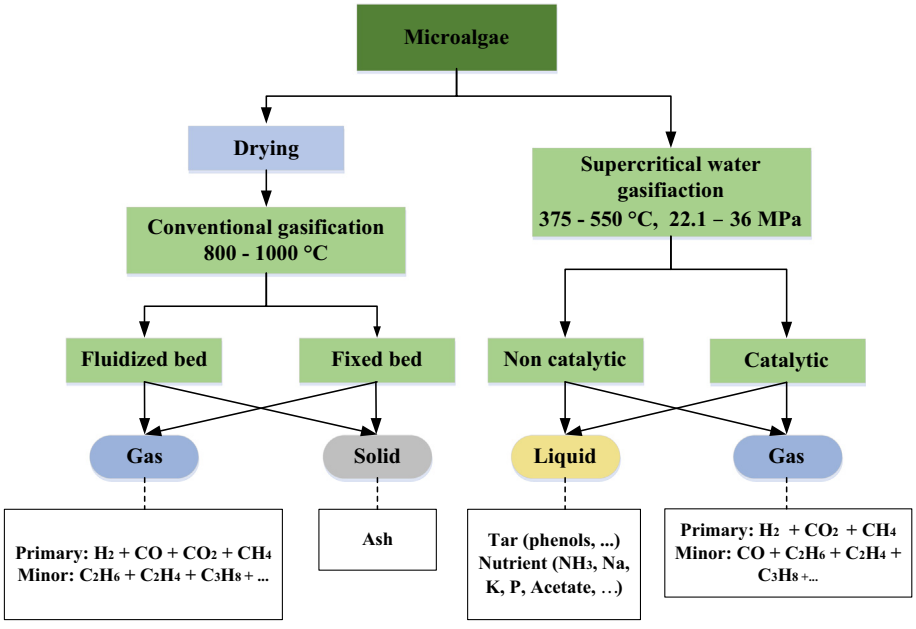

Fig. 4. A schematic of microalgae gasification.

Table 5
A list of operating conditions and performance of microalgae conventional gasification.

Microalgae	Operation conditions			Production		References
	Reactor	Temperature (°C)	Agent gas	Performance	Primarily gases composition (vol%)	
Nannochloropsis sp. residue	Fixed bed	850	Nitrogen, 650 ml min^{-1}	HHV of gases = 38.3 MJ/kg; 140% T.E.[a]	H_2, CO, CO_2, CH_4, totally 85%	Khoo et al. (2013)
Nannochloropsis gaditana	TGA[b]	850	Ar/steam, Ar: 200 ml min^{-1}		H_2 (46), CO (33), CO_2 (12), CH_4 (<5)	Sanchez-Silva et al. (2013)
Nannochloropsis oculata residue	Fixed bed	600–850	Steam	42–70% C.C.[c]	H_2 (40–52), CO (<6), CH_4 (~10), CO_2 (32–38)	Duman et al. (2014)
Spirulina platensis (torrefied pellet)	Fluidized bed	800	Air/steam	Syngas LHV = 5–8 MJ/kg	H_2 (20), CO (35), CO_2 (40), CH_4 (<4) (ER[e] = 0.4)	Yang et al. (2013)
Spirulina platensis[d] (torrefied pellet)	Fluidized bed	800	Air/steam	Higher MR[f] with higher CO, but fewer H_2	H_2 (19), CO (40), CO_2 (25), CH_4 (8) (ER = 0.4, MR = 7:3)	Yang et al. (2013)
Spirulina	Fluidized bed	850–1000	O_2: steam = 0.39 ml: 0.25 g (min^{-1})	93–103% C.C.	H_2 (35–48), CO (10–18), CO_2 (31–36), CH_4 (9–11)	Hirano et al. (1998)
Tetraselmis sp.[g]	Fluidized bed	820–885	Air/steam, air: 35 L min^{-1}		H_2 (9), CO (12), CO_2 (13), CH_4 (<2) (at 860 °C)	Alghurabie et al. (2013)

[a] Thermal efficiency (gases).
[b] Thermogravimetric analysis.
[c] Carbon conversion.
[d] Co-gasification with coal.
[e] Ratio of the desired air flow rate to the stoichiometric air flow rate for complete combustion.
[f] Mixing ratio of woody biomass and microalgal.
[g] Co-gasification with woody biomass.

high ash content microalgae should not be utilized to avoid ash agglomeration. The related studies of conventional microalgae gasification are summarized in Table 5.

5.3. Supercritical water gasification (SCWG)

Microalgae usually have high moisture contents. A drying process of microalgae (at least 90 wt% of dry mass) for conventional gasification requires much heating energy due to the high latent heat of water vaporization (Haiduc et al., 2009). In SCWG, microalgae are directly converted to gas product beyond the water critical point (374 °C and 22.1 MPa) without drying (Amin, 2009), the process is thus a promising method for gas fuel production using microalgae as feedstocks. Similar to liquefaction, SCWG also uses water as a reaction medium. Unlike the goal of liquefaction to preserve the C–C bonds for synthesizing liquid fuels within certain carbon ranges (i.e., C_4–C_{12} for gasoline and C_{10}–C_{15} for diesel), the aim of SCWG is to break C–C bonds to produce combustible gases such as CH_4 or H_2 (Yeh et al., 2012). The operating conditions and gas products from microalgae SCWG are given in Table 6.

5.3.1. Principle of SCWG

SCWG is typically operated at 400–500 °C (up to 700 °C) and 24–36 MPa in the absence/presence of catalysts. The dielectric constant, which is a measure of the solvent's polarity, decreases drastically in the supercritical region. This results in water behaving like a non-polar solvent and makes water be a suitable solvent for microalgae gasification. The residual organics content in the effluent is usually very low (reduction of organic carbon > 99%) (Haiduc et al., 2009). The process can be implemented with residence times of the order of minutes or even seconds for complete gasification of the organic matter; hence the reactor volumes can be reduced.

The components in the effluent contain gases, tar, aqueous phase, and solid residue. The major gaseous species are H_2, CO_2, and CH_4; lesser amounts of CO and C_2–C_4 compounds can also be found (Onwudili et al., 2013). In the aqueous phase, ammonium, sodium, potassium, phosphate, and acetate may be detected. Therefore, the recovered solution from SWCG can be used as nitrogen nutrient for microalgae cultivation, thereby reducing a part of energy consumption for the cultivation. The compounds in tar included phenols, alkyl benzenes, and polycyclic aromatic hydrocarbons. However, tar and char formation may be avoided from SCWG (Haiduc et al., 2009). In the residual solid, in addition to unreacted microalgae, some salts are also contained if catalytic SCWG is performed. For example, when NaOH is used for SCGW, both sodium carbonate and bicarbonate are found in the solid residues. The study of Minowa and Sawayama (1999) revealed that all nitrogen in *C. vulgaris* was converted to ammonia in the course of gasification, and the gas dissolved in the solution could be used as nitrogen nutrient.

5.3.2. Effects of operating parameters

In general, higher temperatures, longer holding times, and higher water densities in association with lower microalgae loads provide higher gas yields per unit weight of microalgae. Increasing temperature, time, and water density also increases the carbon yield and energy recovery.

Guan et al. (2012) studied *Nannochloropsis* sp. gasification at 450 °C and found that CO_2 was the most abundant product; at 550 °C the CH_4, CO_2, and H_2 yields were all about the same at the longer reaction times. The carbon yield went up with increasing temperature and time, and approached 60% at 550 °C when the reaction time was as long as around 80 min. The microalga load strongly affected the H_2 yield. For example, the H_2 yield at 500 °C was more than tripled when the load was reduced from 15 to 1 wt%. The gas composition was almost independent of water density, whereas the carbon yield was a strong function of water density, with a higher density leading to higher gas and carbon yields.

Catalysts, including homogeneous and heterogeneous catalysts, can be used in SCWG to accelerate microalgae reaction rates and control the ultimate product distribution. Alkali compounds, such as NaOH and KOH are the primary homogeneous catalysts and have been shown to be effective gasification catalysts. Watanabe et al. (2003) addressed that the H_2 yield from *n*-hexadecane (*n*-C_{16}) gasification with NaOH (at 400 °C, 15 min, and 0.35 g cm^{-3} of water density) was 4 times higher than that without the catalyst. The catalytic effect of NaOH was able to enhance the decomposition of intermediate (aldehyde and ketone) into CO. In fact, NaOH intensified not only the partial oxidation of *n*-C_{16} but also

Table 6
A list of operating conditions and performance of microalgae supercritical water gasification.

Microalgae	Operation conditions				Production		References
	Temperature (°C)	Pressure (MPa)	Catalyst	Microalgal loading	C.C. (%)	Primarily gases composition	
Chlorella vulgaris	350	18	Nickel	0.5–1 (g dry-cell/L)	35–70	H_2 (10–35), CO_2 (44–49), CH_4 (16–38) (vol%)	Minowa and Sawayama (1999)
Chlorella vulgaris	400–700	24	Ru/TiO_2	7.3 (wt%)	14–82	H_2 (7), CO (22), CO_2 (26), CH_4 (25) (mol%, at 600 °C)	Chakinala et al. (2010)
Chlorella vulgaris	500	36	NaOH; $Ni–Al_2O_3$	5.9, 7.0 (wt%)	90–97	H_2 (18–68), CH_4 (12–29), CO_2 (35–51), CO (1–5) (mol%)	Onwudili et al. (2013)
Nannochloropsis sp.	400–500	35		21 (wt%)	42	H_2 (19), CH_4 (37), CO_2 (36), C_2H_6 (11) (mol%, at 500 °C)	Brown et al. (2010)
Nannochloropsis sp.	450–500	24		4.7 (wt%)	60	H_2 (32), CH_4 (30), CO_2 (34), CO (0.2) (vol%, at 500 °C)	Guan et al. (2012)
Nannochloropsis sp.	450	24	Ru/C	4.8 (wt%)		H_2 (48), CH_4 (15), CO_2 (36), CO (0.6) (mol%)	Guan et al. (2013)
Phaeodactylum tricornutum	400	30	Ru/C	2.5–13 (wt%)	4–74	H_2 (6–8), CH_4 (34–46), CO_2 (40–84) (vol%)	Haiduc et al. (2009)
Spirulina platensis	>400	30	Ru/ZrO_2; Ru/C	2.5 (wt%)	18–93	H_2 (6–29), CH_4 (2–52), CO_2 (38–77), C_2H_6 (1–9) (vol%)	Stucki et al. (2009)

the water gas shift reaction; hence the H_2/CO_2 ratio was almost or more than unity. The Guan et al. (2013) also showed that H_2 and CH_4 yields from *Nannochloropsis* sp. gasification were dramatically improved by NaOH and KOH.

In contrast to homogeneous catalysts, more heterogeneous catalysts such as Ru/C, Ru/ZrO_2, Pt/C, Pd/C, and $Ni/SiO_2–Al_2O_3$ have been utilized for microalgae SCWG. Guan et al. (2013) adopted Ru/C and Pd/C as catalysts to explore *Nannochloropsis* sp. gasification where H_2 and CH_4 yields were enhanced markedly by the catalysts, and explained that those catalysts could enhance the gasification of recalcitrant intermediate products which led to an efficient gasification of the microalga. Among the four catalysts of NaOH, KOH, PdC, and Ru/C, the last one was the most efficient catalyst. Stucki et al. (2009) used Ru/C (2 wt% of Ru) and Ru/ZrO_2 (2 wt% of Ru) catalysts to perform *S. platensis* gasification at temperatures of 399–409 °C, and emphasized that the microalga could be gasified completely to a CH_4-rich gas, with 60–70% of the heating value contained in the microalgal biomass being recovered as CH_4. Haiduc et al. (2009) employed a Ru/C catalyst (2 wt% of Ru) to carry out *Phaeodactylum tricornutum* gasification and produce a CH_4-rich gas. The gasification efficiency was high and 68–74% of carbon in the microalga was recovered in the gas phase, with very low organic carbon retained in the remaining liquid.

With the aid of catalysts in SCWG, the production of H_2 and CH_4 depends on microalgae composition as well as microalgae and catalyst loads. For the low-temperature (at 350 °C) or subcritical gasification of *C. vulgaris* (Minowa and Sawayama, 1999), the CH_4 yield increased with increasing Ni-catalyst load, but the H_2 yield decreased. Overall, the gas yield and carbon conversion increased with increasing the catalyst load. The gasification of *S. platensis* at 400 °C (Stucki et al., 2009) also suggested that an increase in catalyst-to-microalga ratio increased the CH_4/H_2 ratio from favoring H_2 to favoring CH_4. On the other hand, CH_4 was always favored over H_2 from *P. tricornutum* gasification at 400 °C (Haiduc et al., 2009).

Chakinala et al. (2010) found that the dry gas composition from *C. vulgaris* gasification without catalysts mainly comprised of CO_2, CO, CH_4, H_2, and some $C_2–C_3$ compounds. Higher temperatures, low microalgal concentrations, and longer residence times favored the gasification efficiency. The addition of catalysts to the slurry resulted in higher H_2 yields and lower CO yields, due to enhanced water gas shift reaction. The addition of Ni-catalysts accelerated the gasification efficiency up to a maximum of 84% at 600 °C and 2 min reaction time. Complete gasification was achieved at a higher temperature (700 °C) with excess amounts of Ru/TiO_2 catalyst.

In summary, for microalgae in inert or oxygen-free environments, torrefaction and pyrolysis can be employed to produce solid fuels and bio-oils, respectively, depending on the reaction temperature. Using water as a reaction medium under sub-critical states, bio-oils can be produced from microalgae, whereas large amounts of H_2 and CH_4 are contained in the product gas when water is at super-critical states. When microalgae are in high-temperature and partial oxidation environments, syngas (i.e., $H_2 + CO$) can be produced as gas fuels. Homogeneous and heterogeneous catalysts can be employed to aid in chemical reaction in pyrolysis, liquefaction, and super-critical water gasification of microalgae. Accordingly, using different thermochemical conversion routes, solid, liquid, and gas biofuels can be produced from microalgae as substitute to fossil fuels.

6. Challenges

In torrefaction, the solid yield and calorific value are two important indicators for biomass torrefaction. Unfortunately, a higher

calorific value of torrefied biomass is accompanied by a lower solid yield, and vice versa. Therefore, how to obtain an feasible operation to improve microalgae as solid fuels used in industry is an important issue in torrefaction. Meanwhile, very little research has been performed on the direct combustion of microalgae and the impact of torrefaction upon microalgae burning. On account of limited data, these issues deserve further investigation in the future. In hydrothermal liquefaction, certain amount of organic carbon in microalgae is contained in the aqueous phase, rendering a loss of carbon efficiency and the reduction in bio-oil yields (Biller et al., 2011). Meanwhile, the combustion of bio-oils from the liquefaction may lead to high NOx emissions, due to the high amounts of nitrogen in chlorophyll and proteins which are abundant in microalgae cells. De-NOx processes in flue gases are thus required, and bio-oils should be upgraded through deoxygenation and denitrogenation to remove the higher composition of O and N in the oils. Bio-oils obtained from microalgae pyrolysis have higher oil yield and HHV compared with those from lignocellulosic biomass. However, algal pyrolytic bio-oil still requires to be further upgraded to enhance stability, prevent polymerization and condensation reactions, decrease acidity, and increase the energy density (Liang, 2013). The ash content is high in some microalgae (Chen et al., 2014a). High mineral matter or ash in microalgae will make conventional gasification impossible. The gasification temperature is often above the melting point of the ash in microalgae, resulting in clinkering and/or slagging in the hearth and subsequent feed blockages. In SCWG, though Ru/C is an efficient catalyst, the presence of sulfur in microalga had an adverse effect on the performance of the Ru/C catalyst in that sulfur was probably a chief contributor to the deactivation of the catalyst (Haiduc et al., 2009; Guan et al., 2013). The aforementioned challenging issues in the thermochemical conversion of microalgae need to be overcome in order to achieve the technologies from microalgae utilization for the production of solid, liquid, and gas fuels.

7. Conclusions

On account of abundant lipids, carbohydrates, and proteins contained in microalgal biomass, microalgae are a promising feedstock for third-generation biofuels. Solid, liquid, and gas biofuels can be produced from microalgae through the thermochemical conversion technologies. A comprehensive review of recent progress and development of torrefaction, liquefaction, pyrolysis, and gasification using microalgae as feedstocks has been presented in this paper. Solid biofuels are produced by torrefaction. The main product of liquefaction and pyrolysis is bio-oils, whereas combustible gases can be generated from gasification. The developed biofuels are renewable fuels which can replace fossil fuels and abate atmospheric greenhouse effect.

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