Renewable and Sustainable Energy Reviews 49 (2015) 990–999

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

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

Thermochemical conversion of microalgal biomass for biofuel production

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ARTICLE INFO

Article history:
Received 5 June 2014
Received in revised form
30 April 2015
Accepted 30 April 2015

Keywords:
Microalgae
Thermochemical
Gasification
Pyrolysis
Liquefaction
Bioremediation

ABSTRACT

Reliable and sustainable energy supply is critical to effective natural resource management, and it encompasses functioning efficiency of energy resources as well as socio-economic and environmental impact considerations. The complete reliance on fossil fuels is recognized as unsustainable throughout the world, and this is due to, amongst others, the rapid declining of fossil fuel reserves and the emission of significant quantities of greenhouse gases associated with their production and combustion. This has resulted in escalating interest in research activities aiming to develop alternative and somewhat carbon neutral energy sources. Algal biofuels, so called third generation biofuels, appear to be promising in delivering sustainable and complementary energy platforms essential to formulate a major component of the renewable and sustainable energy mix for the future. Algal biomass can be converted into various portfolios of biofuel products, such as bio-hydrogen, biodiesel, bioethanol and biogas, via two different pathways: biochemical and thermochemical pathways. Thermochemical conversion is considered as a viable method to overcome the existing problems related with biochemical conversion such as lengthy reaction time, low conversion efficiency by microbes and enzymes, and high production costs. This paper discusses process technologies for microalgae-to-biofuel production systems, focusing on thermochemical conversion technologies such as gasification, pyrolysis, and liquefaction. The benefits of exploiting upstream microalgal biomass development for bioremediation such as carbon dioxide mitigation and wastewater treatment are also discussed.

Contents

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http://dx.doi.org/10.1016/j.rser.2015.04.186
1364-0321/

1. Introduction

The supply of sustainable energy at an affordable price is a major global endeavor. Energy is viewed as a baseline for economic and social development as it improves living standards and social strata [1]. However, the number of human activities and extensive use of fossil fuels for transportation, manufacturing and power generation has significantly contributed to the emission of greenhouse gases (GHG) and other harmful pollutants resulting in global undesired climate change [2–5]. In addition, anthropogenic emission of carbon dioxide is expected to be 2×10^{10} t/year, most of which is a result of fossil fuels combustion [6]. It has therefore become important to reduce carbon emissions by promoting sustainable alternative resources for energy and implementing policies to reduce the impacts. More renewable and sustainable sources of energy seem to be an auspicious approach to tackle the problem. Notable renewable energy portfolios include solar energy, wind power, nuclear energy, hydropower and biomass [7,8]. In recent years, biomass has gained significant attention as it is considered as a potential renewable energy source for future sustainable energy mix [9,10]. Examples of biomass being explored for biofuel production include plants, trees, food materials, bio-wastes and cellular materials from algae and bacteria.

1.1. Algae technology

Energy harnessing from algal biomass is not a new idea. Many studies have reported the production of biofuels from algal biomass [11,12]. Algae are unicellular, microscopic and photosynthetic organisms typically found in fresh water or marine systems. These organisms consume three primary components: sunlight, carbon dioxide and water to produce significant quantities of lipids, proteins, carbohydrates and other bioactive compounds within a short period of time [13,14].

Algae can be classified into macroalgae (filamentous) and microalgae (phytoplankton) as shown in Table 1. Macroalgae, also known as seaweed, is further divided into three main categories based on pigmentation. These are *Phaeophyceae* (Brown seaweed), *Rhodophyceae* (Red seaweed) and Chlorophyceae (Green seaweed). In contrast, microalgae are unicellular organisms divided into four classes. These are *Bacillariophyceae* (diatom), *Chlorophyceae* (green algae), Cyanophyceae (blue algae) and Chrysophyceae (golden algae) [15]. Algal biomass generally consists of 9.5–42% lipid, 17–57% carbohydrate and 20–50% protein (dry weight basis) depending on the species and some species possess oil content up to 79.5% [16].

1.2. Advantages of microalgae

There are numerous advantages of microalgal biomass as a feedstock for biofuel production compared to existing biomass such as Jatropha, grains, sugarcane, oil seeds and corn. These include:

1. Microalgae are capable of fixing high CO_2 from the environment [7]. Microalgae can utilise CO_2 emissions from power plants and other industrial sources for their growth in a CO_2 biosequestration process. Typically 1 kg of microalgal biomass synthesis requires about 1.8 kg of CO_2 [17,18].
2. Microalgae can grow in different types of environments. They do not require traditional agricultural resources, as they can be cultivated with or without land and in seawater or freshwater [7,19]. They also require lesser volumes of water for cultivation compared to terrestrial crops.
3. The photosynthesis mechanism in microalgae is similar to other plants. However, microalgae can convert more solar energy (at about 4–7.5%) during cellular metabolism compared to 0.5% for land based crops [20].
4. Microalgae have a high growth rate within a short duration of time compared to land based crops and it could be harvested throughout the year. They double up in mass by converting carbon dioxide and sunlight into energy within 24 h. Some species require only 3.5 h for biomass production [17,18].
5. Microalgal biomass can be used to generate numerous valuable products such as food, feed for animals and fuels, including jet fuel, aviation gas, biodiesel, gasoline, bioethanol. Residual microalgal biomass may be used as feed or fertilizer.

2. Application of microalgae

2.1. Microalgae as a source of food

Microalgae are one of the most important biomass sources on the earth containing proteins, carbohydrates, enzymes and vitamins A & C and minerals such as iodine, potassium, iron and calcium. Green microalgae have been used in Asian countries, including China, Japan and Korea, as the source of certain food nutrients for hundreds of years [21]. Commercially used microalgae as food supplements and additives for humans and animals are *Chlorella vulgaris*, *Haematococcu spluvialis*, *Dunaliella salina* and Cyanobacteria *Spirulina maxima* [22]. Blue–green microalga *Spirulina platens* are considered as one of the major nutritious food sources and has gained acceptance as a food supplement globally [23]. Currently, numerous by-products of microalgal biomass are used as fruit and vegetable

Table 1
Comparison between the characteristics of macroalgae and microalgae.

Macroalgae	Microalgae
• Multicellular plants which grow in salt and fresh water.	• Unicellular plants which grow in salt and fresh water.
• Able to grow up to 60 m in length	• Small size (1 μm)
• High nutrient storage capacity and has low growth rate	• More nutrient uptake and has fast growth rate
• Utilized for food production and extraction of hydrocolloid.	• Utilized for food production, medical supplements and biofuels.

preservatives. The microalga *D. salina* is an important source of beta-carotene and it is used as vitamin C supplement. *Chlorella* and *Spirulina sps* have been identified to have high protein content and nutritional value [24,25]. The products from microalgal biomass are formulated and marketed forms such as liquid, powder, capsules, and tablets. *Chlorella* and *Arthrospira sps* are used as 'skin foods'in the cosmetic and skin care industry as thickening agents, water-binding agents, and antioxidants [21,22]. Commonly used microalgae species and their applications in the food industry are given in Table 2.

2.2. Microalgal biomass as biofuel feedstock

Biofuels from microalgal biomass are referred to as third generation biofuels. Microalgae have a higher capacity to produce 30–100 times more energy per hectare compared to terrestrial corps [14]. A wide range of research on biofuels from microalgae has been presented, including bioethanol, biodiesel, biohydrogen and syngas [29–31]. Biomass from microalgal cells are also used to produce biohydrogen and biomethane from anaerobic digestion and fermentation [32,33]. In USA and Brazil, oil and carbohydrate producing crops such as sunflower, sugar beet, soybean, and sugarcane are used as feedstock for the production of biodiesel and bioethanol [34]. Biofuels from oleaginous crops are advantageous and possess significant potential to be carbon-neutral fuel. Table 3 shows the oil content of various microalgae species in comparison to plant crops. Different species of microalgae have been studied for their biofuels production potential. Table 4 shows microalgae species currently used to synthesize various types of biofuel. The conversion process depends on different factors relating to biomass composition, desired biofuel product, process time, process economics, and operating conditions.

3. Conversion technologies for microalgal biofuels production

Photosynthetically grown microalgal biomass is widely regarded to produce environmental friendly biofuels such as solid fuel, biohydrogen, biodiesel, bioethanol and syngas via two different pathways: biochemical and thermo-chemical conversion processes as illustrated in Fig. 1. The selection of the right conversion technology is a key step to ensuring that biofuel production is economically viable and environmentally sustainable. Currently, there are no clear established advantages between biochemical and thermochemical pathways. However, a review by Sims et al. [46], reported that thermochemical conversion is considered more advantageous. One of the major problems with biochemical conversion is the feedstock characteristics. Feedstock improvements which involve pretreatment processes require high capital cost and this increases the production cost. In addition, conversion efficiency of biomass into biofuel via biochemical pathways is low. Also, the biochemical pathway only produced single end product for each technology compared to thermochemical pathway which can produces several types of end products from a single process.

3.1. Biochemical conversion technologies

Biochemical conversion of microalgal biomass can be carried out using several different approaches such as fermentation, anaerobic digestion, and photobiological production techniques [47]. These conversion technologies mostly involve microorganisms and enzymatic processes to convert the biomass into biofuels [48]. However, this conversion method, environmentally benign, is usually not preferable from an industrial perspective due to lengthy reaction steps, low conversion efficiency by microbe and/or enzyme, and high production costs.

Table 2
Composition of commonly used microalgae cells for applications in human nutrition.

Microalgae	Major applications	Country of production	World production (t/year)	Protein (% dry matter)	Carbohydrates (% dry matter)	Lipids (% dry matter)	References
Spirulina (Arthrospira)	Pasta, powders, beverages,	China, USA	3000	45–65	20–28	8–10	[25,26]
Chlorella-vulgaris	Noodles, tablets, powders, capsules.	Taiwan, Germany	2000	41–58	12–17	10–22	[25,27]
Dunaliella salina	Beta-carotene	Australia	1200	57	32	6	[25,27,28]

Table 3
Lipid composition of various microalgae species and crop plants [7,17].

Species	Oil content (% dry weight)
Botryococcus braunii	25–75
Chlorella sp.	28–32
Crypthecodinium cohnii	20
Cylindrotheca sp.	16–37
Nitzschia sp.	45–47
Nannochloropsis sp.	31–68
Schizochytrium sp.	50–77
Tetraselmis suecica	15–23
Corn/Maize (*Zea mays*)	44
Hemp (*Cannabis sativa*)	33
Soybean (*Glycine max*)	18
Jatropha (*Jatropha curcas*)	28
Camelina (*Camelina sativa* L.)	42
Canola (*Brassica napus*)	41
Sunflower (*helianthus annuus*)	40
Palm Oil (*elaeis guineensis*)	36

Table 4
Commonly used microalgae species for biofuel production.

Biofuel type	Microalgae	References
Biodiesel	*Botryococcus braunii*	[17]
	Schizochytrium sp.	[17]
	Chlorella sp.	[7]
Bioethanol	*Chlorococcum* sp.	[35]
	Spirogyra	[36]
	Undaria pinnatifida	[37]
	Chlorella vulgaris	[37]
	Chlamydomonas reinhardtii	[37]
Bio-oil	*Corallina pilulifera*	[38]
	Nannochloropsis sp.	[39]
	Dunaliella tertiolecta	[40]
	Chlorella sp.	[41]
Bio Syngas	*Chlorella vulgaris*	[42]
	Chlorella vulgaris	[43]
	Cladophora fracta	[44]
	Botryococcus braunii	[45]

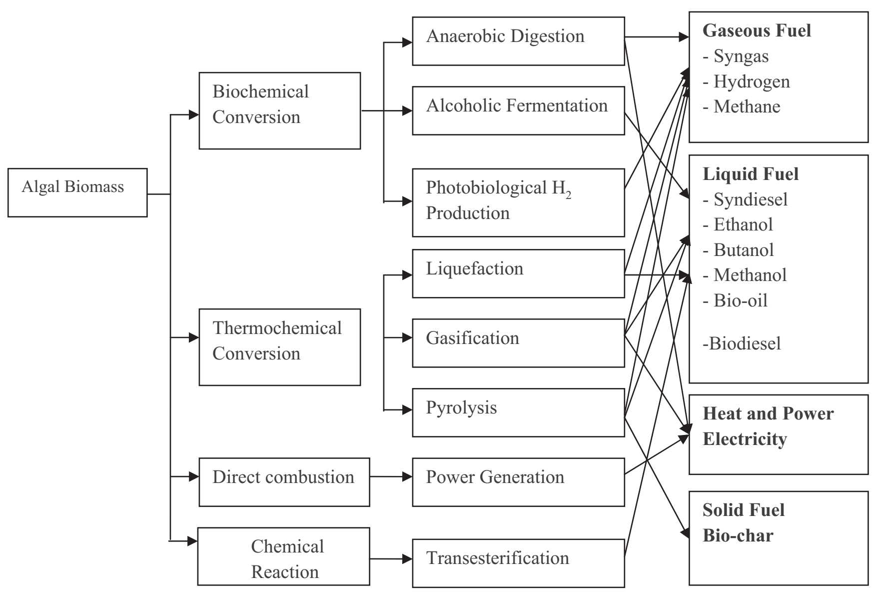

Fig. 1. Energy conversion processes from algal biomass.

3.2. Thermochemical conversion technologies

Thermochemical conversion encompasses the thermal decomposition of organic compounds present in the biomass to produce biofuels [48]. The conversion process can be by liquefaction, gasification, pyrolysis or direct combustion [14,49]. During thermochemical conversion, the biomass is heated with oxygen/air or steam under deficient conditions to produce synthetic gas or syngas which primarily consist of hydrogen (H) and carbon monoxide (CO). The gases produced from the thermochemical process can be directly burnt in the boiler or further processed into other gaseous or liquid product such as methanol or diethyl ether (DME). Thermochemical conversion is studied extensively and more applied than biochemical conversion. Table 5 shows algae species currently used for biofuel production via thermochemical pathways.

3.2.1. Gasification

Gasification converts organic or fossil based carbonaceous materials into clean fuel gases or synthetic gases. This is achieved by reacting materials at high temperature (800–1000 °C) without combustion in partial oxidation of air, oxygen or steam [61,62]. The chemical reactions the in gasification of carbonaceous materials entail different processes such as drying, pyrolysis, combustion and reduction. The initial process of gasification is the thermochemical breaking of biomass. After the gasification process, the produced syngas, primarily consists of H_2 (6–55%) and CO (8–53%) and CH_4 as co-product (2–26% [63,64]. Fig. 2 shows gaseous products from gasification along with some unwanted products such as tar, ash and water. These unwanted products highly affect the yield of the main product [30]. The composition of tar during gasification ranges from 0.1–21% depending on the gasifying agent and reactor type [65]. The biomass for gasification is suitable when the moisture not more than 15% [66]. However, algal biomass with moisture up to 40% is acceptable. Higher moisture content in the biomass reduces the efficiency of the gasifier and also the energy content of the syngas. The calorific value (CV) of the produced syngas at moisture content (5–30%) ranges from 3.45–5.9 MJ kg^{-1} [67]. Fig. 2 illustrates the gasification process of microalgal biomass.

According to the process flow diagram in Fig. 2, the gasification of microalgal biomass undergoes three phases: dewatering or moisture removal, devolatization or pyrolysis, and oxidation or char combustion. The drying process takes place at a range of temperature

Table 5
Algae sources studied for thermochemical conversion of biomass.

Algae type	Species	Reaction	References
Macroalgae	*Enterimorpha prolifera*	Liquefaction	[50]
	porphyra yezoensis	Pyrolysis	[38]
	Plocamium telfairiae	Pyrolysis	[38]
	Corallina pilulifera	Pyrolysis	[38]
	Enteromorpha clathrata	Pyrolysis	[51]
	Enteromorpha clathrata	Pyrolysis	[51]
	Ulva lactuca L	Pyrolysis	[51]
	Undaria pinnatifida (Harvey)	Pyrolysis	[51]
Microalgae	*Chlorella vulgaris*	Gasification	[42,43]
	Spirulina platensis	Gasification	[52]
	Nannochloropsis sp.	Gasification	[53]
		Liquefaction	[53]
		Pyrolysis	[39]
	Cladophora fracta	Gasification	[44]
	Chlorella protothecoides	Gasification	[44]
		Pyrolysis	[54,55]
	Spirulina sp.	Gasification	[56]
	Phaeodactylum tricomutum	Gasification	[57]
	Dunaliella tertiolecta	Gasification	[45]
		Pyrolysis	[40]
		Liquefaction	[58]
	Botryococcus braunii	Gasification	[45]
		Liquefaction	[59,60]
	Microcystis aeruginosa Chlorella sp.	Pyrolysis	[54]
		Pyrolysis	[41]

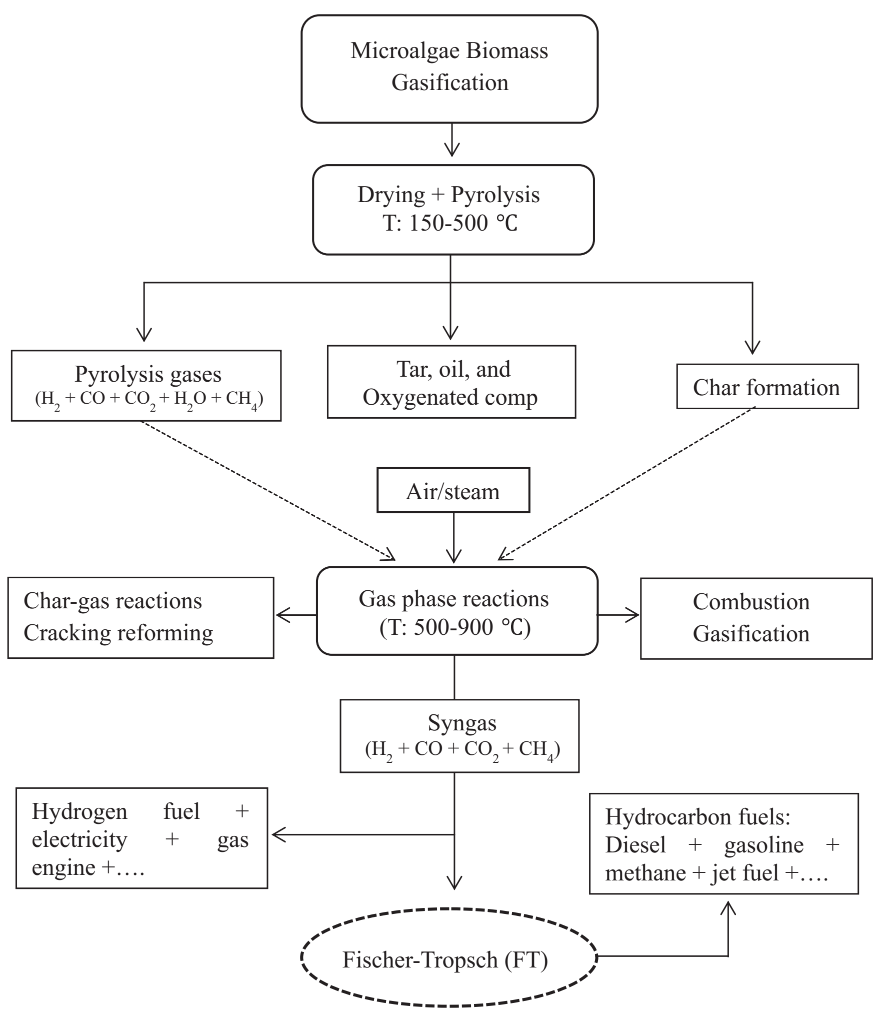

Fig. 2. Processes entailed in microalgal biomass gasification.

increase from 0 to 150 °C. When the temperature reaches 500 °C, the dried biomass changes into combustible gases, such as CO_2, H_2 and CO, vaporized tar/oil, and solid char. Partial oxidation or combustion occurs when the gasifying agent (steam/oxygen) reacts with the combustible gases at high temperatures up to 900 °C yielding residual carbon monoxide (CO), hydrogen (H_2), methane (CH_4), carbon dioxide (CO_2) and traces of hydrocarbon products. Producer gas is primarily suitable for power generation. It can also be utilized in chemical industries for different applications such as hydrogenation reactant, saturation compounds [68], and transportation fuels by means of water–gas-shift (WGS) reaction [69]. WGS reaction consumes CO and H_2O to produce H_2 and CO_2, thus, it can be used to promote the conversion of the producer gas into syngas by enhancing the H_2 yield. In addition, increasing reactor temperature and catalyst concentration can enhance overall gasification efficiency. Syngas resulted from the gasification process has a low calorific value (typical 4–6 MJ m^{-3}) but can be utilized directly for heating, electricity generation or as a fuel for gas engines/turbines [70]. The gasification of microalgal biomass has been studied to produce variety of liquid fuels using Fischer–Tropsch synthesis (FTS). FTS is a well-established technique to clean the impurities of produced gases and upgrade them to usable liquid fuels [71]. The gasification reactions are described below:

$$C+H_2O\rightarrow CO+H_2 \tag{1}$$

$$C+CO_2 \rightarrow 2CO \tag{2}$$

$$CO+H_2O \rightarrow H_2+CO_2 \tag{3}$$

During gasification, methane could also be produced by thermal splitting of the organic material [72] according to the reaction:

$$CO_2+ 4H_2 \rightarrow CH_4+2H_2O \tag{4}$$

Gasification of microalgal biomass has been carried out by Hirano et al. [56] by partially oxidizing *Spirulina* sp. by at three different temperatures; 850 °C, 950 °C and 1000 °C. The biomass slurries of 0.25 g min^{-1} and O_2 of 0.39 ml min^{-1} were continuously supplied to the system. The gaseous composition from *Spirulina* sp. gasification mainly comprised of H_2, CO, CO_2 and CH_4 with small quantities of O_2, N_2 and C_2H_4. The increased in temperature enhanced H_2 content while decreasing CO_2, CO and CH_4 contents in the produced syngas. The study showed increasing carbon conversion from 93% to 100% with increasing reaction temperature from 850 °C to 1000 °C.

Several studies have been reported on gasification of *Chlorella* sp. [42,44,54,55]. *Chlorella* sp. is a single cell green microalgae belonging to *Chlorophyta* and abundantly found in fresh waters. Minowa and Sawayama [43] studied the gasification of *C. vulgaris* in a nitrogen cycling system at a low temperature of 350 °C under Ni-catalyst. The process resulted in the production of methane-rich fuels. The CH_4 production increased at higher catalyst concentrations, whereas H_2 production declined. The carbon conversion and gas yield increased due to the catalyst loading. The study also reported that all the nitrogen in the biomass was converted to ammonia during the gasification process and the produced ammonia can be converted to high quality fertilizer. Chakinala et al. [42] studied catalytic and non-catalytic supercritical water gasification of *C. vulgaris* and reported that excessive use of catalyst to the slurry resulted in higher H_2 production and lower CO yield via enhanced water–gas-shift activity. Also, the addition of a nickel based catalyst was found to increase the gasification efficiency up to 84% at 600 °C with 2 min of reaction time. The complete gasification was achieved at 700 °C using an excess amount of Ru/TiO_2 catalyst. The study also found that the application of high temperature, low microalgae concentration and longer residence time is important for optimal gasification efficiency. Another study on catalytic gasification at 400 °C has been reported for *S. platensis* [52]. In this study, a novel method based on cultivation of microalgae using CO_2 emission from fossil fuel and the catalytic hydrothermal process in the presence of ruthenium catalyst has been proposed. It was observed that a high yield of carbon gasification up to 50% and methane concentration up to 40% could be achieved by increasing the catalyst loading. Increasing of catalyst-to-microalgae ratio increases the CH_4/H_2 ratio. Similar result was found with *Phaeodactylum tricornutum* [57]. While examining the effect of temperature on gasification of *Cladophora fracta* and *Chlorella* sp., Demirbas [44] showed that syngas yield increased from 28 to 57% by increasing reaction temperature from 552 to 952 °C. High temperatures and catalyst loading play important roles in gasification to increase H_2 yield. The commonly used catalysts are alkali catalysts. These include nickel, dolomite, and potassium carbonate [73]. Amongst all these catalysts, nickel-based catalysts are more capable of reducing tar production up to 5% at 500–900 °C [74]. The gasification efficiency of microalgal biomass increased in the presence of catalyst, up to 85% [42]. The yield of syngas produced from gasification is dependent on the gasifying agent. Air as a gasification agent can produce high yield of syngas richer in H_2 than steam [75,76]. However, more tar is expected to be produced by this technique. Tar production can possibly be reduced by increasing flow rate of air during the gasification process.

3.2.2. Pyrolysis

Biomass pyrolysis is a thermochemical process which occurs at 200–750 °C in the absence of oxygen to produce renewable bio oil, char and gases. The operational conditions of pyrolysis are categorized into two different stages: fast pyrolysis and slow pyrolysis as shown in Fig. 3. Fast pyrolysis of biomass produces 19–57% of bio oil (as the final product) and char [54,77]. The products produced from pyrolysis of microalgae are bio char and a gaseous mixture of methane and carbon dioxide. The concentration of these gases increases with temperature [55].

Many studies have been reported on the pyrolysis of microalgal biomass with promising results [51,55,77,78]. Table 6 shows some microalgae species studied in different pyrolytic processes. According to Peng et al. [55], maximum pyrolytic rate up to 78% can be achieved in the temperature range of 300–600 °C. In general, the bio-oils from microalgae are more stable compared

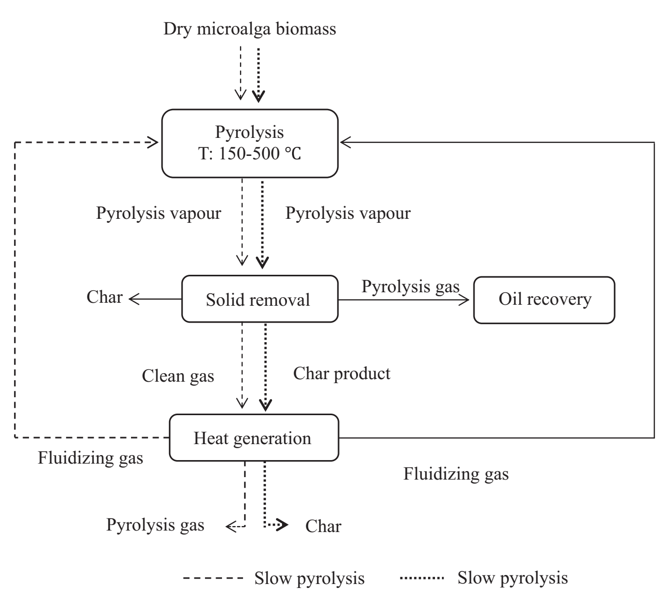

Fig. 3. Schematic process description and products formation from pyrolysis [85].

to those from terrestrial crops such as wood [81]. This is demonstrated with Table 7. Bio-oils produced from pyrolysis of lignocellulosic feedstock are unstable as it holds solids with chemically dissolved oxygen concentrations, thus require upgrading to facilitate their conversion [61,82]. In contrast, bio-oils from microalgal biomass contain various types and amounts of linear hydrocarbons and nitrogenous species, resulting from its lipids and proteins [78]. The calorific value of bio oil from microalgae feedstock ranges between 31 and 42 MJ kg^{-1} with a viscosity of 0.060 Pa s [54,82]. Miao et al. [79] indicated that higher calorific values of bio-oils could be achieved from fast pyrolysis of microalgae at a lower oxygen contents compared to bio-oils obtained from lignocellulosic biomass. The lower concentrations of oxygen in bio-oils derived from microalgae offers better storage stability over wood derived bio-oils [78].

Grierson et al. [77] studied the slow pyrolysis of six different microalgae species namely *Tetraselmis Chuii, Chlorella* sp., *C. vulgaris*, *Chaetocerous muelleri*, *Dunaliella tertiolecta* and *Synechococcus* sp. showed a total production of 30–63%, 13–25% and 24–43% char, gas and bio-oils respectively for the different microalgal biomass. The pyrolytic bio-oils were also composed of fatty acids, alkenes, phenols and amides.

Another study of fast pyrolysis conducted by Miao and Wu [54] for *Chlorella protothecoides* and *Microcystis aeruginosa* reported 18% and 24% conversion of total biomass into bio oil respectively. It was found that the bio-oil content of *C. protothecoides* (heterotrophic) was 3.4 time higher than *M. aeruginosa* (autotrophic), with lower oxygen concentrations, higher calorific value (41 MJ kg^{-1}), lower density (0.91 kg 1^{-1}), and lower viscosity (0.02 Pa s). It was concluded that the heterotrophic macroalgae cell displayed better performance in fast pyrolysis than the autotroph and wood. The product composition from the pyrolysis of microalgae is completely influenced by temperature, pressure and holding time [55,39,84]. The temperature range of 200 to 520 °C is considered to be optimum for thermal degradation of microalgal biomass. However, it has been reported that there is no significant difference in bio oil yield from 300 to 500 °C at a residence time of 20 min [55]. Recent studies have proposed that catalytic pyrolysis is a suitable approach to upgrade bio-oils from microalgal biomass in terms of quality and quantity with lower oxygenic compounds [85]. For instance, a study by Pan et al. [39] discovered that the produced oil from the catalytic activity of *Nannochloropsis* sp. gave a lower concentration of oxygen (19 wt%) and a higher heating value of 32.5 MJ kg^{-1} compared to direct pyrolysis of biomass which contained a high concentrations of oxygen (30 wt%) and a calorific value of 24.6 MJ kg^{-1}. Babich et al. [41] pyrolyzed *Chlorella* with/without Na_2CO_3, and achieved higher gaseous product as compared to non-catalytic pyrolysis. Du et al. [82] used *Chlorella* sp. for pyrolysis in a microwave oven and obtained a maximum bio-oil of 28.6 wt% at 750 W. The produced bio-oil had a lower oxygen content with aromatic hydrocarbons, non-condensable gas (H_2, CO, CO_2) and trace amounts of hydrocarbon gases.

3.2.3. Liquefaction

Microalgal biomass typically contains approximately 80–90% moisture content and this causes major problems for energy production [86]. Thus, microalgal biomass requires effective dewatering to reduce the moisture content prior to biofuel production process. However, the dewatering process increases the energy cost and makes biofuels from microalgae less economically viable. Hence, liquefaction is considered useful in overcoming the high moisture content of microalgal biomass.

Liquefaction is a thermochemical method of producing liquid fuels from wet biomass. Liquefaction occurs at lower temperatures (200–500 °C) and high pressures (5–20 bar) in the presence of a catalyst [72]. The process can achieve 10–73% of bio oil, gaseous mixture content of 8–20% and an ash content of 0.2 to 0.5% [87,88]. The reactors and fuel requirements for liquefaction are slightly complex and this makes the process more expensive [70]. The liquefaction process however have various advantages based on their capability of converting wet biomass into biofuels [89]. In liquefaction, the wet biomass is decomposed into

Table 6
Microalgae species used for biofuel production via pyrolysis.

Microalgae	Production	Temp (°C)	Liquid content (wt%)	HHV MJ kg^{-1}	Gas content (wt%)	Solid content (wt%)	References
Nannochloropsis sp.	Phototrophic	400	19.7	32.7	25	25	[39]
Chlorella protothecoides	Phototrophic	500	18	30	–	–	[79]
Chlorella protothecoides	Heterotrophic	450	57.9	41	32	10.1	[54]
Microcystis aeruginosa	Phototrophic	500	24	29	–	–	[79]
Chlorella sp.	Phototrophic	450	55	27	20	30	[41]
Tetraselmis Chuii	Phototrophic	500	43	–	20	37	[77]
Chlorella like	Phototrophic	500	41	–	22	37	[77]
Chlorella vulgaris	Phototrophic	500	41	–	25	34	[77]
Chaetocerous muelleri	Phototrophic	500	33	–	14	53	[77]
Dunaliella tertiolecta	Phototrophic	500	24	–	13	63	[77]
Synechococcus	Phototrophic	500	38	–	18	44	[77]
Emiliania huxleyi	Phototrophic	400					[80]

Table 7
Comparison between petroleum oil and bio oil from the pyrolysis of wood and microalgae [82,79,83].

Properties	Bio-oil		Petroleum
	Wood	Microalgae	
C (%)	55.9	65.0–65.76	83.0–87.0
H (%)	5.9	7.84–8.50	10.0–14.0
O (%)	37.3	11.24–16.48	0.05–1.5
N (%)	0.2	9.75–10.28	0.01–0.7
Density (kg l^{-1})	1.3	0.98–1.06	0.75–1.0
Viscosity (Pa s)	0.04–0.2	0.10	2–1000
HHV (MJ kg^{-1})	21	29–45.9	42

small molecules which undergo depolymerization into oily products with a wide range of molecular weight distribution and high energy density [86]. Liquefaction can be classified as direct or indirect. Direct liquefaction is the fast pyrolysis of biomass to produce bio oil, liquid tar and condensable organic vapour. In contrast, indirect liquefaction is performed in the presence of catalyst to convert non-condensable products (organic vapour and liquid tar) and gases from pyrolysis or gasification into liquid products [90].

Several studies have been reported on liquefaction of microalgal biomass. A successful study on thermochemical liquefaction of *Botryococcus braunii* was conducted by Dote et al. [60], achieving 64% yield of bio oil at 300 °C with a higher heating value (HHV) of 45.8% MJ kg^{-1}. Another study performed with *D. tertiolecta* reported a bio oil yield of 42% on dry basis and HHV of 34.9 MJ kg^{-1} [58]. Protein rich *Spirulina* sp. was reported by Matsui et al. [91] to produce 54% of oil without the presence of a catalyst. These results show that liquefaction is a promising technology for microalgal biomass conversion into liquid fuels. The various factors significantly affecting the microalgal biomass liquefaction process and the resulting product composition are temperature, biomass loading, holding time and the presence/concentration of a catalyst. The conversion of microalgal biomass into bio-oil is greatly dependent on the liquefaction reaction temperature [92,53]. The optimum conditions for liquefaction reaction as proposed by Yang et al. [93] are 340 °C, a holding time of 30 min and 5% catalyst loading.

The bio-oil content and calorific value are normally in the range of 30–65 wt% and 30–50 MJ kg^{-1}. This calorific value is comparable to that of petroleum oil (41 MJ kg^{-1}) [53]. Hence, the liquefied bio-oils can be readily utilized as a combustion fuel. Raw microalgae have higher oxygen content compared to its bio-oils [87]. For instance, the weight percentages of elemental oxygen of *D. tertiolecta* and bio-oil obtained from its liquefaction (360 °C, 30 min) are 53 and 25 wt%, respectively [87]. A summary of thermochemical methods is shown in Table 8.

3.2.4. Direct combustion

Direct combustion is a thermochemical technique used to burn biomass in the presence of excess air. In the process, photosynthetically stored chemical energy in the biomass is converted into hot gases [72]. Typically, combustion takes place inside a boiler, furnace or in a steam turbine at a temperature around 850 °C. The combustion process accepts various types of biomass, but the moisture content should be less than 50% [70]. The heat produced from the combustion process does not have suitable options for storage; hence it is best utilized immediately [89]. The cost of energy production from direct combustion is slightly higher as the biomass requires pretreatment, such as dehydrating, cutting and crushing, prior to the process [72]. One of the simplest approaches in the literature for microalgal biomass utilization is combined heat and power production [97]. Another possibility for sustainable operation of microalgal biomass in direct combustion is coal-algae co-firing. It is projected that coal-algae co-firing will lead to lower emissions of greenhouse gases (GHG) into the atmosphere [98]. The idea of co-firing algal biomass with coal or natural gas in a boilers and the reduction of CO_2 emission by recycling CO_2 from the combustion process for algae cultivation has been proposed [98]. There is currently no extensive study carried out to determine the viability of this technology.

4. Benefits of microalgae

4.1. CO_2 mitigation using microalgae

Biomass derived energy is not only environment friendly and carbon neutral but it also reduces our dependence on fossil fuels, thereby contributing efficiently to energy security and clean climate change mitigations. Kyoto 1997 protocol was aimed to act in order to reduce greenhouse gas emissions, particularly carbon dioxide, from different anthropogenic activities [99]. As microalgae possess photosynthetic efficiency higher than terrestrial plants with efficient carbon biosorption, it has a great potential for biosequestration of CO_2 released from power plants and industrial processes [94,100] which would otherwise go into the atmosphere. Microalgae species tested and proven to be viable for CO_2 fixation are *Chlorella* sp. *Nannochloropsis* sp. *Phaeodactylum*, *Emiliania huxley* and *S. platensis* [101]. Some microalgal species have a high capacity to capture 5–15% of CO_2 from intense CO_2 streams such as flue gases and flaring gases [102,103]. In contrast, existing biofuel crops usually absorb only 0.03–0.06% of CO_2 from environment. This is mainly due to the slow growth rate of plants as they are not efficient converters of energy from the sun. Microalgae are able to mitigate CO_2 10 to 50 times higher than terrestrial plants [104,105]. Microalgae have considerable advantages for CO_2 mitigation: (1) CO_2 produced from power plants and boilers can be recycled for energy production via photosynthesis and then converted into fuels by using existing technologies; (2) Direct fixation of CO_2 by microalgae can enhance the sequestration significantly. It has been reported that the cost of CO_2 separation via conventional technologies such as scrubbing is estimated to be about 70% of energy production cost [94]. The mitigation of CO_2 can be made more economically effective by combining other processes such as wastewater treatment as a medium for microalgae cultivation. CO_2 mitigation could prove profitable for producing biofuels and other value added products such as bulk chemical.

4.2. Algal wastewater treatment systems

Microalgae utilize various nutrients for its growth. The application of wastewater for algae cultivation offers significant economic advantages in biofuel production. In general, wastewater could contain different essential nutrients, such as nitrates, phosphates and metal ions that support microalgae growth. It has been reported that microalgae are efficient to reduce chemical oxygen

Table 8
Summary of thermochemical conversion methods with key operating parameters.

Process	Feedstock conditions	Reaction conditions				Products		Reference
	Moisture level (%)	Temperature (°C)	Pressure (MPa)	Gasifying agent	Catalyst	Main products	Co-products	
Gasification	< 40	600–1000	1–25	Air, steam, nitrogen or combination of these	Required	H_2: 5–56%, CO: 9–52%	CH_4,CO_2, tar and other hydrocarbons	[85,89,94]
Pyrolysis	< 5	350–700	0.1–0.5	Not required	Not required	Bio-oil, fuel gas	Bio-char	[95,40,85]
Liquefaction	> 75	250–500	5–20	–	Required	Bio-oil	Mixture of gas	[87,96]

demand (COD) and biochemical oxygen demand (BOD) in wastewater [85]. Microalgae species such as *Scendesmus* sp., *Chlorella* sp., and *Chlamydomonas reinhardtii* have been found to be favorable for wastewater treatment [106,107]. Metal ions such as calcium, ferum, magnesium and aluminum have removal rates which vary amongst microalgae species in the range 50–99% [108]. Several studies have been successfully conducted by using microalgae to treat wastewater with high concentrations of nitrogenous and phosphorus compound [109,110]. Microalgae require nitrogen and phosphorus for protein, nucleic acid and phospholipid synthesis [111]. A study on wastewater treatment using *Chlorella kesseleri* showed that microalgae is able to remove nitrates in wastewater from 168.1 mg NO_3–N/ml to 136.5 and 154.1 NO_3–N/ml respectively for continuous and diurnal illumination [112]. The results indicate that there is an enormous potential for the application of microalgal cells for industrial-scale wastewater treatment. However more work is required in the development of a commercially viable bioprocess for full-scale application of microalgae for wastewater treatment.

5. Conclusion

The environmental issues associated with anthropogenic activities, such as global warming and climate change, mostly resulting from energy production and utilization cannot be ignored much longer as they affect nature and human lives. In response to the problem, microalgae are considered a sustainable biofuel feedstock and with attractive bioremediation capabilities. Its continuous higher production rate compared to other biofuel biomass will promote the sustenance of biofuels as a key component of the future sustainable energy mix. Thermochemical conversion of microalgal biomass provides significant advantages in terms of simplicity, shorter conversion time, higher productivity and compatibility.

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