

Biofuels from algae for sustainable development

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ABSTRACT

Microalgae are photosynthetic microorganisms that can produce lipids, proteins and carbohydrates in large amounts over short periods of time. These products can be processed into both biofuels and useful chemicals. Two algae samples (*Cladophora fracta* and *Chlorella protothecoid*) were studied for biofuel production. Microalgae appear to be the only source of renewable biodiesel that is capable of meeting the global demand for transport fuels. Microalgae can be converted to biodiesel, bioethanol, bio-oil, biohydrogen and biomethane via thermochemical and biochemical methods. Industrial reactors for algal culture are open ponds, photobioreactors and closed systems. Algae can be grown almost anywhere, even on sewage or salt water, and does not require fertile land or food crops, and processing requires less energy than the algae provides. Microalgae have much faster growth-rates than terrestrial crops. The per unit area yield of oil from algae is estimated to be from 20,000 to 80,000 liters per acre, per year; this is 7–31 times greater than the next best crop, palm oil. Algal oil can be used to make biodiesel for cars, trucks, and airplanes. The lipid and fatty acid contents of microalgae vary in accordance with culture conditions. The effect of temperature on the yield of hydrogen from two algae (*C. fracta* and *C. protothecoid*) by pyrolysis and steam gasification were investigated in this study. In each run, the main components of the gas phase were CO₂, CO, H₂, and CH₄. The yields of hydrogen by pyrolysis and steam gasification processes of the samples increased with temperature. The yields of gaseous products from the samples of *C. fracta* and *C. protothecoides* increased from 8.2% to 39.2% and 9.5% to 40.6% by volume, respectively, while the final pyrolysis temperature was increased from 575 to 925 K. The percent of hydrogen in gaseous products from the samples of *C. fracta* and *C. protothecoides* increased from 25.8% to 44.4% and 27.6% to 48.7% by volume, respectively, while the final pyrolysis temperature was increased from 650 to 925 K. The percent of hydrogen in gaseous products from the samples of *C. fracta* and *C. protothecoides* increased from 26.3% to 54.7% and 28.1% to 57.6% by volume, respectively, while the final gasification temperature was increased from 825 to 1225 K. In general, algae gaseous products are higher quality than gaseous products from mosses.

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1. Introduction

For some time now we have been living with environmental dilemmas which challenge human creativity and capacity to venture sustainable solutions to protect the life on our planet and our existence upon it. Among these are the needs to protect fresh water and agricultural lands for food production, to combat the greenhouse effect and to produce energy from non fossil sources [1–8].

In a period when fossil hydrocarbons are likely to become scarce and costly, methods to convert biomass to competitive liquid biofuels are increasingly attractive. In recent years considerable attention has been focused on lowering biofuel costs, GHG emissions, and land and water resource needs, and on improving compatibility with fuel distribution systems and vehicle engines.

Policy priorities should be aligned with these research and development objectives as well as with other policies addressing climate, agriculture, forestlands and international trade [9–22].

Competitive liquid biofuels from various biomass materials by chemically and biochemically have been found promising methods for near future. Liquid biofuels may offer a promising alternative to petroleum based transportation fuels. There are two global liquid transportation biofuels: bioethanol and biodiesel, respectively. Among emerging feedstocks, jatropha currently can be converted to biodiesel with commercial processes, while processes capable of converting algae, crop wastes, perennial grasses, wood and wood wastes are still at pre-commercial stages [23–26,15,27,13].

Algae use enormous amount of CO₂ removing from power plant emissions. Allied to this is the enormous capacity of the algae to convert CO₂ into biomass, liberating via photosynthesis more oxygen for the atmosphere than forests. An additional advantage of algae is depolluted the waters by absorbing the urea expelled by these animals and at the same time increases the CO₂ conversion

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into biomass. The algae can then be converted into various kinds of biofuel using liquefaction, pyrolysis, gasification, extraction and transesterification, fermentation, and anaerobic digestion [28–35].

Produce biofuels such as biodiesel via transesterification of algal oil, and alcohol from microalgae biomass via hydrolysis and fermentation are promise well the future. Biomass conversion processes fall into three major categories: chemical, biological, and thermochemical [36–39]. The most efficient processes may be those that combine two or more processes and use the entire plant. Transesterification to produce biodiesel is more energy-efficient than fermentation to produce ethanol [40–42].

Bioethanol production from microalgae begins with the collection and drying of algae that have been cultivated in a suitable for water environment. In the next step of the process, the algal mass is ground and hydrolyzed and then the hydrolyzed mass is fermented and finally distilled [33].

One hectare algae farm on wasteland can produce over 10–100 times of oil as compared to any other known source of oil-crops. While a crop cycle may take from three months to three years for production, algae can start producing oil within 3–5 days and thereafter oil can be harvested on daily basis. Algae can be grown using sea water and non-potable water on wastelands where nothing else grows. It is firmly reinforced that algae' farming for biofuels is expected to provide a conclusive solution to food vs. fuel debate [43]. The carbon dioxide fixation and the main steps of algal biomass technologies are illustrated in Fig. 1.

Microalgae are photosynthetic microorganisms with simple growing requirements (light, sugars, CO_2 , N, P, and K) that can produce lipids, proteins and carbohydrates in large amounts over short periods of time. These products can be processed into both biofuels and useful chemicals [44]. The microalgae species most used for biodiesel production are presented and their main advantages described in comparison with other available biodiesel feedstocks [45,46].

This paper presents a brief review on algal production technology and the main processes such as thermochemical, chemical and biochemical conversion of microalgae becoming energy. Energy conversion using thermochemical, chemical and biochemical con-

version processes will produce biodiesel, bio-oil, ethanol, hydrogen rich gas mixture, and methane, respectively.

2. Biofuels

The term biofuel is referred to as solid, liquid, or gaseous fuels that are predominantly produced from biorenewable feedstocks [24]. There are two global biorenewable liquid transportation fuels: bioethanol and biodiesel. Bioethanol is good alternate fuel that is produced almost entirely from food crops [47–49]. Biodiesel has become more attractive recently because of its environmental benefits [50]. Biofuels can be classified based on their production technologies: first generation biofuels (FGBs); second generation biofuels (SGBs); third generation biofuels (TGBs); and fourth generation biofuels. "Advanced biofuels" include bioethanol made from cellulosic material, hemicelluloses, sugar, starch, and waste, as well as biomass-based biodiesel, biogas, biohydrogen, and other fuels made from cellulosic biomass or other nonfood crops [50,51].

Second and third generation biofuels are also called advanced biofuels. Second generation biofuels made from non food crops, wheat straw, corn, wood, energy crop using advanced technology. Algae fuel, also called oilgae or third generation biofuel, is a biofuel from algae. Algae are low-input, high-yield feedstocks to produce biofuels. Definition of a fourth generation biofuel is crops that are genetically engineered to consume more CO_2 from the atmosphere than they will produce during combustion later as a fuel. Some fourth generation technology pathways include: pyrolysis, gasification, upgrading, solar-to-fuel, and genetic manipulation of organisms to secrete hydrocarbons. On the other hand, an appearing fourth generation is based in the conversion of vegoils and biodiesel into biogasoline using most advanced technology.

Biofuels provide the prospect of new economic opportunities for people in rural areas in oil importer and developing countries. Renewable energy sources that use indigenous resources have the potential to provide energy services with zero or almost zero emissions of both air pollutants and greenhouse gases [52–56]. Biofuels are expected to reduce dependence on imported petroleum with associated political and economic vulnerability, reduce greenhouse

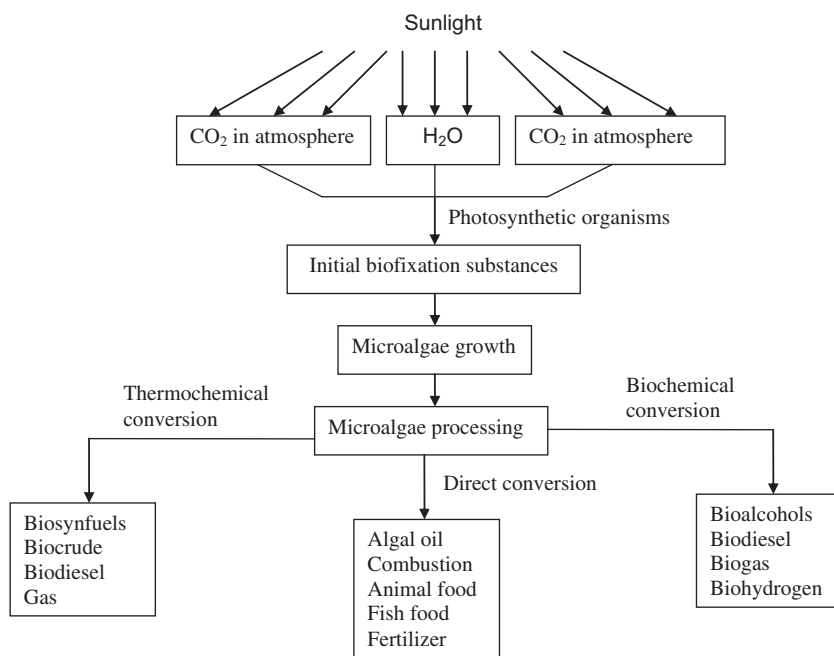


Fig. 1. Carbon dioxide fixation and main steps of algal biomass technologies.

gas emissions and other pollutants, and revitalize the economy by increasing demand and prices for agricultural products [57–59].

Renewable resources, such as waste and virgin biomass, can contribute to shift to energy resources and also can serve as an alternative to raw materials. Waste and virgin biomass such as tree, agricultural crop waste and residues, wood waste and residues, municipal wastes, microalgae, and other waste materials is seen as attractive potential and feasible resource due to cheapness, worldwide abundance, plentiful and renewable basis widely available [56–63].

3. Algae cultivation technology

The algal organisms are photosynthetic macroalgae or microalgae growing in aquatic environments. Algae are simple organisms that are mainly aquatic and microscopic. Microalgae are unicellular photosynthetic micro-organisms, living in saline or freshwater environments that convert sunlight, water and carbon dioxide to algal biomass [30]. They are categorized into four main classes: diatoms, green algae, blue–green algae and golden algae. There are two main species of algae: filamentous and phytoplankton algae. These two species, in particular phytoplankton, increase in numbers rapidly to form algae blooms. Many species exhibit rapid growth and high productivity, and many microalgal species can be induced to accumulate substantial quantities of lipids, often greater than 60% of their dry biomass [43]. Microalgae are very efficient solar energy converters and they can produce a great variety of metabolites.

Industrial reactors for algal culture are at present. There are open ponds, photobioreactors and closed systems. Photobioreactors are different types of tanks or closed systems in which algae are cultivated. Open pond systems are shallow ponds in which algae are cultivated. Nutrients can be provided through runoff water from nearby land areas or by channelling the water from sewage/water treatment plants. Technical and biological limitations of these open systems have given rise to the development of enclosed photoreactors. Microalgae cultivation using sunlight energy can be carried out in open or covered ponds or closed photobioreactors, based on tubular, flat plate or other designs. A few open systems are presented for which particularly reliable results are available. Emphasis is then put on closed systems, which have been considered as capital intensive and are justified only when a fine chemical is to be produced. Microalgae production in closed photobioreactors is highly expensive. Closed systems are much more expensive than ponds. However, the closed systems require much less light and agricultural land to grow the algae. High oil species of microalgae cultured in growth optimized conditions of photobioreactors have the potential to yield 19,000–57,000 liters of microalgal oil per acre per year. The yield of oil from algae is over 200 times the yield from the best-performing plant/vegetable oils [64]. Photobioreactors have the ability to produce algae while performing beneficial tasks, such as scrubbing power plant flue gases or removing nutrients from wastewater.

Algae can also be grown in a photo-bioreactor (PBR). A PBR is a close bioreactor which incorporates some type of light source. A variation on the basic open-pond system is to enclose it with a transparent or translucent barrier. Like this, a pond covered with a greenhouse could be considered as a PBR. Because PBR systems are closed, all essential nutrients must be introduced into the system to allow algae to grow and be cultivated. It is possible to introduce a continuous stream of sterilized water containing nutrients, air and carbon dioxide. As algae grows, excess culture overflows and is harvested.

Macroalgae are classified into three broad groups based on their pigmentation: brown seaweed (*Phaeophyceae*); red seaweed (*Rhodophyceae*) and green seaweed (*Chlorophyceae*). Microalgae

are veritable miniature biochemical factories, and appear more photosynthetically efficient than terrestrial plants and are efficient CO₂ fixers. Microalgae are microscopic organisms that grow in salt or fresh water. The three most important classes of microalgae in terms of abundance are the diatoms (*Bacillariophyceae*), the green algae (*Chlorophyceae*), and the golden algae (*Chrysophyceae*). In this report the cyanobacteria (blue–green algae) (*Cyanophyceae*) are also referred to as micro-algae, this applies for example to *Spirulina* (*Arthrospira platensis* and *Arthrospira maxima*) [65–69].

Open ponds are the oldest and simplest systems for mass cultivation of microalgae. The pond is designed in a raceway configuration, in which a paddlewheel circulates and mixes the algal cells and nutrients. The raceways are typically made from poured concrete, or they are simply dug into the earth and lined with a plastic liner to prevent the ground from soaking up the liquid. Baffles in the channel guide the flow around the bends in order to minimize space. The system is often operated in a continuous mode, i.e., the fresh feed is added in front of the paddlewheel, and algal broth is harvested behind the paddlewheel after it has circulated through the loop.

Fig. 2 shows the open pond systems “algae farms”. The “algae farms” are large ponds. The ponds are “raceway” designs, in which the algae, water and nutrients circulate around a racetrack. Paddlewheels provide the flow. The algae are thus kept suspended in water. Algae are circulated back up to the surface on a regular frequency. The ponds are kept shallow because of the need to keep the algae exposed to sunlight and the limited depth to which sunlight can penetrate the pond water. The ponds are operated continuously; that is, water and nutrients are constantly fed to the pond, while algae-containing water is removed at the other end. The size of these ponds is measured in terms of surface area, since surface area is so critical to capturing sunlight. Their productivity is measured in terms of biomass produced per day per unit of available surface area. Such algae farms would be based on the use of open, shallow ponds in which some source of waste CO₂ could be efficiently bubbled into the ponds and captured by the algae. Careful control of pH and other physical conditions for introducing CO₂ into the ponds allowed greater than 90% utilization of injected CO₂. Raceway ponds, usually lined with plastic or cement, are about 15–35 cm deep to ensure adequate exposure to sunlight. They are typically mixed with paddlewheels, are usually lined with plastic or cement, and are between 0.2 and 0.5 ha in size. Paddlewheels provide motive force and keep the algae suspended in the water. The ponds are supplied with water and nutrients, and mature algae are continuously removed at one end.

Fig. 3 depicts a tubular photobioreactor with parallel run horizontal tubes [27]. A tubular photobioreactor consists of an array of straight transparent tubes that are usually made of plastic or glass. The solar collector tubes are generally 0.1 m or less in diameter. Tube diameter is limited because light does not penetrate too deeply in the dense culture broth that is necessary for ensuring a high biomass productivity of the photobioreactor. Microalgal broth is circulated from a reservoir to the solar collector and back to the reservoir.

Flat-plated photobioreactors are usually made of transparent material. The large illumination surface area allows high photosynthetic efficiency, low accumulation of dissolved oxygen concentration, and immobilization of algae [70]. Rectangular tanks are another example of photobioreactors. Unlike the circular tank design, rectangular tanks do not require a stirring device when a sufficiently high gas velocity is used. Drain pipes and gas spargers are located at the bottom of the tank.

In hybrid systems, both open ponds as well as closed bioreactor system are used in combination to get better results. Open ponds are a very proficient and lucrative method of cultivating algae, but they become contaminated with superfluous species very

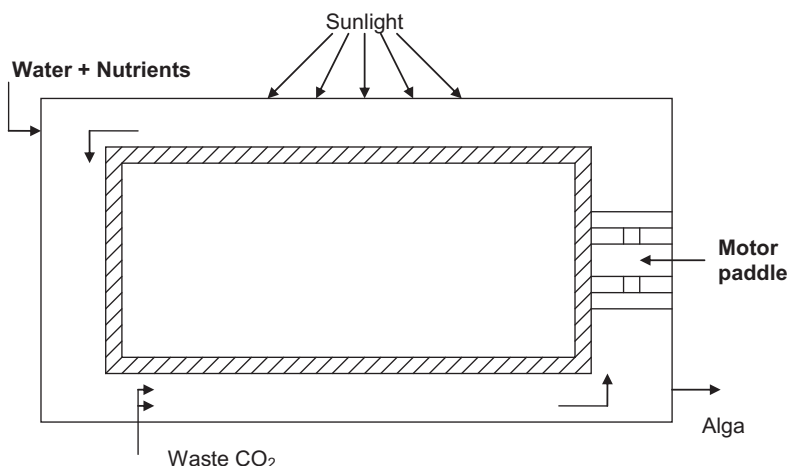


Fig. 2. Open pond system.

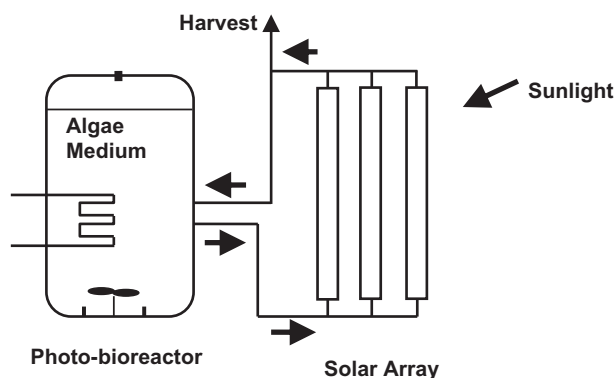


Fig. 3. A tubular photobioreactor with parallel run horizontal tubes.

quickly. A combination of both systems is probably the most logical choice for cost-effective cultivation of high yielding strains for biofuels. Open ponds are inoculated with a desired strain that was invariably cultivated in a bioreactor, whether it be as simple as a plastic bag or a high tech fiber optic bioreactor. Importantly, the size of the inoculums needs to be large enough for the desired species to establish in the open system before an unwanted species. Therefore to minimize contamination issues, cleaning or flushing the ponds should be part of the aquaculture routine, and as such, open ponds can be considered as batch cultures [71–74].

4. Biofuels production from algae

Algae will become the most important biofuel source in the near future. The idea of using microalgae to produce fuel is not new, but it has received renewed attention recently in the search for sustainable energy. Biodiesel is typically produced from plant oils, but there are widely voiced concerns about the sustainability of this practice [29–33].

Biodiesel produced from microalgae is being investigated as an alternative to using conventional crops such as rapeseed; microalgae typically produce more oil, consume less space, and could be grown on land unsuitable for agriculture [75–77]. Using microalgae as a source of biofuels could mean that enormous cultures of algae are grown for commercial production, which would require large quantities of fertilizers [78–80]. While microalgae are estimated to be capable of producing 10–20 times more biodiesel than rapeseed, they need 55–111 times more nitrogen fertilizer – 8 to 16 tons/ha/year.

Advantages and disadvantages of biofuel production using microalgae are shown in Table 1. The high growth rate of microalgae makes it possible to satisfy the massive demand on biofuels using limited land resources without causing potential biomass deficit. Microalgal cultivation consumes less water than land crops. The tolerance of microalgae to high CO_2 content in gas streams allows high-efficiency CO_2 mitigation. Microalgal farming could be potentially more cost effective than conventional farming. Nitrous oxide release could be minimized when microalgae are used for biofuel production [33].

On the other hand, one of the major disadvantages of microalgae for biofuel production is the low biomass concentration in the microalgal culture due to the limit of light penetration, which in combination with the small size of algal cells makes the harvest of algal biomasses relatively costly. The higher capital costs of and the rather intensive care required by a microalgal farming facility compared to a conventional agricultural farm is another factor that impedes the commercial implementation of the biofuels from microalgae strategy.

Main thermochemical processes include liquefaction, pyrolysis and gasification. Hydrocarbons of algal cells have been separated by extraction with organic solvent after freeze-drying and sonicating the algal cells. However, these procedures are not suitable for separation on a large scale because these are costly. Therefore, an effective method is liquefaction for separating hydrocarbons as liquid fuel from harvested algal cells with high moisture content.

The feasibility of producing liquid fuel or bio-oil via pyrolysis or thermochemical liquefaction of microalgae has been demonstrated for a range of microalgae [81–83,35]. Since algae usually have high moisture content, a drying process requires much heating energy [84,85]. A novel energy production system using microalgae with nitrogen cycling combined with low temperature catalytic gasification of the microalgae has been proposed. The gasification process produces combustible gas such as H_2 , CH_4 , CO_2 and ammonia, whereas the product of pyrolysis is bio-oil [84,86,87].

Table 1
Advantages and disadvantages of biofuel production using microalgae.

Advantages	Disadvantages
High growth rate	Low biomass concentration
Less water demand than land crops	Higher capital costs
High-efficiency CO_2 mitigation	
More cost effective farming	

Microalgae were directly liquefied and oil from liquefaction products extracted by dichloromethane (CH_2Cl_2). The liquefaction was performed in an aqueous solution of alkali or alkaline earth salt at about 575 K and 10 MPa [88]. Liquefaction can be performed by using a stainless steel autoclave with mechanical mixing. The direct liquefaction product is extracted with dichloromethane in order to separate the oil fraction. Past research in the use of hydrothermal technology for direct liquefaction of algal biomass was very active. Minowa et al. [88] report an oil yield of about 37% (organic basis) by direct hydrothermal liquefaction at around 575 K and 10 MPa from *Dunaliella tertiolecta* with a moisture content of 78.4 wt%. The oil had viscosity of 150–330 mPas and heating value of 36 MJ/kg.

The liquefaction technique was concluded to be a net energy producer from the energy balance. In a similar study on oil recovery from *Botryococcus braunii*, a maximum yield 64% dry wt. basis of oil was obtained by liquefaction at 575 K catalyzed by sodium carbonate [89]. The hydrothermal liquefaction technique was more effective for extraction of microalgal biodiesel than using the supercritical carbon dioxide [90]. From these two studies, it is reasonable to believe that, among the selected techniques, the hydrothermal liquefaction is the most effective technological option for production of bio-diesel from algae. Nevertheless, due to the level of limited information in the hydrothermal liquefaction of algae, more research in this area would be needed.

Liquefaction of *B. braunii*, a colony-forming microalga, with high moisture content was performed with or without sodium carbonate as a catalyst for conversion into liquid fuel and recovery of hydrocarbons. A greater amount of oil than the content of hydrocarbons in *B. braunii* (50 wt% db) was obtained, in a yield of 57–64 wt% at 575 K. The oil was equivalent in quality to petroleum oil. The recovery of hydrocarbons was a maximum (>95%) at 575 K [91].

Algal cells were liquefied by hexane extraction obtaining for the primary oil. Hexane solubles of the algal cells are shown in Table 2. The yield of the primary oil obtained at 575 K was 52.9% and that at 475 K was 56.5%; these values were a little lower than the yield of the hexane soluble of the raw algal cells. This suggests that hydrocarbons of the raw algal cells were partly converted to dichloromethane insoluble materials such as char [92].

The viscosity of the primary oil obtained at 575 K was as low (94 cP) as that of the hexane soluble of the raw algal cells. However, the viscosity of the primary oil obtained at 475 K was too high to measure it: the primary oil was like a rubber. Therefore, the primary oil obtained at 575 K could be used as fuel oil. The oxygen content of the primary oil obtained at 575 K was a little higher than that of the hexane soluble of the algal cells. However, it was much lower than that of the oil obtained by liquefaction of other biomass [92].

The properties of the hexane soluble of primary oil are shown in Table 3. The yield of the hexane soluble of the primary oil obtained at 575 K was 44% and that at 475 K was 39% on a dry algal cells basis. This meant that the primary oil obtained at 575 K contained 83% of hexane soluble and that at 475 K contained 69% of hexane soluble. The elemental composition of the three hexane solubles was almost equal. The hexane solubles of the primary oil obtained at 575 K and 475 K had good fluidity as well as the hexane soluble of the raw algal cells. In spite of thermal treatment at high temper-

Table 3

Properties of the hexane soluble of algal cells.

Yield (%) ^a	Heating value (MJ/kg)	Viscosity (cP, at 323 K)	Elemental analysis (%)			
			C	H	N	O
58.0	49.4	56.0	84.6	14.5	0.1	0.9

^a On a dry algal cells basis.

ature, the same properties of the hexane soluble of primary oil as that of the hexane soluble of the algal cells [92].

One alga sample (*Cladophora fracta*), and one microalga sample (*Chlorella protothecoides*) were used by Demirbas in the earlier work [93]. The yield of bio-oil from pyrolysis of the samples increased with temperature, as expected. The yields were increased up to 750 K in order to reach the plateau values at 775 K. The maximum yields were 48.2% and 55.3% of the sample for *C. fracta* and *C. protothecoides*, respectively.

The chemical compositions of algae are given in Table 4 [94]. One alga sample (*C. fracta*), and one microalga sample (*C. protothecoides*) were subjected to pyrolysis and steam gasification for producing hydrogen-rich gas.

The yield of bio-oil from pyrolysis of the samples increased with temperature, as expected. The yields were increased up to 750 K in order to reach the plateau values at 775 K. The maximum yields for *C. fracta* and *C. protothecoides* were 45.0% and 50.8% of the sample at 925 K, respectively. Bio-oil comparable to fossil oil was obtained from microalgae [91]. In the pyrolysis process, the yield of charcoal decreases with increasing pyrolysis temperature. The yield of the liquid product is highly excessive at temperatures between 625 and 725 K.

Demirbas reported [93] that the yields of bio-oil by pyrolysis from alga samples (Table 5). As can be seen from Table 5, the

Table 4

Chemical compositions of algae on a dry matter basis (%).

Species of sample	Proteins	Carbohydrates	Lipids	Nucleic acid
<i>Scenedesmus obliquus</i>	50–56	10–17	12–14	3–6
<i>Scenedesmus quadricauda</i>	47	–	1.9	–
<i>Scenedesmus dimorphus</i>	8–18	21–52	16–40	–
<i>Chlamydomonas reinhardtii</i>	48	17	21	–
<i>Chlorella vulgaris</i>	51–58	12–17	14–22	4–5
<i>Chlorella pyrenoidosa</i>	57	26	2	–
<i>Spirogyra sp.</i>	6–20	33–64	11–21	–
<i>Dunaliella bioculata</i>	49	4	8	–
<i>Dunaliella salina</i>	57	32	6	–
<i>Euglena gracilis</i>	39–61	14–18	14–20	–
<i>Prymnesium parvum</i>	28–45	25–33	22–38	1–2
<i>Tetraselmis maculata</i>	52	15	3	–
<i>Porphyridium cruentum</i>	28–39	40–57	9–14	–
<i>Spirulina platensis</i>	46–63	8–14	4–9	2–5
<i>Spirulina maxima</i>	60–71	13–16	6–7	3–4.5
<i>Synechococcus sp.</i>	63	15	11	5
<i>Anabaena cylindrica</i>	43–56	25–30	4–7	–

Table 2

Properties of microalga used for liquefaction.

Moisture content (%)	Dry solid (%)	Ash (%) ^a	Organics (%) ^a	Elemental analysis (%) ^a			
				C	H	N	O
92.0	8.0	2.0	98.0	68.7	10.9	1.3	19.1

^a On a dry algal cells basis.

Table 5
Yields of bio-oil by pyrolysis from alga samples at different temperatures (K).

Sample	575	625	675	725	775	825	875
<i>Cladophora fracta</i>	10.5	23.5	33.2	43.4	48.2	46.8	44.6
<i>Chlorella protothecoides</i>	12.8	27.4	38.4	50.2	55.3	53.7	51.6

bio-oil yield for *C. protothecoides* (a microalga sample) rose from 12.8% to 55.3% as the temperature rose from 575 to 775 K, and then gradually decreased to 51.8% was obtained at 875 K with a heating rate of 10 K/s [90]. For alga, maximum bio-oil yields of between 48.2% and 46.8%, and for alga 55.3% and 53.7% were obtained at temperature ranging from 775 to 825 K, whereas for wood, cotton stalk, tobacco stalk and sunflower bagasse, maximum oil yields between 39.7% and 49.4% were obtained at temperature in the range 775–825 K [95,96].

Demirbas reported [93] that the yields the yields of gaseous product by pyrolysis from moss and alga samples (Table 6). From Tables 5 and 6, the yields of gaseous products for *C. protothecoides* increased from 9.5% to 39.5% as the temperature rose from 575 to 875 K.

At high pressure, wet algal biomass can be converted into pyrolysis oil, synthesis gas (a CO/H₂ mixture) or natural gas (CH₄), processes still being developed [97]. A novel energy production system using microalgae with nitrogen cycling combined with low temperature catalytic gasification of the microalgae has been proposed. The gasification process produces combustible gas such as H₂, CH₄, CO₂ and ammonia, whereas the product of pyrolysis is bio-oil [84,87,98].

Stucki et al. [99] proposed a novel process based on microalgae cultivation using dilute fossil CO₂ emissions and the conversion of the algal biomass through a catalytic hydrothermal process. They showed that complete gasification of microalgae (*Spirulina platensis*) to a methane-rich gas is now possible in supercritical water using ruthenium catalysts [99].

The project was developed by Elliot et al. [97] an understanding of catalytic hydrothermal gasification as applied to feedstocks generated in biorefinery applications and algae. The gasification reactor was a 1-inch ID X 72-inch-long 304 SS tube. The gas product recovered was typical of catalytic hydrothermal gasification: 59%–62% methane, 36%–40% carbon dioxide and 1% hydrogen. Four tests were performed using different algae feedstocks provided by Genifuel. Dried solids were provided in the first three tests and a dewatered material in the fourth. This material was mixed with additional water to process through our wet mill to make the feed slurry. The test was performed at 350 °C and 204 atm. The Ru/C gasification catalyst was used with a pelletized Raney nickel sulfur scrubbing bed [97].

With interaction of water and char from decomposition of biomass intermediate products occurs which leads to more hydrogen-rich gas yield by the steam reforming. The pyrolysis was carried out at the moderate temperatures and steam gasification at the highest temperatures. In order to clarify the steam gasification mechanism in detail, more kinetic study is necessary. These results suggest that the fundamental information obtained in the gasification of each component could possibly be used to predict the composition of product gas generated in air–steam gasification of biomass.

Table 6
Yields of gaseous product by pyrolysis from alga samples at different temperatures (K).

Sample	575	625	675	725	775	825	875
<i>Cladophora fracta</i>	8.2	19.7	28.2	32.6	35.7	38.0	39.7
<i>Chlorella protothecoides</i>	9.5	21.8	29.5	33.7	36.3	38.1	39.5

Microalgae contain oils, or 'lipids', that can be converted into biodiesel. Biodiesel is typically produced from plant oils, but there are widely-voiced concerns about the sustainability of this practice. Biodiesel produced from microalgae is being investigated as an alternative to using conventional crops, such as rapeseed: microalgae typically produce more oil, consume less space and could be grown on land unsuitable for agriculture. However, many technical and environmental issues, such as land use and fertilizer input still need to be researched and large-scale commercial production has still not been attained [33].

Using microalgae as a source of biofuels could mean that enormous cultures of algae are grown for commercial production, which would require large quantities of fertilizers. While microalgae are estimated to be capable of producing 10–20 times more biodiesel than rapeseed, they need 55–111 times more nitrogen fertilizer: 8–16 tons/ha/year. Such quantities of nitrogen and phosphorus could damage the environment.

Microalgae contain lipids and fatty acids as membrane components, storage products, metabolites and sources of energy. Algae present an exciting possibility as a feedstock for biodiesel, and when you realize that oil was originally formed from algae.

Transesterification is a process of exchanging the alkoxy group of an ester compound by another alcohol. Transesterification is the reaction of a fat or oil with an alcohol to form esters and glycerol. The algal oil is converted into biodiesel through a transesterification process. Oil extracted from the algae is mixed with alcohol and an acid or a base to produce the fatty acid methylesters that makes up the biodiesel [74].

Many algae are exceedingly rich in oil, which can be converted to biodiesel. The oil content of some microalgae exceeds 80% of dry weight of algae biomass. The use of algae as energy crops has potential, due to their easy adaptability to growth conditions, the possibility of growing either in fresh- or marine-waters and avoiding the use of land. Furthermore, two thirds of earth's surface is covered with water, thus algae would truly be renewable option of great potential for global energy needs [33].

Fermentation is used commercially on a large scale in various countries to produce ethanol from sugar crops and starch crops. Chemical reaction is composed of enzymatic hydrolysis of sucrose followed by fermentation of simple sugars. Fermentation of sucrose is performed using commercial yeast such as *Saccharomyces cerevisiae*. Gluco-amylase enzyme converts the starch into D-glucose. The enzymatic hydrolysis is then followed by fermentation, distillation and dehydration to yield anhydrous bioethanol. Corn (60–70% starch) is the dominant feedstock in starch-to-bioethanol industry worldwide.

The algal biomass is ground, and the starch is converted by enzymes to sugar. The sugar is converted to ethanol by yeast. Production of ethanol by using microalgal as raw material can be performed according to the following procedure. In the first step, the starch of microalgae is released from the cells with the aid of mechanical equipment or an enzyme. When the cells begin to degrade, *Saccharomyces cerevisiae* yeast is added to the biomass to begin fermentation. The product of fermentation is ethanol. The ethanol is drained from the tank and pumped to a holding tank to be fed to a distillation unit. Ethanol was produced with microalgal photosynthesis and intracellular anaerobic fermentation [100–102].

5. Conclusion

Microalgae are photosynthetic microorganisms that can produce lipids, proteins and carbohydrates in large amounts over short periods of time. These products can be processed into both biofuels and useful chemicals.

It has been reviewed main processes such as thermochemical, chemical and biochemical conversion of microalgae becoming energy. Energy conversion using thermochemical, chemical and biochemical conversion processes will produce bio-oil, biodiesel, ethanol, and hydrogen-rich gas mixture [103]. This paper describes hydrogen production from biomass such as moss and algae by laboratory-scale tests of pyrolysis and steam-gasification. The conversion of biomass into hydrogen is interested in the viewpoint of hydrogen production from renewable resource.

The yields of hydrogen from biomass by the pyrolysis and the steam gasification increase with increasing of temperature. In general, the steam gasification temperature is higher than that of pyrolysis and the yield of hydrogen from the air–steam gasification is higher than that of the pyrolysis.

Industrial reactors for algal culture are open ponds, photobioreactors and closed systems. Algae are very important as a biomass source. Algae will someday be competitive as a source for biofuel. Different species of algae may be better suited for different types of fuel. Algae can be grown almost anywhere, even on sewage or salt water, and does not require fertile land or food crops, and processing requires less energy than the algae provides.

Most current research on oil extraction is focused on microalgae to produce biodiesel from algal-oil. Algal-oil processes into biodiesel as easily as oil derived from land-based crops. Algae biomass can play an important role in solving the problem between the production of food and that of biofuels in the near future. Most current research on oil extraction is focused on microalgae to produce biodiesel from algal-oil. Algal-oil processes into biodiesel as easily as oil derived from land-based crops.

References

- [1] Yan J, Lin T. Biofuels in Asia. *Appl Energy* 2009;86:S1–S10.
- [2] Hertel TW, Tyner WE, Birur DP. The global impacts of biofuel mandates. *Energy J* 2010;31:75–100.
- [3] Yumurtaci M, Kecebas A. Renewable energy and its university level education in Turkey. *Energy Educ Sci Technol Part B* 2011;3:143–52.
- [4] Yee KF, Tan KT, Abdullah AZ, Lee KT. Life cycle assessment of palm biodiesel: revealing facts and benefits for sustainability. *Appl Energy* 2009;86:S189–96.
- [5] Demirbas A. Political, economic and environmental impacts of biofuels: a review. *Appl Energy* 2009;86:S108–17.
- [6] Sahin Y. Environmental impacts of biofuels. *Energy Educ Sci Technol Part A* 2011;26:129–42.
- [7] Demirbas A. Progress and recent trends in biodiesel fuels. *Energy Convers Manage* 2009;50:14–34.
- [8] Calik M. How did creating a constructivist learning environment influence my graduate students' views? *Energy Educ Sci Technol Part B* 2011;3:1–13.
- [9] Tian Y, Zhao L, Meng H, Sun L, Yan J. Estimation of un-used land potential for biofuels development in (the) People's Republic of China. *Appl Energy* 2010;86:S77–85.
- [10] Demirbas AH. Biofuels for future transportation necessity. *Energy Educ Sci Technol Part A* 2010;26:13–23.
- [11] Demirbas A. Social, economic, environmental and policy aspects of biofuels. *Energy Educ Sci Technol Part B* 2010;2:75–109.
- [12] Kecebas A, Alkan MA. Educational and consciousness-raising movements for renewable energy in Turkey. *Energy Educ Sci Technol Part B* 2009;1:157–70.
- [13] Demirbas A. Concept of energy conversion in engineering education. *Energy Educ Sci Technol Part B* 2009;1:183–97.
- [14] Cardak O. The determination of the knowledge level of science students on energy flow through a word association test. *Energy Educ Sci Technol Part B* 2009;1:139–55.
- [15] Balat H. Prospects of biofuels for a sustainable energy future: a critical assessment. *Energy Educ Sci Technol Part A* 2010;24:85–111.
- [16] Demirbas A. Progress and recent trends in biofuels. *Prog Energy Combust Sci* 2007;33:1–18.
- [17] Demirbas B. Biomass business and operating. *Energy Educ Sci Technol Part A* 2010;26:37–47.
- [18] Arpa O, Yumurtas R, Demirbas A. Production of diesel-like fuel from waste engine oil by pyrolytic distillation. *Appl Energy* 2010;87:122–7.
- [19] Kirtay E. The role of renewable energy sources in meeting Turkey's electrical energy demand. *Energy Educ Sci Technol Part A* 2009;23:15–30.
- [20] Phalan B. The social and environmental impacts of biofuels in Asia: an overview. *Appl Energy* 2009;86:S21–9.
- [21] Prabhakar SVRK, Elder M. Biofuels and resource use efficiency in developing Asia: back to basics. *Appl Energy* 2009;86:S30–6.
- [22] Demirbas A. Competitive liquid biofuels from biomass. *Appl Energy* 2011;88:17–28.
- [23] Demirbas MF. Biorefineries for biofuel upgrading: a critical review. *Appl Energy* 2009;86:S151–61.
- [24] Aksoy F, Bayrakceken H, Eryilmaz T, Aksoy L. Analyzing the impact of using different methyl esters in a diesel engine on engine performance and emissions. *Energy Educ Sci Technol Part A* 2011;27:25–34.
- [25] Balat M, Balat H. Recent trends in global production and utilization of bio-ethanol fuel. *Appl Energy* 2009;86:2273–82.
- [26] Demirbas A. Energy concept and energy education. *Energy Educ Sci Technol Part B* 2009;1:85–101.
- [27] Kita K, Okada S, Sekino H, Imou K, Yokoyama S, Amano T. Thermal pretreatment of wet microalgae harvest for efficient hydrocarbon recovery. *Appl Energy* 2010;87:2420–3.
- [28] Demirbas AH. Inexpensive oil and fats feedstocks for production of biodiesel. *Energy Educ Sci Technol Part A* 2009;23:1–13.
- [29] Ozkurt I. Qualifying of safflower and algae for energy. *Energy Educ Sci Technol Part A* 2009;23:145–51.
- [30] Demirbas MF. Microalgae as a feedstock for biodiesel. *Energy Educ Sci Technol Part A* 2010;25:31–43.
- [31] Demirbas A. Production of biodiesel from algae oils. *Energy Source Part A* 2009;31:163–8.
- [32] Demirbas A, Demirbas MF. Algae energy: algae as a new source of biodiesel. London: Springer-Verlag; 2010.
- [33] Chaumont D. Biotechnology of algal biomass production: a review of systems for outdoor mass culture. *J Appl Phycol* 2005;5:593–604.
- [34] Tsukahara K, Sawayama S. Liquid fuel production using microalgae. *J Jpn Petrol Inst* 2005;48:251–9.
- [35] Ertaş M, Alma MH. Slow pyrolysis of chinaberry (*Melia azedarach* L.) seeds: characterization of bio-oils and bio-chars. *Future Energy Source* 2010;2:149–70.
- [36] Balat M, Balat H. Progress in biodiesel processing. *Appl Energy* 2010;87:1815–35.
- [37] Miao XL, Wu QY, Yang CY. Fast pyrolysis of microalgae to produce renewable fuels. *J Anal Appl Pyrol* 2004;71:855–63.
- [38] Balat H. Social, political and economic impacts of biodiesel. *Social Polit Econ Cult Res* 2009;1:89–125.
- [39] Xu H, Miao X, Wu Q. High quality biodiesel production from a microalga *Chlorella protothecoides* by heterotrophic growth in fermenters. *J Biotechnol* 2006;126:499–507.
- [40] Keskin A, Emiroglu AO. Catalytic reduction techniques for post-combustion diesel engine exhaust emissions. *Energy Educ Sci Technol Part A* 2010;25:87–103.
- [41] Gao C, Zhai Y, Ding Y, Wu Q. Application of sweet sorghum for biodiesel production by heterotrophic microalga *Chlorella protothecoides*. *Appl Energy* 2010;87:756–61.
- [42] Schenk PM, Thomas-Hall SR, Stephens E, Marx U, Mussgnug JH, Posten C, et al. Second generation biofuels: high-efficiency microalgae for biodiesel production. *Bioenergy Res* 2008;1:20–43.
- [43] Brennan L, Owende P. Biofuels from microalgae – a review of technologies for production, processing, and extractions of biofuels and co-products. *Renew Sustain Energy Rev* 2010;14:557–77.
- [44] Mata TM, Martins AA, Caetano NS. Microalgae for biodiesel production and other applications: a review. *Renew Sustain Energy Rev* 2010;14:217–32.
- [45] Scott SA, Davey MP, Dennis JS, Horst I, Howe CJ, Lea-Smith DJ, et al. Biodiesel from algae: challenges and prospects. *Current Opin Biotechnol* 2010;21:277–86.
- [46] Hammond GP, Kallu S, McManus MC. Development of biofuels for the UK automotive market. *Appl Energy* 2008;85:506–15.
- [47] Tan RR, Foo DCY, Aviso KB, Ng DKS. The use of graphical pinch analysis for visualizing water footprint constraints in biofuel production. *Appl Energy* 2009;86:605–9.
- [48] Börjesson P. Good or bad bioethanol from a greenhouse gas perspective – what determines this? *Appl Energy* 2009;86:589–94.
- [49] Altun S. Fuel properties of biodiesels produced from different feedstocks. *Energy Educ Sci Technol Part A* 2011;26:165–74.
- [50] Ertaş M, Alma MH. Slow pyrolysis of chinaberry (*Melia azedarach* L.) seeds. Part I: the influence of pyrolysis parameters on the product yields. *Energy Educ Sci Technol Part A – Energy Sci Res* 2011;26:143–54.
- [51] Najafi G, Ghobadian B, Tavakoli T, Buttsworth DR, Yusaf TF, Faizollahnejad M. Performance and exhaust emissions of a gasoline engine with ethanol blended gasoline fuels using artificial neural network. *Appl Energy* 2009;86:630–9.
- [52] Dennis Y, Leung C, Wu X, Leung MKH. A review on biodiesel production using catalyzed transesterification. *Appl Energy* 2010;87:1083–95.
- [53] Taleghani M, Ansari HR, Jennings P. Renewable energy education in sustainable architecture: lessons from developed and developing countries. *Energy Educ Sci Technol Part B* 2010;2:111–31.
- [54] Kan A. General characteristics of waste management: a review. *Energy Educ Sci Technol Part A* 2009;23:55–69.
- [55] Yumurtaci M, Kecebas A. Renewable energy and its university level education in Turkey. *Energy Educ Sci Technol Part B* 2011;3:143–52.
- [56] Darici B, Ocal FM. The structure of European financial system and financial integration. *Energy Educ Sci Technol Part B* 2010;2:133–45.
- [57] Tatli ZH. Computer based education: Online learning and teaching facilities. *Energy Educ Sci Technol Part B* 2009;1:171–81.

- [59] Balat H. Prospects of biofuels for a sustainable energy future: a critical assessment. *Energy Educ Sci Technology Part A* 2010;24:85–111.
- [60] Qi DH, Chen H, Geng LM, Bian YZH, Ren XCH. Performance and combustion characteristics of biodiesel–diesel–methanol blend fuelled engine. *Appl Energy* 2010;87:1679–86.
- [61] Leduc S, Natarajan K, Dotzauer E, McCallum I, Obersteiner M. Optimizing biodiesel production in India. *Appl Energy* 2009;86:S125–31.
- [62] Mahlia TMI, Saidur R, Husnawan M, Masjuki HH, Kalam MA. An approach to estimate the life-cycle cost of energy efficiency improvement of room air conditioners. *Energy Educ Sci Technol Part A* 2010;26:1–11.
- [63] Sahin Y. Environmental impacts of biofuels. *Energy Educ Sci Technol Part A* 2011;26:29–142.
- [64] Chisti Y. Biodiesel from microalgae. *Biotechnol Adv* 2007;25:294–306.
- [65] Matsumoto N, Sano D, Elder M. Biofuel initiatives in Japan: Strategies, policies, and future potential. *Appl Energy* 2009;86:S69–76.
- [66] Tian Y, Zhao L, Meng H, Sun L, Yan J. Estimation of un-used land potential for biofuels development in (the) People's Republic of China. *Appl Energy* 2009;86:S77–85.
- [67] Yang J, Huang J, Qiu H, Rozelle S, Sombilla MA. Biofuels and the Greater Mekong Subregion: Assessing the impact on prices, production and trade. *Appl Energy* 2009;86:S37–46.
- [68] Malik US, Ahmed M, Sombilla MA, Cuono SL. Biofuels production for smallholder producers in the Greater Mekong Sub-region. *Appl Energy* 2009;86:S58–68.
- [69] Zhou A, Thomson E. The development of biofuels in Asia. *Appl Energy* 2009;86:S11–20.
- [70] Ugwu CU, Aoyagi H, Uchiyama H. Photobioreactors for mass cultivation of algae. *Biore Technol* 2008;99:4021–8.
- [71] Williamson A-M, Badr O. Assessing the viability of using rape methyl ester (RME) as an alternative to mineral diesel fuel for powering road vehicles in the UK. *Appl Energy* 2010;59:187–214.
- [72] Ganapathy T, Murugesan K, Gakkhar RP. Performance optimization of *Jatropha* biodiesel engine model using Taguchi approach. *Appl Energy* 2010;86:2476–86.
- [73] Wen Z, Yu X, Tu S-T, Yan J, Dahlquist E. Synthesis of biodiesel from vegetable oil with methanol catalyzed by Li-doped magnesium oxide catalysts. *Appl Energy* 2010;87:743–8.
- [74] Altun S. Performance and emission characteristics of a diesel engine fueled with biodiesel obtained from a hybrid feedstock. *Energy Educ Sci Technol Part A* 2011;27:79–86.
- [75] Huang G, Chen F, Wei D, Zhang X, Chen G. Biodiesel production by microalgal biotechnology. *Appl Energy* 2010;87:38–46.
- [76] Thamsirirot J, Murphy JD. Is it better to import palm oil from Thailand to produce biodiesel in Ireland than to produce biodiesel from indigenous Irish rape seed? *Appl Energy* 2009;86:595–604.
- [77] Hazar H, Aydin H. Performance and emission evaluation of a CI engine fueled with preheated raw rapeseed oil (RRO)-diesel blends. *Appl Energy* 2010;87:786–90.
- [78] Divakara BN, Upadhyaya HD, Wani SP, Gowda CLL. Biology and genetic improvement of *Jatropha curcas* L.: a review. *Appl Energy* 2010;87:732–42.
- [79] Becker EW. In: Baddiley J et al., editors. *Microalgae: biotechnology and microbiology*. Cambridge, New York: Cambridge Univ. Press; 1994.
- [80] Banerjee A, Sharma R, Chisti Y, Banerjee UC. *Botryococcus braunii*: a renewable source of hydrocarbons and other chemicals. *Critic Rev Biotechnol* 2002;22:245–79.
- [81] Sawayama S, Inoue S, Yokoyama S. Continuous culture of hydrocarbon-rich microalga *Botryococcus braunii* in secondarily treated sewage. *Appl Microbiol Biotechnol* 1994;41:729–31.
- [82] Peng WM, Wu QY, Tu PG. Effects of temperature and holding time on production of renewable fuels from pyrolysis of *Chlorella protothecoides*. *J Appl Phycol* 2000;12:147–52.
- [83] Sawayama S, Minowa T, Yokoyama SY. Possibility of renewable energy production and CO₂ mitigation by thermochemical liquefaction of microalgae. *Biomass Bioenergy* 1999;17:33–9.
- [84] Minowa T, Sawayama S. A novel microalgal system for energy production with nitrogen cycling. *Fuel* 1999;78:1213–5.
- [85] Yang YF, Feng CP, Inamori Y, Maekawa T. Analysis of energy conversion characteristics in liquefaction of algae. *Res Conser Recyc* 2004;43:21–33.
- [86] Cohen E, Koren A, Arad SM. A closed system for outdoor cultivation of microalgae. *Biomass Bioenergy* 1991;1:83–8.
- [87] Chisti Y. Microalgae as sustainable cell factories. *Environ Eng Manage J* 2006;5:261–74.
- [88] Minowa T, Yokoyama S-Y, Kishimoto M, Okakura T. Oil production from algal cells of *dunaliella tertiolecta* by direct thermochemical liquefaction. *Fuel* 1995;74:1735–8.
- [89] Sawayama S, Inoue S, Dote Y, Yokoyama S-Y. CO₂ fixation and oil production through microalga. *Energy Convers Manage* 1995;36:729–31.
- [90] Aresta M, Dibenedetto A, Barberio G. Utilization of macro-algae for enhanced CO₂ fixation and biofuels production: Development of a computing software for an LCA study. *Fuel Proc Technol* 2005;86:1679–93.
- [91] Banerjee A, Harma RS, Chisti Y, Banerjee UC. *Botryococcus braunii*: A renewable source of hydrocarbons and other chemicals. *Critic Rev Biotechnol* 2002;22:245–79.
- [92] Dote Y, Sawayama S, Yokoyama S. Liquefaction of hydrocarbon-rich microalga. National Institute for Resources and Environment 16-3 Onogawa. Tsukuba, Ibaraki 305, Japan; 1995.
- [93] Demirbas A. Oily products from mosses and algae via pyrolysis. *Energy Edu Sci Technol Part A* 2006;28:933–40.
- [94] Pimentel D, Marklein A, Toth MA, Karpoff M, Paul GS, McCormack R, et al. Biofuel impacts on world food supply: use of fossil fuel, land and water resources. *Energies* 2008;1:41–78.
- [95] Putun AE. Biomass to bio-oil via fast pyrolysis of cotton straw and stalk. *Energy Source* 2002;24:275–85.
- [96] Gercel HF. The effect of a sweeping gas flow rate on the fast pyrolysis of biomass. *Energy Source* 2002;24:633–42.
- [97] Elliott DC, Neuenschwander GG, Hart TR, Rotness LJ, Zacher AH, Santosa DM, et al. Catalytic hydrothermal gasification of lignin-rich biorefinery residues and algae. US Department of Energy, Pacific Northwest National Laboratory Richland: Washington; October 2009.
- [98] Cohen E, Koren A, Arad SM. A closed system for outdoor cultivation of microalgae. *Biomass Bioenergy* 1991;1:83–8.
- [99] Stucki S, Vogel F, Ludwig C, Haiduc AG, Brandenberger M. Catalytic gasification of algae in supercritical water for biofuel production and carbon capture. *Energy Environ Sci* 2009;2:535–41.
- [100] Hirano A, Ueda R, Hirayama S. CO₂ fixation and ethanol production with microalgal photosynthesis and intracellular anaerobic fermentation. *Energy* 1997;22:137–42.
- [101] Pimentel D. Ethanol fuels: energy balance, economics, and environmental impacts are negative. *Natural Res Res* 2003;12:127–34.
- [102] Pimentel D, Patzek TW. Ethanol production using corn, switchgrass, and wood; biodiesel production using soybean and sunflower. *Natural Res Res* 2005;14:65–76.
- [103] Sheth PN, Babu BV. Experimental studies on producer gas generation from wood waste in a downdraft biomass gasifier. *Biores Technol* 2009;100:3127–33.