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Use of algae as biofuel sources

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ABSTRACT

The aim of this study is to investigate the algae production technologies such as open, closed and hybrid systems, production costs, and algal energy conversions. Liquid biofuels are alternative fuels promoted with potential to reduce dependence on fossil fuel imports. Biofuels production costs can vary widely by feedstock, conversion process, scale of production and region. Algae will become the most important biofuel source in the near future. 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 bio-oil, bioethanol, bio-hydrogen and bimethane via thermochemical and biochemical methods. Microalgae are theoretically very promising source of biodiesel.

1. Introduction

The world has been confronted with an energy crisis due to depletion of finite resources of fossil fuel. The use of fossil fuels as energy is now widely accepted as unsustainable due to depleting resources and also due to the accumulation of greenhouse gases in the environment. Biomass provides a number of local environmental gains [1–3]. The thermochemical transformation of biomass generates gases, liquids and solid fuels. Among all the procedures used to transform biomass into useful products, liquefaction, pyrolysis and gasification are the most appropriate methods [4].

Amongst the renewable energies, one of the most important energy sources in near future is biomass. Biofuel is a renewable energy source produced from biomass, which can be used as a substitute for petroleum fuels. The benefits of biofuels over traditional fuels include greater energy security, reduced environmental impact, foreign exchange savings, and ü socioeconomic issues [5–7].

Billions of years ago the earth atmosphere was filled with CO_2. Thus there was no life on earth. Life on earth started with *Cyanobacterium* and algae. These humble photosynthetic organisms sucked the atmospheric CO_2 and started releasing oxygen. As a result, the levels of CO_2 started decreasing to such an extent that life evolved on earth. Once again these smallest organisms are poised to save us from the threat of global warming.

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 [8]. There are two main populations of algae: filamentous and phytoplankton algae. They are categorized into four main classes: diatoms, green algae, blue–green algae and golden algae.

The algal organisms are photosynthetic macroalgae or microalgae growing in aquatic environments. Macroalgae are classified into three broad groups based on their pigmentation: (1) brown seaweed (*Phaeophyceae*); (2) red seaweed (*Rhodophyceae*) and (3) green seaweed (*Chlorophyceae*).

Microalgae are microscopic photosynthetic organisms that are found in both marine and freshwater environments. Biologists have categorized microalgae in a variety of classes, mainly distinguished by their pigmentation, life cycle and basic cellular structure. The three most important classes of microalgae in terms of abundance are the diatoms (*Bacillariophyceae*), the green algae (*Chlorophyceae*), and the golden algae (*Chrysophyceae*). The cyanobacteria (blue–green algae) (*Cyanophyceae*) are also referred to as microalgae. This applies for example to Spirulina (*Arthrospira platensis* and *Arthrospira maxima*). Diatoms are the dominant life form in phytoplankton and probably represent the largest group of biomass producers on earth. Minimal nutritional requirements can be estimated using the approximate molecular formula of the microalgal biomass that is $CO_{0.48}H_{1.83}N_{0.11}P_{0.01}$. This formula is based on data presented by Grobbelaar [9].

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. Closed systems are much more

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expensive than ponds, and present significant operating challenges, and due to gas exchange limitations, among others, cannot be scaled-up much beyond about a hundred square meters for an individual growth unit.

Nutrients can be provided through runoff water from nearby land areas or by channelling the water from sewage/water treatment plants. Microalgae cultivation using sunlight energy can be carried out in open or covered ponds or closed photobioreactors. Algal cultures consist of a single or several specific strains optimized for producing the desired product. Water, necessary nutrients and CO_2 are provided in a controlled way, while oxygen has to be removed [10]. Algae receive sunlight either directly through the transparent container walls or via light fibers or tubes that channel it from sunlight collectors. A great amount of developmental work to optimize different photobioreactor systems for algae cultivation has been carried out and is reviewed [11–14].

Microalgae are a potential source of renewable energy, and they can be converted into energy such as biofuel oil and gas [15]. Since microalgae have high water content, not all biomass energy conversion processes can be applied. By using thermochemical processes, oil and gas can be produced, and by using biochemical processes, ethanol, biodiesel and bio-hydrogen can be produced [15].

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 conversion processes will produce bio-oil, biodiesel, and ethanol, methane and hydrogen, respectively.

2. Algae production technology

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.

Open pond systems are shallow ponds in which algae are cultivated. Nutrients can be provided through runoff water from nearby land areas or by channeling the water from sewage/water treatment plants [10]. The water is typically kept in motion by paddle wheels or rotating structures, and some mixing can be accomplished by appropriately designed guides. Algal cultures can be defined (one or more selected strains), or are made up of an undefined mixture of strains [16,17]. The only practicable methods of large-scale production of microalgae are raceway ponds [18,19] and tubular photobioreactors [19–21].

Fig. 1 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 CO_2 could be efficiently bubbled into the ponds and captured by the algae. Careful control of pH and other physical conditions for introducing CO_2 into the ponds allowed greater than 90% utilization of injected CO_2. 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 hectares 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 [22].

Raceway ponds for mass culture of microalgae have been used since the 1950s. Extensive experience exists on operation and engineering of raceways. The largest raceway-based biomass production facility occupies an area of 440,000 m^2 [23]. Productivity is affected by contamination with unwanted algae and micro-organisms that feed on algae. Raceway ponds and other open culture systems for producing microalgae are further discussed by Terry and Raymond [18].

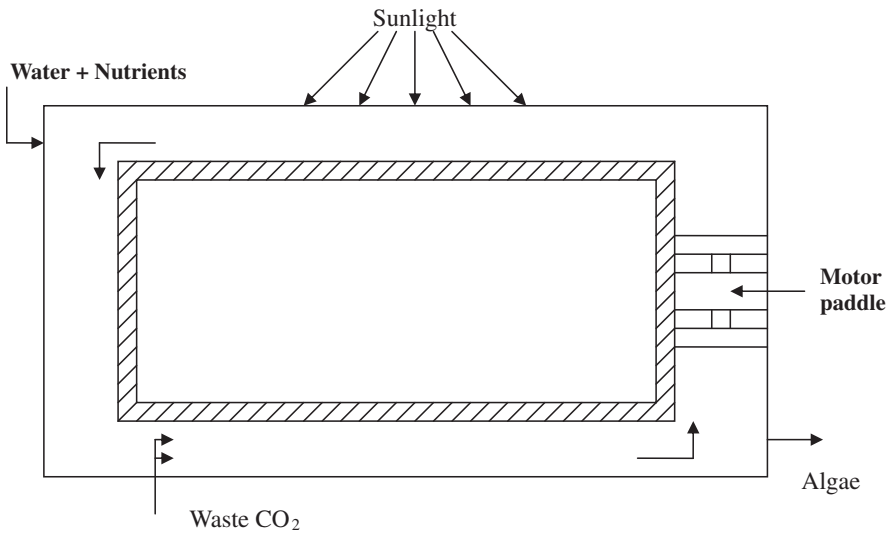

Fig. 1. Open pond system.

Photobioreactors have the ability to produce algae while performing beneficial tasks, such as scrubbing power plant flue gases or removing nutrients from wastewater [10]. Photobioreactors are different types of tanks or closed systems in which algae are cultivated [22].

Most of algal species are obligate phototrophs and thus require light for their growth. The phototropic microalgae are most commonly grown in open ponds and photobioreactors [24]. The open pond cultures are economically more favorable, but raise the issues of land use cost, water availability, and appropriate climatic conditions. Photobioreactors offer a closed culture environment, which is protected from direct fallout, relatively safe from invading micro-organisms. This technology is relatively expensive compared to the open ponds because of the infrastructure costs. An ideal biomass production system should use the freely available sunlight.

Photobioreactors have higher efficiency and biomass concentration (2–5 g/L), shorter harvest time (2–4 weeks), and higher surface-to-volume ratio (25–125/m) than open ponds [25,26]. Closed systems consist of numerous designs: tubular, flat-plated, rectangular, continued stirred reactors, etc. Regulation of carbon dioxide and dissolved oxygen levels in the bioreactor is another key element to algal growth. The highest cost for closed system is the energy cost associated with the mixing mechanism [27].

Tubular photobioreactors consist of transparent tubes that are made of flexible plastic or glass. Tubes can be arranged vertically, horizontally, inclined, helical, or in a horizontal thin-panel design. Tubes are generally placed in parallel to each other or flat above the ground to maximize the illumination surface-to-volume ratio of the reactor. The diameter of tubes is usually small and limited (0.2 m diameter or less) to allow light penetration to the center of the tube where the light coefficient and linear growth rate of culture decrease with increasing unit diameter [28,29]. Growth medium circulates from a reservoir to the reactor and back to the reservoir. A turbulent flow is maintained in the reactor to ensure distribution of nutrients, improve gas exchange, minimize cell sedimentation, and circulate biomass for equal illumination between the light and dark zones.

Fig. 2 depicts s tubular photobioreactor with parallel run horizontal tubes [30]. A tubular photobioreactor consists of an array of straight transparent tubes that are usually made of plastic or glass. This tubular array, or the solar collector, is where the sunlight is captured as seen in Fig. 2. 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.

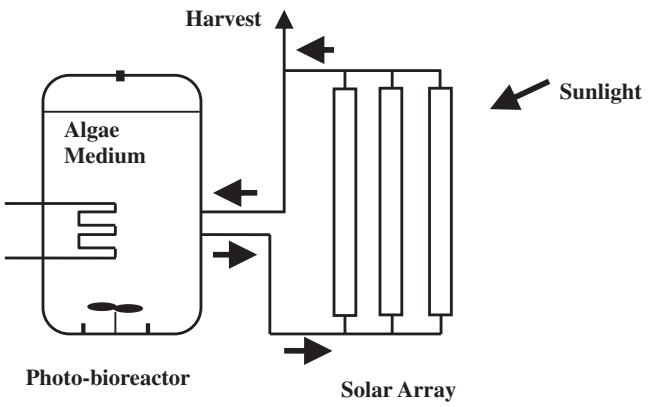

Fig. 2. A tubular photobioreactor with parallel run horizontal tubes.

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 [31]. The reactors are inexpensive and easy to construct and maintain. However, the large surface area presents scale-up problems, including difficulties in controlling culture temperature and carbon dioxide diffusion rate, and the tendency for algae adhering to the walls.

An inclined triangular tubular photobioreactor was designed to install adjacent to a power plant utilizing flue gas as the feed gas. Flue gas entered the reactor from the bottom of the inclined tube. Gas bubbles traveled along the inner surface of the tube generating eddies for mixing and preventing fouling. The upper surface of the inclined tube absorbed natural light. The mixing to the algal culture and the flow rate of flue gas influences the growth rate of algae. The system worked, and 15–30% of algae were harvested each day. The setup was able to remove 82% carbon dioxide on a sunny day and 50% carbon dioxide on a cloudy day. Nitrogen oxide was also lowered by 86% [32].

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.

Continuous stirred tank reactors (CSTR) consists of a wide, hollow, capped cylindrical pipe that operates both indoor and outdoor with low contamination risk. Mechanical stirrer and light source are inserted from the top of the reactor. Drain channels and gas injectors position at the bottom (and midsection) of the reactor. The uniform turbulent flow established within the reactor promotes algal growth and prevents fouling.

Another photobioreactor uses helical coils made of plastic tubing placed across a column-like structure. A group of helical coils make up one unit of photobioreactor. Each helical coil runs independently with its own gas injector, pump, and gas removal system. The helical coils operate both indoor (fluorescent light) and outdoor (sunlight). Similar to the helical coils, square tubular reactors consist of plastic tubing arranged in a series of squares. Compared with the helical coils, the square tubing is longer that holds more algal volume.

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 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 [33].

2.1. Harvesting of microalgae

Harvesting the algae from tanks and separating the oil from the algae are difficult and energy intensive processes [34]. The culture of algae in ponds or tanks and, the harvesting of the algae is major problem. Because algae are mostly water, harvesting the algae from the cultural tanks and separating the oil from the algae, is a difficult and energy intensive process [35].

Conventional processes used to harvest microalgae include concentration through centrifugation [36], foam fractionation [37], flocculation [38,39], membrane filtration [40] and ultrasonic separation [41]. Harvesting costs may contribute 20–30% to the total

cost of algal biomass [42]. The microalgae are typically small with a diameter of 3–30 μm, and the culture broths may be quite dilute at less than 0.5 g l–1. Thus, large volumes must be handled. The harvesting method depends on the species, on the cell density, and often also on the culture conditions [10].

Algae pressing is very similar to the techniques used to press flowers, and is used widely by scientists as a means of preserving algal specimens and observing their features.

Algae can be harvested by centrifugation, flocculation or froth flotation. Alum and ferric chloride are chemical flocculants used to harvest algae. Water that is brackish or salty requires additional chemical flocculants to induce flocculation. Harvesting by chemical is a method that is often too expensive for large operations. However, interrupting the carbon dioxide supply to an algal system can cause algae to flocculate on its own, which is called "auto-flocculation". In froth flotation, the water and algae are aerated into froth and algae in then removed from the water.

2.2. Production costs

Producing microalgal biomass is generally more expensive than growing crops. Photosynthetic growth requires light, carbon dioxide, water and inorganic salts. Temperature must remain generally within 293–303 K. To minimize expense, biodiesel production must rely on freely available sunlight, despite daily and seasonal variations in light levels [43].

Microalgae production in closed photobioreactors (PBRs) 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 PBRs have the potential to yield 19,000–57,000 l 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 [43].

Water, containing the essential salts and minerals for growth, is the second requirement. Fresh water is a valuable resource as are the salts and minerals needed; however, algae cultivation can be coupled to another type of environmental remediation that will enhance productivity while mitigating pollution. High nutrient wastewater from domestic or industrial sources, which may already contain nitrogen and phosphate salts, can be added to the algal growth media directly [44]. This allows for algae production to be improved cheaply, while simultaneously treating wastewater. Alternately, salt water can be used, either from saline aquifer or sea water. This means that competition for water will be low.

Nutrients such as phosphorus must be supplied in significant excess because the phosphates added complex with metal ions, therefore, not all the added P is bio-available. Sea water supplemented with commercial nitrate and phosphate fertilizers and a few other micronutrients is commonly used for growing marine microalgae [19]. Genetic and metabolic engineering are likely to have the greatest impact on improving the economics of production of microalgal diesel [45,46].

Growth media are generally inexpensive. Microalgal biomass contains approximately 50% carbon by dry weight [47]. All of this carbon is typically derived from carbon dioxide. Producing 100 ton of algal biomass fixes roughly 183 ton of carbon dioxide. Feeding controlled in response to signals from pH sensors minimizes loss of carbon dioxide and pH variations.

Algae can grow practically anywhere where there is enough sunshine. Some algae can grow in Microalgae are very efficient solar energy converters and they can produce a great variety of metabolites [48]. The culture of algae can yield 30–50% oil. Oil supply is based on the theoretical claims that 47,000–308,000 l/hectare/year of oil could be produced using algae. The calculated cost per barrel would be only $20. Currently, a barrel of oil in the U.S. Market is selling for over $100 per barrel. Despite all the claims and research dating from the early 1970s to date, none of the projected algae and oil yields has been achieved [49,50]. Algae, like all plants, require large quantities of nitrogen fertilizer and water, plus significant fossil energy inputs for the functioning system [51].

Open ponds can be categorized into natural waters (lakes, lagoons, ponds) and artificial ponds or containers. The most commonly used systems include shallow big ponds, tanks, circular ponds and raceway ponds. The polymers can be used in very small amounts, without contributing a major cost to the overall process. The base case (30 g/m^2/d) capital costs were estimated at almost $72,000/ha, without working capital, or almost twice as high as the prior effort [52]. This was due to higher costs for many components, such as earthworks, which were several-fold higher. Among other things, higher costs were assumed for rough and fine (laser) grading, which depends on the type of site assumed to be available. Also the 1987 study estimated about $5000/ha to provide a 3–5 cm crushed rock layer, specified to reduce the suspension of silt from the pond bottom. There is, however, little evidence for a need for such erosion prevention, except perhaps for some areas around the paddle wheel and perhaps the turns. Further, the Weissman and Goebel [53] study selected slip form poured concrete walls and dividers (baffles) as the design choice. A power generation system can be specified to produce electricity from the methane generated from the algal residues (at about 10% of total costs).

The operating costs were discussed in terms of mixing, carbon utilization, nutrient, flocculants, salt disposal, maintenance, labor and the accumulation of photosynthetically produced oxygen [54]. The comparative economics of open ponds and closed photobioreactors (PBRs) are given in Table 1.

3. Energy from algae

While the general idea of using algae for energy production has been around for over 50 years [55], the concept of using lipids derived from algal cells to produce liquid fuels arose more recently [15]. The research of liquid fuel produced from microalga was begun at middle 1980s in 20 centuries [56]. Aquatic biomass may represent a convenient solution, because it has a higher growth-rate than terrestrial plants. Microalgae have been extensively studied so far, as they can grow both in fresh- and salty-waters.

Microalgae can potentially be employed for the production of biofuels in an economically effective and environmentally sustainable manner. Algae can be used to produce biofuel, called algae fuel, algal fuel or even third generation biofuel. Compared with second generation biofuels, algal fuels have a higher yield: they can produce 30–100 times more energy per hectare compared to terrestrial crops. Microalgae have been investigated for the production of a number of different biofuels including bioethanol, vegetable oils, biodiesel, bio-oil, bio-syngas, and bio-hydrogen. The production of these biofuels can be coupled with flue gas CO_2 mit-

Table 1
Comparative economics of open ponds and closed photobioreactors (PBRs).

Parameter	Relative advantage
Capital/operating costs	Open ponds $\ll$ PBRs
Biomass concentration	Open ponds < PBRs
Oxygen inhibition	Open ponds > PBRs
Contamination risk	Open ponds < PBRs
Water losses	Open ponds $\sim$ PBRs
Carbon dioxide losses	Open ponds $\sim$ PBRs
Process control	Open ponds $\sim$ PBRs
Space required	Open ponds $\sim$ PBRs

Table 2
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	

igation, wastewater treatment, and the production of high-value chemicals. Developments in microalgal cultivation and downstream processing are expected to further enhance the cost effectiveness of the biofuel from microalgae strategy [57].

Advantages and disadvatages of biofuel production using microalgae are shown in Table 2. 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.

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.

3.1. Historical perspective

Historically, algae have been seen as a promising source of protein and have been actively cultured by man for centuries, mainly for food. Growing algae as a source of protein on a large scale in open ponds was first conceived by German scientists during World War II [58]. The first attempt in the USA to translate the biological requirements for algal growth into engineering specifications for a large scale plant was made at the Stanford Research Institute (1948–1950).

Under certain growth conditions, many microalgae can produce lipids that are suitable for conversion to liquid transportation fuels [59]. In the late 1940s, nitrogen limitation was reported to significantly influence microalgal lipid storage. Spoehr and Milner [60] published detailed information on the effects of environmental conditions on algal composition, and described the effect of varying nitrogen supply on the lipid and chlorophyll content of Chlorella and some diatoms. Investigations by Collyer and Fogg [61] demonstrated that the fatty acid content of most green algae was between 10% and 30% DCW. Werner [62] reported an increase in the cellular lipids of a diatom during silicon starvation. Coombs et al. [63] reported that the lipid content of the diatom *Navicula pelliculosa* increased by about 60% during a 14 h silicon starvation period. In addition to nutrition, fatty acid and lipid composition and content were also found to be influenced by a number of other factors such as light [64–66] and low temperatures [67]. With the advent of the oil embargo in the early 1970s, a search for alternative energy sources set the stage for an almost 20-year research effort devoted to biofuel production from algal lipids.

3.2. Thermochemical conversion

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 direct thermochemical liquefaction can convert wet biomass such as wood and sewage sludge to liquid fuel at around 575 K and 10 MPa using catalyst such as sodium carbonate [68]. At the same time, the liquid oil can be easily separated [69].

The feasibility of producing liquid fuel or bio-oil via pyrolysis or thermochemical liquefaction of microalgae has been demonstrated for a range of microalgae [70–75]. Since algae usually have high moisture content, a drying process requires much heating energy [76]. 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 [77–79].

3.2.1. Liquefaction of algal cells

Processes relating to liquefaction of biomass are based on the early research of Appell et al. [80]. These workers reported that a variety of biomass such as agricultural and civic wastes could be converted, partially, into a heavy oil-like product by reaction with water and carbon monoxide/hydrogen in the presence of sodium carbonate. The heavy oil obtained from the liquefaction process is a viscous tarry lump, which sometimes caused troubles in handling. For this purpose, some organic solvents were added to the reaction system. These processes require high temperature and pressure.

In the liquefaction process, biomass is converted to liquefied products through a complex sequence of physical structure and chemical changes. The feedstock of liquefaction is usually a wet matter. In the liquefaction, biomass is decomposed into small molecules. These small molecules are unstable and reactive, and can repolymerize into oily compounds with a wide range of molecular weight distribution [81].

Liquefaction can be accomplished directly or indirectly. Direct liquefaction involves rapid pyrolysis to produce liquid tars and oils and/or condensable organic vapors. Indirect liquefaction involves the use of catalysts to convert non-condensable, gaseous products of pyrolysis or gasification into liquid products. Alkali salts, such as sodium carbonate and potassium carbonate, can act the hydrolysis of cellulose and hemicellulose, into smaller fragments. The degradation of biomass into smaller products mainly proceeds by depolymerization and deoxygenation [81].

Direct hydrothermal liquefaction in sub-critical water conditions is a technology that can be employed to convert wet biomass material to liquid fuel. A number of technical terminologies have been used in the literature to refer to this technology, but it essentially utilize the high activity of water in sub-critical conditions in order to decompose biomass materials down to shorter and smaller molecular materials with a higher energy density or more valuable chemicals.

Direct liquefaction of microalgae and oil from liquefaction products by dichloromethane (CH_2Cl_2) extraction is presented in Fig. 3. The liquefaction is performed in an aqueous solution of alkali or alkaline earth salt at about 575 K and 10 MPa [82]. 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. [82] 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 MPa s 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 [83]. The hydrothermal liquefaction technique was more effective for extraction of microalgal biodiesel than using the supercritical carbon dioxide [84]. 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 biodiesel 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 [85].

3.2.1.1. Liquefaction of algal cells by hexane extraction. Fig. 4 shows the liquefaction of algal cells by hexane extraction obtaining for the primary oil. Hexane solubles of the algal cells are shown in Table 3. soluble was obtained in the high yield of 58% of its dry weigh, and had the good fluidity with viscosity of 56 cP and the high heating value (49 MJ/kg). The properties of primary oil are shown in Table 4. 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 [86].

The heating value of the primary oil obtained at 575 K was 47.5 MJ/kg and that at 475 K was 42.0 MJ/kg; these values were equivalent to petroleum oil. Especially, the heating value of the primary oil obtained at 575 K was much higher than that of the oil obtained by liquefaction of other biomass. 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 [86].

The properties of the hexane soluble of primary oil are shown in Table 4. 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 temperature, the same properties of the hexane soluble of primary oil as that of the hexane soluble of the algal cells [86].

3.3. Production of bio-oil and hydrogen by pyrolysis

Five moss samples (*Polytrichum commune*, *Dicranum scoparium, Thuidium tamarascinum, Sphagnum palustre, Drepanocladus revolvens);* one alga sample (*Cladophora fracta*), and one microalga sample (*Chlorella protothecoides*) were used in the earlier work [75]. The yields of bio-oil from the samples via pyrolysis are presented

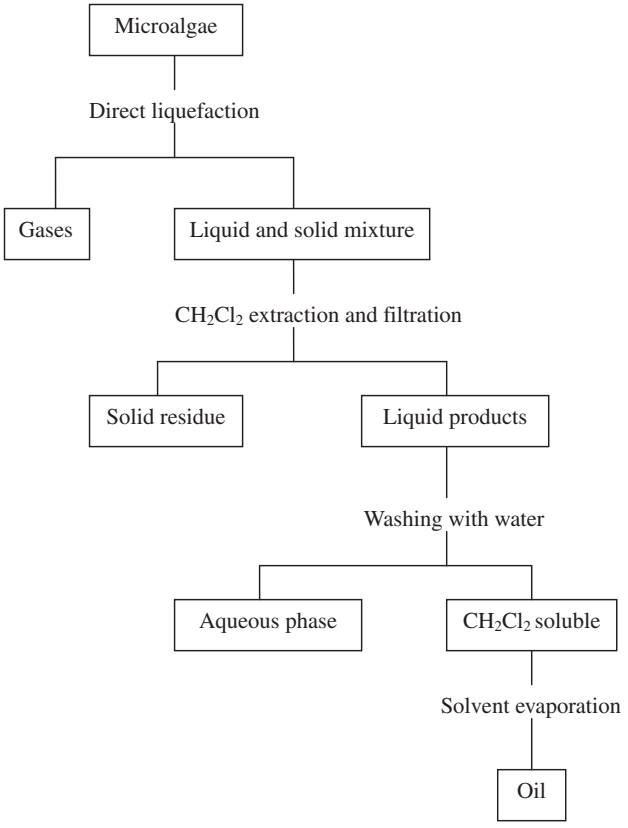

Fig. 3. Direct liquefaction of microalgae and oil from liquefaction products by CH_2Cl_2 extraction.

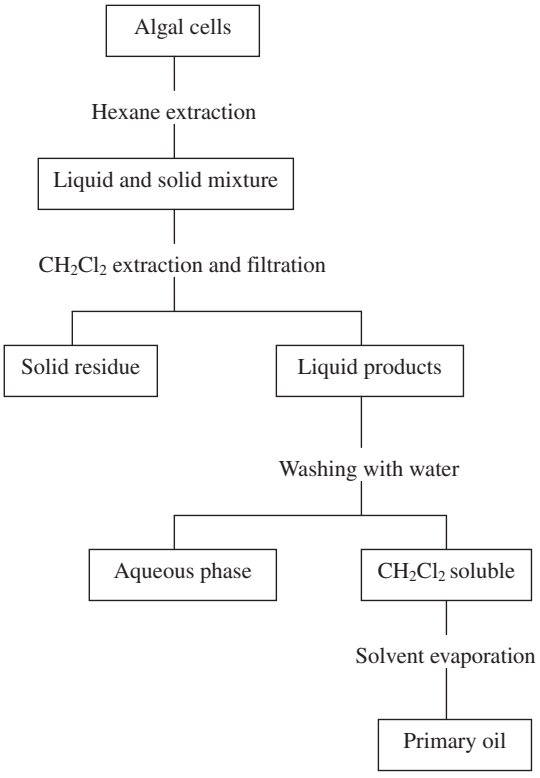

Fig. 4. Primary oil from algal cells by liquefaction of hexane extraction.

Table 3
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 4
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.

as a function of the temperature (K) in Fig. 5. 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 39.1%, 34.3%, 33.6%, 37.0%, 35.4%, 48.2% and 55.3% of the sample for *P. commune*, *D. scoparium*, *T. tamarascinum*, *S. palustre*, *D. revolvens*, *C.* fracta and *C. prototheco*ides, respectively.

The chemical compositions of algae are given in Table 5 [68]. Two moss samples (*P. commune*, *T. tamarascinum*); one alga sample (*C. fracta*), and one microalga sample (*C. prototheco*ides) were subjected to pyrolysis and steam gasification for producing hydrogen-rich gas.

The temperature of the reaction vessel was measured with an iron-constantan thermocouple and controlled at ±3 K. The pyrolysis experiments were performed at temperatures of 575, 625, 675, 725, 775, 825 and 925 K. The steam gasification experiments were carried out at temperatures of 825, 875, 925, 975, 1025, 1075, 1125, 1175 and 1225 K.

The yields of bio-oil from the samples via pyrolysis are presented as a function of the temperature (K) in Fig. 6. 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 *P. commune*, *T. tamarascinum*, *C. fracta and C. prototheco*ides were 31.6, 37.3, 45.0 and 50.8% of the sample at 925 K, respectively. The bio-oil yields of pyrolysis from algae were higher than those of mosses. Bio-oil comparable to fossil oil was obtained from microalgae [87]. 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.

The HHVs for bio-oils from mosses 21.5–24.8 MJ/kg and the HHVs for bio-oils from alga and microalga 32.5 and 39.7 MJ/kg, respectively, were obtained by pyrolysis at temperature ranging from 775 to 825 K. In general, algae bio-oils are higher quality than bio-oils from mosses.

Fig. 7 shows the effect on temperature on yields of gaseous products from the samples by pyrolysis. As can be seen in Fig. 6, The yields of gaseous products from the samples of *P. commune*, *T. tamarascinum*, *C. fracta and C. prototheco*ides increased from 5.3% to 40.6%, 6.5% to 42.2%, 8.2% to 39.2% and 9.5% to 40.6% by volume, respectively, while the final pyrolysis temperature was increased from 575 to 875 K.

Fig. 8 shows the plots for yields of hydrogen in gaseous products from the samples by pyrolysis. The percent of hydrogen in gaseous products from the samples of *P. commune*, *T. tamarascinum*, *C. fracta and C. prototheco*ides increased from 21.3% to 38.7%, 23.0% to 41.3%,

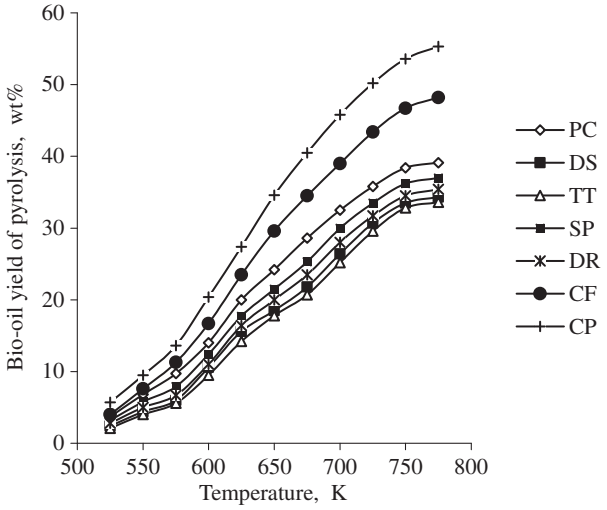

Fig. 5. Curves for yields of bio-oil from pyrolysis of the samples: *Polytrichum commune* (PC), *Dicranum scoparium* (DS), *Thuidium tamarascinum* (TT), *Sphagnum palustre* (SP), *Drepanocladus revolvens* (DR), *Cladophora fracta* (CF), and *Chlorella prototheco*ides (CP).

Table 5
Chemical compositions of algae on a dry matter basis (%).

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

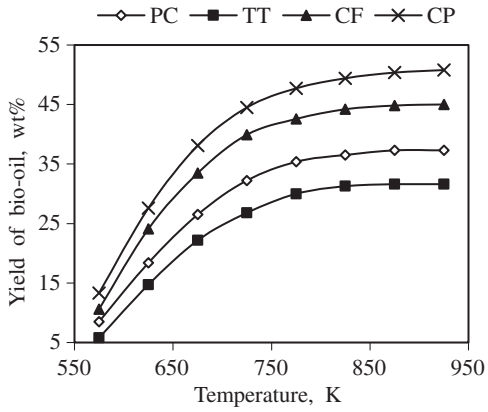

Fig. 6. Plots for yield of bio-oil from moss and alga samples by pyrolysis at different temperatures (K). *Polytrichum commune* (PC), *Thuidium tamarascinum* (TT), *Cladophora fracta* (CF), and *Chlorella protothecoides* (CP).

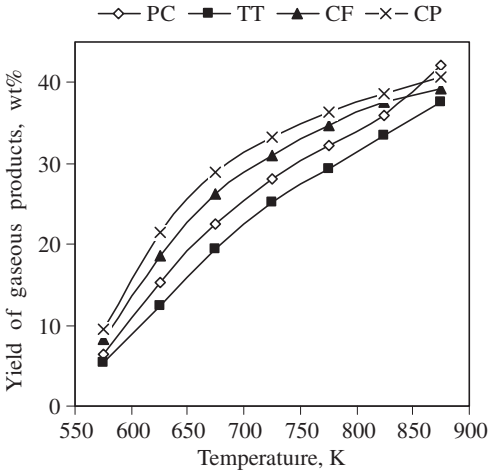

Fig. 7. Plots for yields of gaseous products from the samples by pyrolysis: *Polytrichum commune* (PC), *Thuidium tamarascinum* (TT), *Cladophora fracta* (CF), and *Chlorella protothecoides* (CP).

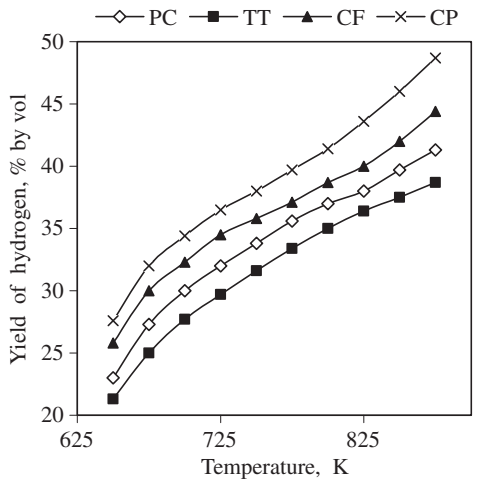

Fig. 8. Plots for yields of hydrogen in gaseous products from the samples by pyrolysis: *Polytrichum commune* (PC), *Thuidium tamarascinum* (TT), *Cladophora fracta* (CF), and *Chlorella protothecoides* (CP).

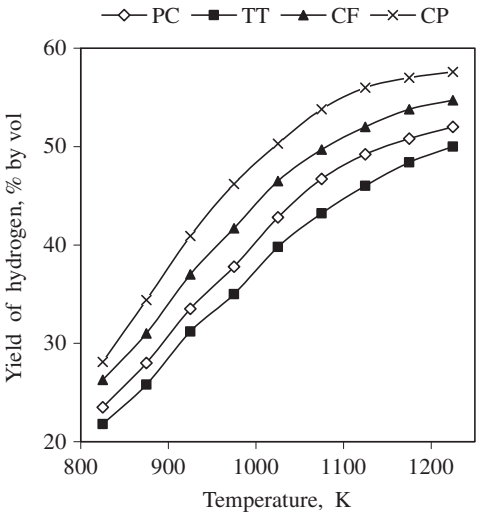

Fig. 9. Plots for yields of hydrogen in gaseous products from the samples by steam gasification: *Polytrichum commune* (PC), *Thuidium tamarascinum* (TT), *Cladophora fracta* (CF), and *Chlorella protothecoides* (CP).

25.8% to 44.4% and 27.6% to 48.7% by volume, respectively, while the final pyrolysis temperature was increased from 650 to 875 K.

Fig. 9 shows the plots for yields of hydrogen in gaseous products from the samples by steam gasification. The percent of hydrogen in gaseous products from the samples of *P. commune*, *T. tamarascinum*, *C. fracta and C. protothecoides* increased from 21.8% to 50.0%, 23.5% to 52.0%, 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.

Fig. 10 shows the plots for yields of hydrogen in gaseous products from microalga and wood samples by pyrolysis. The percent of hydrogen in gaseous products from the samples of beech wood and spruce wood increased from 31.5% to 40.5% and 33.3% to 42.3% by volume, respectively, while the final pyrolysis temperature was increased from 650 to 875 K [88]. Microalgae gaseous products are higher quality than gaseous products from wood (Fig. 10). In gen-

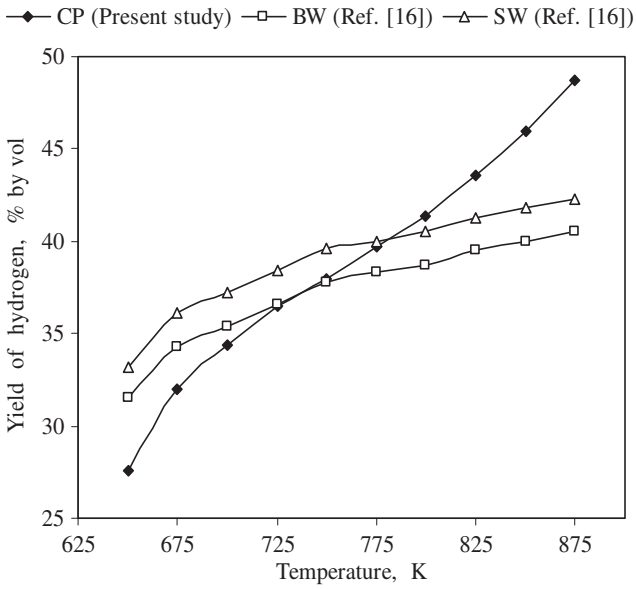

Fig. 10. Plots for yields of hydrogen in gaseous products from microalga and wood samples by pyrolysis: *Chlorella protothecoides* (CP), beech wood (BW) and spruce wood (SW).

Table 6
Yields of bio-oil by pyrolysis from moss and alga samples at different temperatures (K).

Sample	575	625	675	725	775	825	875
Polytrichum commune	10.3	20.0	27.5	35.8	39.1	38.4	36.7
Dicranum scoparium	6.0	15.5	21.8	30.7	34.3	33.8	31.7
Thuidium tamarascinum	5.6	14.2	20.7	29.5	33.6	33.4	31.3
Sphagnum palustre	7.9	17.7	25.3	33.5	37.0	36.3	34.6
Drepanocladus revolvens	6.7	16.4	23.5	31.7	35.4	34.7	32.9
Cladophora fracta	10.5	23.5	33.2	43.4	48.2	46.8	44.6
Chlorella protothecoides	12.8	27.4	38.4	50.2	55.3	53.7	51.6

Table 7
Yields of gaseous product by pyrolysis from moss and alga samples at different temperatures (K).

Sample	575	625	675	725	775	825	875
Polytrichum commune	6.5	14.8	22.6	26.4	29.2	36.6	42.2
Dicranum scoparium	5.8	12.5	19.8	25.0	27.6	35.0	40.8
Thuidium tamarascinum	5.3	11.2	17.9	23.5	25.6	33.2	39.3
Sphagnum palustre	5.5	11.9	18.3	24.2	26.5	34.0	39.8
Drepanocladus revolvens	5.6	12.3	18.9	24.7	27.0	34.5	40.4
Cladophora fracta	8.2	19.7	28.2	32.6	35.7	38.0	39.7
Chlorella protothecoides	9.5	21.8	29.5	33.7	36.3	38.1	39.5

eral, algae gaseous products are higher quality than gaseous products from mosses.

Table 6 shows the yields of bio-oil by pyrolysis from moss and alga samples [75]. As can be seen from Table 6, the 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 than gradually decreased to 51.8% was obtained at 875 K with a heating rate of 10 K/s. The bio-oil yield for *P. commune* (a moss sample) rose from 10.3% to 39.1% as the temperature rose from 575 to 775 K, and than gradually decreased to 36.7% was obtained at 875 K with a heating rate of 10 K/s [75]. For alga, maximum bio-oil yields of between 48.2% and 46.8%, and for microalga 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 [89,90].

Table 7 shows the yields of gaseous product by pyrolysis from moss and alga samples [75]. From Tables 5.12 and 5.13, the yields of gaseous products for *C. protothecoides* increased from 9.5% to 39.5% as the temperature rose from 575 to 875 K. The char yields of pyrolysis from mosses were higher than those of algae.

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.

3.4. Biodiesel production via chemical process

Microalgae contain oils, or 'lipids', that can be converted into biodiesel. The idea of using microalgae to produce fuel is not new, but has received recent renewed attention 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. 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.

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 per hectare per year. Such quantities of nitrogen and phosphorus could damage the environment. Additionally, it could limit the economic viability of using microalgae. Nitrogen and phosphorus found in algal waste, after the oils have been extracted, must therefore be recycled.

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 [43].

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.

3.5. Biochemical processes

3.5.1. Fermentation

Fermentation is used commercially on a large scale in variouscountries to produce ethanol from sugar crops and starch crops. Ethanol can be produced from a large variety of carbohydrates with a general formula of $(CH_2O)_n$. 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 ceveresiae*. First, invertase enzyme in the yeast catalyzes the hydrolysis of sucrose to convert it into glucose and fructose.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} \rightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6} \quad (1)$$

Second, zymase, another enzyme also present in the yeast, converts the glucose and the fructose into ethanol.

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2 \quad (2)$$

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.

3.5.1.1. Bioethanol. 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, *Saccharomycess 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 [91].

3.5.1.2. Biomethane. The concept of using algae as a fuel was first proposed by Meier [55] for the production of methane gas from the carbohydrate fraction of cells. This idea was further developed by Oswald and Golueke [92], who introduced a conceptual techno-economic engineering analysis of digesting microalgal biomass grown in large raceway ponds to produce methane gas. In the 1970s, as the cost of conventional fuels began rising rapidly, the possibility of using algae as a fuel source received renewed attention. A more detailed design and engineering analysis of this concept was carried out by Benemann et al. [93], who concluded that such systems could produce biogas competitively with projected fossil fuel prices.

Anaerobic digestion of bio-wastes occurs in the absence of air, the resulting gas called as biogas is a mixture consisting mainly of methane and carbon dioxide. Biogas is a valuable fuel which is produced in digesters filled with the feedstock like dung or sewage. The digestion is allowed to continue for a period of from ten days to a few weeks.

Algal biomass can be used for biogas production. In Poland, there are numerous active biogas installations, from large-scale ones to small ones fed with straw and green plant fuel that serve a few farms; so far, however, algae have not been used as such a fuel. Some macroalgal species like *Macrocystis pylifera*, and genera such as *Sargassum*, *Laminaria*, *Ascophyllum*, *Ulva*, *Cladophora*, *Chaetomorpha* and *Gracilaria*, have been explored as potential methane sources [94]. But in spite of the large seaweed biomass in various regions of the world, anaerobic digestion for biogas generation appears to be unsatisfactory and therefore uneconomic [95,96].

Anaerobic digestion of the algal waste produces carbon dioxide, methane and ammonia. Left over nitrogen and phosphorus compounds can be reused as fertilizer to the algal process. Using the methane as an energy source can further enhance energy recovery from the process.

The researchers highlighted some key issues to be addressed in microalgal production:

- Sodium (in salt) can inhibit the anaerobic digestion process when using marine algae, although researchers suggest suitable bacteria (anaerobic digesters) can adapt.
- Digestion of the algae can be enhanced and the methane yield increased by physical or chemical pre-treatment to break down cell walls and make the organic matter in the cells more accessible.
- The nitrogen content of certain algae can be high, resulting in greater levels of ammonia which can also inhibit the digestion process. One strategy to overcome this problem uses a 'co-digestion' process, whereby other organic waste, which is higher in carbon and lower in nitrogen, is added to the algal waste.

3.5.1.3. Anaerobic bio-hydrogen production. In microbial fermentation of biomass, different waste materials can be used as substrates. A new and unique process has been developed when substrates such as carbohydrates are fermented by a consortium of bacteria; they produce hydrogen and carbon dioxide. Highly concentrated organic waste water is one of the most abundantly available biomass which can be exploited for microbial conversion into hydrogen [97]. Municipal solid wastes and digested sewage sludge have the potential to produce large amount of hydrogen by suppressing the production of methane by introducing low voltage electricity into the sewage sludge. The substrate from the acidogenesis of fruit and vegetable market wastes gives higher hydrogen evolution rates (about threefold) compared to synthetic medium. Mixed culture of photosynthetic anaerobic bacteria provides a method of utilization of a variety of resources for bio-hydrogen-production [98].

Hydrogen produced by photosynthetic organisms is one of a range of popular scenarios for renewable energy. Hydrogen can be produced by algae under specific conditions. Three different ways to produce hydrogen have been proposed: direct and indirect photolysis, and ATP-driven hydrogen-production. Direct photolysis is possible when the resulting hydrogen and oxygen are continuously flushed away. Photosynthesis and water-splitting are coupled, resulting in the simultaneous production of hydrogen and oxygen. This results in major safety risk, and costs to separate the hydrogen and oxygen. Major factors affecting the cost of hydrogen production by microalgae are (a) the cost of the huge photobioreactor and (b) the cost of hydrogen storage facilities that guarantee continuous hydrogen supply also through the night or during cloudy periods of the day.

Anaerobic hydrogen production proceeds photofermentative as well as without the presence of light. Anaerobic bacteria use organic substances as the sole source of electrons and energy, converting them into hydrogen.

$$\text{Glucose} + 2H_2O \rightarrow 2\text{Acetate} + 2CO_2 + 4H_2 \quad (3)$$

$$\text{Glucose} \rightarrow \text{Butyrate} + 2CO_2 + 2H_2 \quad (4)$$

The reactions involved in hydrogen production (Eqs. (3) and (4)) are rapid and these processes do not require solar radiation, making them useful for treating large quantities of wastewater by using a large fermentor.

Since they cannot utilize light energy, the decomposition of organic substrates is incomplete. Further decomposition of the acetic acid is not possible under anaerobic conditions. Nevertheless, these reactions are still suitable for the initial steps of wastewater treatment and hydrogen production followed by further waste treatment stages.

A new fermentation process that converts valueless organic waste streams into hydrogen-rich gas has been developed by Van Ginkel et al. [99]. The process employs mixed microbial cultures readily available in the nature, such as compost, anaerobic digester sludge, soil etc. to convert organic wastes into hydrogen-rich gas. The biodegradation efficiencies of the pollutants were examined by changing hydraulic retention time (HRT) as a main operating variable. An enriched culture of hydrogen producing bacteria such as *Clostridia* was obtained by heat treatment, pH control and HRT control of the treatment system. The bio-hydrogen fermentation technology could enhance the economic viability of many processes utilizing hydrogen as a fuel source or as raw materials.

Anaerobic fermentative microorganism, cyanobacteria and algae are suitable in biological production of hydrogen via hydrogenase due to reversible hydrogenases [100]. Cyanobacteria and algae can carry out photo-evolution of hydrogen catalyzed by hydrogenases. The reactions are similar to electrolysis involving splitting of water into oxygen and hydrogen [101].

Biological hydrogen can be generated from plants by biophotolysis of water using microalgae (green algae and cyanobacteria), fermentation of organic compounds, and photodecomposition of organic compounds by photosynthetic bacteria. To produce hydrogen by fermentation of biomass, a continuous process using a non-sterile substrate with a readily available mixed microflora is needed [102,103,75,104,105]. A successful biological conversion of biomass to hydrogen depends strongly on the processing of raw materials to produce feedstock, which can be fermented by the micro-organisms.

Hydrogen producing bacteria (*Clostridia*) were found to have growth rates about 5–10 times higher than that of methane producing bacteria [99,103]. In a continuous flow bioreactor system, hydrogen production showed declining trend at the later stage of reactor operation. Based on these findings, it is hypothesized that *Clostridia* may have gone through a phenomenon known as "degeneration" in which they lose their ability to produce hydrogen. Therefore inoculating fresh mixed cultures may be a feasible way to maintain a sustainable hydrogen production. Based on this hypothesis, two-stage anaerobic reactor has been proposed. The first-stage reactor is designed as hydrogen producing reactor whereas the second-stage reactor will be employed to cultivate fresh seed culture to perpetually supply to the first one.

4. Conclusion

In this work, algae production technologies such as open, closed and hybrid systems, production costs, and algal energy conversions were investigated.

Algae are among the fastest growing plants in the world, and about 50% of their weight is oil. Microalgae have much faster growth-rates than terrestrial crops. the per unit area yield of oil from algae is estimated to be from between 20,000 to 80,000 l per acre, per year; this is 7–31 times greater than the next best crop, palm oil. Industrial reactors for algal culture are open ponds, photobioreactors and closed systems. Algae are very important as a biomass source. Algae will some day 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.

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, and ethanol, methane and hydrogen, respectively.

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 biofules in the near future.

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