Chapter 6
Biodiesel from Algae

6.1 Introduction

Continued use of petroleum sourced fuels is now widely recognized as unsustainable because of depleting supplies and the contribution of these fuels to the accumulation of carbon dioxide in the environment. Renewable, carbon-neutral transport fuels are necessary for environmental and economic sustainability (Chisti 2007). Biodiesel can be carbon neutral and produced intensively on relatively small areas of marginal land. The quality of the fuel product is comparable to petroleum diesel and can be incorporated with minimal change into the existing fuel infrastructure. Innovative techniques, including the use of industrial and domestic waste as fertilizer, could be applied to further increase biodiesel productivity (Campbell 2008).

Algae, like corn, soybeans, sugar cane, wood, and other plants, use photosynthesis to convert solar energy into chemical energy. They store this energy in the form of oils, carbohydrates, and proteins. The plant oil can be converted into biodiesel; hence biodiesel is a form of solar energy. The more efficient a particular plant is at converting that solar energy into chemical energy, the better it is from a biodiesel perspective, and algae are among the most photosynthetically efficient plants on earth.

Algae can be a replacement for oil-based fuels, one that is more effective and has no disadvantages. Algae are among the fastest growing plants in the world, and about 50% of their weight is oil. This lipid oil can be used to make biodiesel for cars, trucks, and airplanes. Microalgae have much faster growth rates than terrestrial crops. The per-unit area yield of oil from algae is estimated to be between 20,000 and 80,000 L/acre/year; this is 7 to 31 times greater than the next best crop, palm oil. The lipid and fatty acid contents of microalgae vary in accordance with culture conditions. Most current research on oil extraction is focused on microalgae to produce biodiesel from algal-oil. Algal-oil can be processed into biodiesel as easily as oil derived from land-based crops.

The production of microalgal biodiesel requires large quantities of algal biomass. Macro- and microalgae are currently mainly used for food, in animal feed, in feed

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for aquaculture, and as biofertilizer. A 1-ha algae farm on wasteland can produce over 10 to 100 times as much oil compared to any other known source of oil crops. While a crop cycle may take from 3 months to 3 years for production, algae can start producing oil within 3 to 5 d, and thereafter oil can be harvested on a daily basis (just like milk). Algae can be grown using sea water and nonpotable water on wastelands where nothing else grows. Algae farming for biofuels is expected to provide a conclusive solution to the food vs. fuel debate.

The production of biodiesel has recently received much attention worldwide. In order to resolve the worldwide energy crisis, seeking for lipid-rich biological materials to produce biodiesel effectively has attracted much renewed interest. Algae have emerged as one of the most promising sources for biodiesel production. It can be inferred that algae grown in CO_2-enriched air can be converted into oily substances. Such an approach can contribute to solving the major problems of air pollution resulting from CO_2 emissions and future crises due to a shortage of energy sources (Sharif Hossain *et al.* 2008).

6.2 Biodiesel from Algal Oil

Biodiesel is defined as the monoalkyl esters of vegetable oils or animal fats. The vegetable oils and fats as alternative engine fuels are all extremely viscous, with viscosities ranging from 10 to 17 times greater than petroleum diesel fuel. Biodiesel is produced by transesterifying the parent oil or fat to achieve a viscosity close to that of petrodiesel. The chemical conversion of the oil into its corresponding fatty ester (biodiesel) is called transesterification. The purpose of the transesterification process is to lower the viscosity of the oil. The transesterification reaction proceeds with or without a catalyst by using primary or secondary monohydric aliphatic alcohols having one to four carbon atoms as follows (Demirbas 2007):

$$\text{Triglycerides} + \text{Monohydric alcohol} \rightarrow \text{Glycerin} + \text{Monoalkyl esters (Biodiesel)} \quad (6.1)$$

This is an equilibrium reaction (Figure 6.1) where triglycerides can be processed into biodiesel, usually in the presence of a catalyst, and alkali such as potassium hydroxide (Ma and Hanna 1999; Demirbas 2007).

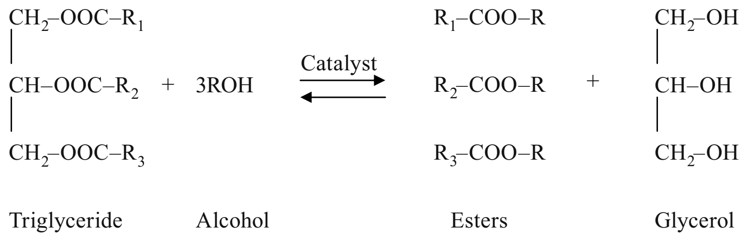

Figure 6.1 Transesterification of triglycerides with alcohol

Transesterification and catalytic cracking has usually been adopted to convert fat in the cell of microalgae into gasoline and diesel. This kind of method was limited by low temperature, and the outcome function was highly influenced by the fat content. What was more, the fat content in the microalgae had to be very high; otherwise good economic performance would be hard to achieve (Xu *et al.* 2006).

Biodiesel is a biofuel commonly consisting of methyl esters that are derived from organic oils, plant or animal, through the process of tranesterification. The biodiesel transesterification reaction is very simple:

$$\text{Triglyceride} + 3\,\text{Methanol} \xrightarrow{\text{Catalyst}} \text{Glycerine} + 3\,\text{Methyl esters (Biodiesel)} \tag{6.2}$$

An excess of methanol is used to force the reaction to favor the right side of the equation. The excess methanol is later recovered and reused.

The triglyceride is a complex molecule that plants and animals use for storing chemical energy; in more simple terms, it is fat. The process of making biodiesel occurs as follows. (1) Triglycerides, methanol, and catalyst are placed in a controlled reaction chamber to undergo transesterification. (2) The initial product is placed in a separator to remove the glycerine byproduct. (3) The excess methanol is recovered from the methyl esters through evaporation. (4) The final biodiesel is rinsed with water, neutralized, and dried (Xu *et al.* 2006). Unlike petroleum fuels, the relative simplicity of biodiesel manufacture makes its production scalable. Many existing vendors are small-time producers. Biodiesel is a somewhat "mature" fuel and was used as a diesel alternative in the early 20th century (Demirbas 2007). This has allowed biodiesel to attain a level of "grassroots" popularity among environmental advocates and visionaries.

The energy density of biodiesel is comparable to petroleum diesel. The higher heating value of petroleum diesel is 42.7 MJ/kg. Values for biodiesel vary depending on the source of biomass. Typically, biodiesel derived from seed oils, such as rapeseed or soybean, produces 39.5 MJ/kg, while biomass derived from algae yields 41 MJ/kg (Demirbas 1998; Rakopoulos *et al.* 2006; Xu *et al.* 2006). Although the lower-energy biodiesels based on seed oils are the most common, they have enough energy density to make them a viable alternative to petroleum diesel.

Biodiesel can be made from virtually any source of renewable oil. Typical sources include restaurant waste oil, animal fats, and vegetable oils. The supply of waste oil is very limited; however, it is a popular source for small-scale, independent producers. Large commercial producers often use vegetable oils, such as soybean, rapeseed, palm, and corn oils. Unfortunately, biodiesel derived from seed oil diverts from the food supply and the increasing competition for seed causes the oil, and resulting biodiesel, to become increasingly expensive (Campbell 2008).

The main advantages of biodiesel as diesel fuel its portability, ready availability, renewability, higher combustion efficiency, and lower sulfur and aromatic content (Demirbas 2007). Adopting biodiesel has a number of advantages. First, because the fuel is derived from biomass, it does not contribute to atmospheric CO_2 emissions. Second, biodiesel emissions are, except for NO_x, lower than petroleum diesel. Combustion of biodiesel alone provides over a 90% reduction in total unburned hydrocarbons, and a 75 to 90% reduction in polycyclic aromatic hydrocarbons (PAHs). Biodiesel further provides significantly greater reductions in particulates and carbon monoxide than petroleum diesel fuel. Biodiesel provides a slight increase or decrease in nitrogen oxides depending on engine family and testing procedures. Many studies on the performances and emissions of compression ignition engines, fueled with pure biodiesel and blends with diesel oil, have been performed and are reported in the literature (Laforgia and Ardito 1994; Cardone *et al.* 1998). Third, the infrastructure needed for biodiesel already exists. Biodiesel can be used in existing diesel engines blended with petroleum diesel, or it can be run unblended in engines with minor modifications (Crookes 2006; Rakopoulos *et al.* 2006; Bowman *et al.* 2006). Because biodiesel has twice the viscosity of petroleum diesel, its lubrication properties can actually improve engine life (Bowman *et al.* 2006). Fourth, biodiesel has low toxicity and is biodegradable (Aresta *et al.* 2005; Demirbas 2007). The biodegradabilities of several biodiesels in the aquatic environment show that all biodiesel fuels are readily biodegradable. After 28 d all biodiesel fuels are 77 to 89% biodegraded; diesel fuel is only 18% biodegraded in the same period (Zhang 1996). The enzymes responsible for the dehydrogenation/oxidation reactions that occur in the process of degradation recognize oxygen atoms and attack them immediately (Zhang *et al.* 1998). Fifth, like petroleum diesel, biodiesel has a more complete combustion than gasoline, giving a cleaner burn (Bowman *et al.* 2006). The oxygen content of biodiesel improves the combustion process and decreases its oxidation potential. The structural oxygen content of a fuel improves its combustion efficiency due to an increase in the homogeneity of oxygen with the fuel during combustion. Because of this, the combustion efficiency of biodiesel is higher than that of petrodiesel. A visual inspection of injector types would indicate no difference between biodiesel fuels when tested on petrodiesel. The overall injector coking is considerably low.

The major disadvantages of biodiesel are its higher viscosity, lower energy content, higher cloud point and pour point, higher nitrogen oxide (NO_x) emissions, lower engine speed and power, injector coking, engine compatibility, high price, and greater engine wear. Biodiesel is not without problems. First, it does produce increased NO_x emissions, relative to petroleum diesel, owing to the higher compression ratios typically used in biodiesel engines (Crookes 2006; Pradeep and Sharma 2007). Second, biodiesel does reduce the power output of a diesel engine compared to petroleum diesel, although this is only around 2% overall (Schneider 2006). Third, the production of biodiesel results in glycerine byproducts and wash wastewater. Fourth, the price of biodiesel is typically higher than that of petroleum diesel. Fifth, and most importantly, the biomass feedstocks for making biodiesel are diverted from other important uses, typically food production.

The algae that are used in biodiesel production are usually aquatic unicellular green algae. This type of algae is a photosynthetic eukaryote characterized by high growth rates and high population densities. Under good conditions, green algae can double their biomass in less than 24 h (Schneider 2006; Chisti 2007). Additionally, green algae can have huge lipid contents, frequently over 50% (Schneider 2006; Chisti 2007). This high-yield, high-density biomass is ideal for intensive agriculture and may be an excellent source for biodiesel production.

The annual productivity and oil content of algae is far greater than that of seed crops. Soybean can only produce about 450 L of oil per hectare. Canola can produce 1,200 L/ha, and palm can produce 6,000 L. Now, compare that to algae, which can yield 90,000 L/ha (Haag 2007; Schneider 2006; Chisti 2007). It is possible that US demand for liquid fuel could be achieved by cultivating algae in one tenth the area currently devoted to soybean cultivation (Scott and Bryner 2006).

The process for producing microalgal oils consists of a microalgal biomass production step that requires light, carbon dioxide, water, and inorganic nutrients. The latter are mainly nitrates, phosphates, iron, and some trace elements. Approximately half of the dry weight of microalgal biomass is carbon, which is typically derived from carbon dioxide. Therefore, producing 100 tons of algal biomass fixes roughly 183 tons of carbon dioxide. This carbon dioxide must be fed continually during daylight hours. It is often available at little or no cost (Chisti 2008). The optimal temperature for growing many microalgae is between 293 and 303 K. A temperature outside this range could kill or otherwise damage the cells.

There are three well-known methods to extract oil from algae: (1) expeller/press, (2) solvent extraction with hexane, and (3) supercritical fluid extraction. A simple process is to use a press to extract a large percentage (70 to 75%) of the oils from algae. Algal oil can be extracted using chemicals. The most popular chemical for solvent extraction is hexane, which is relatively inexpensive. Supercritical fluid extraction is far more efficient than traditional solvent separation methods. Supercritical fluids are selective, thus providing the high purity and product concentrations (Paul and Wise 1971). This method alone can allow one to extract almost 100% of the oils. In supercritical fluid CO_2 extraction, CO_2 is liquefied under pressure and heated to the point where it has the properties of both a liquid and a gas. This liquefied fluid then acts as the solvent in extracting the oil.

The lipid and fatty acid contents of microalgae vary in accordance with culture conditions. Algal oil contains saturated and monounsaturated fatty acids. The fatty acids exist in algal oil in the following proportions: 36% oleic (18:1), 15% palmitic (16:0), 11% stearic (18:0), 8.4% iso-17:0, and 7.4% linoleic (18:2). The high proportion of saturated and monounsaturated fatty acids in this alga is considered optimal from a fuel quality standpoint, in that fuel polymerization during combustion would be substantially less than what would occur with polyunsaturated fatty-acid-derived fuel (Sheehan *et al.* 1998). Table 6.1 shows the oil contents of some microalgae. Oil levels of 20 to 50% are quite common (Chisti 2007; Carlsson *et al.* 2007; Demirbas 2009a).

After oil extraction from algae, the remaining biomass fraction can be used as a high protein feed for livestock (Schneider 2006; Haag 2007). This gives further value to the process and reduces waste.

Table 6.1 Oil contents of some microalgae

Microalga	Oil content (% dry wt)
Botryococcus braunii	25–75
Chlorella spp.	28–32
Crypthecodinium cohnii	20
Cylindrotheca spp.	16–37
Dunaliella primolecta	23
Isochrysis spp.	25–33
Monallanthus salina N	20
Nannochloris spp.	20–35
Nannochloropsis spp.	31–68
Neochloris oleoabundans	35–54
Nitzschia spp.	45–47
Phaeodactylum tricornutum	20–30
Schizochytrium spp.	50–77
Tetraselmis sueica	15–23

6.2.1 Production of Biodiesel from Algal Oils

Most current research on oil extraction is focused on microalgae to produce biodiesel from algal oil. The biodiesel from algal oil in itself is not significantly different from biodiesel produced from vegetable oils.

Dilution, microemulsification, pyrolysis, and transesterification are the four techniques applied to solve the problems encountered with high fuel viscosity. Of the four techniques, transesterification of oil into its corresponding fatty ester (biodiesel) is the most promising solution to the high viscosity problem. This is accomplished by mixing methanol with sodium hydroxide to make sodium methoxide. This liquid is then mixed into vegetable oil. The entire mixture then settles and glycerin is left on the bottom while methyl esters, or biodiesel, is left on top. Biodiesel can be washed with soap and glycerin using a centrifuge and then filtered. Kinematic viscosities of the fatty acid methyl esters vary from 3.23 to 5.61 mm^2/s (Knothe 2005). Methanol is preferred for transesterification because it is less expensive than ethanol (Graboski and McCormick 1998).

For production of biodiesel, a macroalga (*Cladophora fracta*) sample and a microalga (*Chlorella protothecoides*) sample were used in one study (Demirbas 2009b). Proximate analysis data and higher heating values of algae samples are given in Table 6.1. As seen in Table 6.2, the higher heating value of *Chlorella protothecoides* (25.1 MJ/kg) is also higher than that of *Cladophora fracta* (21.1 MJ/kg). Moisture content was determined by drying a 3- to 5-g sample at 378 K to constant weight (Demirbas 1999), ashing was carried out at 1,025 K for 2 h (Demirbas 2001), and protein content was determined by the block digestion method and ether-extractable intramuscular fat content by solvent extraction (Boccard *et al*. 1981). Table 6.3 shows the average chemical composition of algae samples. The oil proportion from the lipid fractions of *Chlorella protothecoides* is considerable higher than that of *Cladophora*

Table 6.2 Proximate analysis data and higher heating values of *Cladophora fracta* (an alga) and *Chlorella protothecoides* (a microalga), percent of dry-matter and ash-free basis (% daf)

Species of sample	Fixed carbon (% daf)	Volatile matter (% daf)	Higher Heating Value (MJ/kg)
Cladophora fracta	28.1	65.6	21.1
Chlorella protothecoides	39.6	54.6	25.1

Table 6.3 Average chemical composition of algae samples on a dry-matter basis (%)

Species of sample	Proteins	Carbohydrates	Lipids	Others
Cladophora fracta	52.3 ± 2.0	15.6 ± 0.9	14.2 ± 0.8	17.5 ± 0.9
Chlorella protothecoides	54.1 ± 2.2	13.7 ± 0.7	29.4 ± 1.5	4.8 ± 0.4

fracta (Demirbas 2009b). Figure 6.2 shows the production of biodiesel from algae.

Oils were obtained by extracting algae with hexane in a Soxhlet extractor for 18 h. Transesterification of algal oils was performed in a 100-mL cylinder using supercritical methanol according to earlier methods (Kusdiana and Saka 2001; Demirbas 2002). The fatty acids of the algal oils were fractionated into saturated, mo-

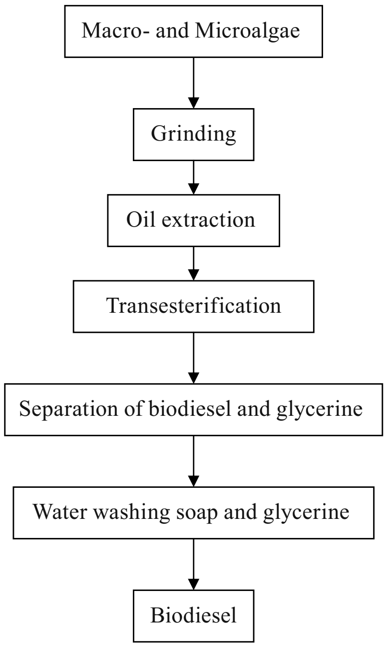

Figure 6.2 Production of biodiesel from algae

nounsaturated, polyunsaturated, and free forms by a preparative chromatographic thin layer on a glass plate coating with a 0.25-μm polyethanol succinate.

The fatty acid compositions of algal oils are given in Table 6.4. Fatty acids come in two varieties: saturated and unsaturated. Saturated fats come from animal products such as meat and dairy. Most vegetable oils are unsaturated. The properties of the various individual fatty esters that comprise biodiesel determine the overall fuel properties of the biodiesel fuel. As seen in Table 6.4, the average polyunsaturated fatty acids of *Chlorella protothecoides* (62.8%) are also higher than those of *Cladophora fracta* (50.9%). Algae generally produce a lot of polyunsaturates, which may present a stability problem since higher levels of polyunsaturated fatty acids tend to decrease the stability of biodiesel. However, polyunsaturates also have much lower melting points than monounsaturates or saturates; thus algal biodiesel should have much better cold weather properties than many other bio-oils (Demirbas 2009b).

Table 6.4 Fatty acid compositions of algal oils on a dry-matter basis (%)

Fatty acids in oils	*Cladophora fracta*	*Chlorella protothecoides*
Saturates	12.5 ± 0.7	10.8 ± 0.6
Monounsaturates	33.7 ± 1.6	24.1 ± 1.2
Polyunsaturates	50.9 ± 1.9	62.8 ± 2.5
Free	3.6 ± 0.3	2.6 ± 0.2

Xu *et al.* (2006) used *Chlorella protothecoides* (a microalga) for the production of biodiesel. Cells were harvested by centrifugation, washed with distilled water, and then freeze dried. The main chemical components of heterotrophic *C. protothecoides* were measured as in a previous study (Miao *et al.* 2004). Microalgal oil was prepared by pulverization of heterotrophic cell powder in a mortar and extraction with *n*-hexane.

Biodiesel was obtained from heterotrophic microalgal oil by acidic transesterification. Figure 6.3 shows the process flow schematic for biodiesel production (Xu *et al.* 2006). The optimum process combination was 100% catalyst quantity (based on oil weight) with 56:1 molar ratio of methanol to oil at a temperature of 303 K, which reduced product-specific gravity from an initial value of 0.912 to a final value of 0.864 in about 4 h of reaction time (Xu *et al.* 2006).

The technique of metabolic control through heterotrophic growth of *C. protothecoides* was applied, and the heterotrophic *C. protothecoides* contained a crude lipid content of 55.2%. To increase the biomass and reduce the cost of algae, corn powder hydrolysate instead of glucose was used as an organic carbon source in heterotrophic culture medium in fermenters. The result showed that cell density significantly increased under heterotrophic conditions, and the highest cell concentration reached 15.5 g/L. A large amount of microalgal oil was efficiently extracted from the heterotrophic cells using *n*-hexane and then transmuted into biodiesel by acidic transesterification (Xu *et al.* 2006).

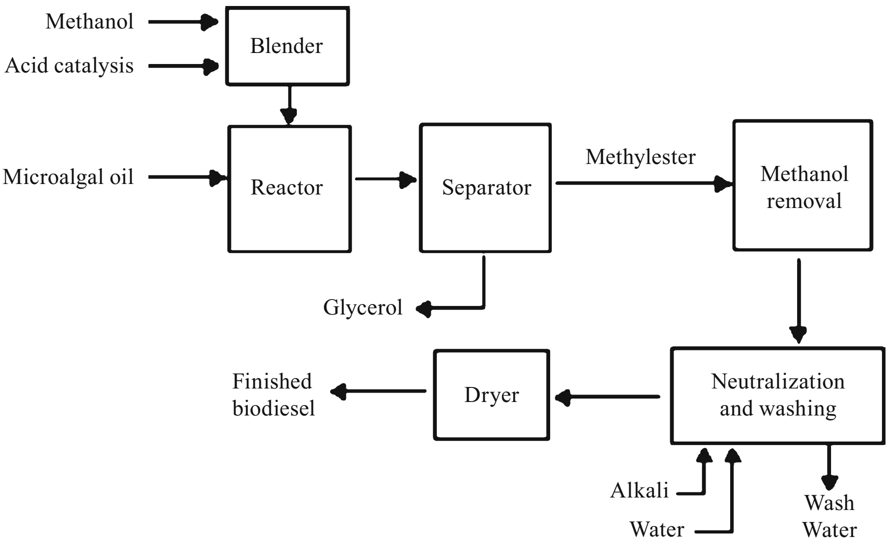

Figure 6.3 Process flow for biodiesel production

6.3 Potential of Microalgal Biodiesel

Algae biomass cultivation confers four important potential benefits that other sources don't have. First, algae biomass can be produced at extremely high volumes, and this biomass can yield a much higher percentage of oil than other sources. Second, algal oil has limited market competition. Third, algae can be cultivated on marginal land, fresh water, or sea water. Fourth, innovations to algae production allow it to become more productive while consuming resources that would otherwise be considered waste (Campbell 2008).

Biodiesel derived from oil crops is a potential renewable and carbon-neutral alternative to petroleum fuels. Unfortunately, biodiesel from oil crops, waste cooking oil, and animal fat cannot realistically satisfy even a small fraction of the existing demand for transport fuels. Microalgae appear to be the only source of renewable biodiesel that is capable of meeting the global demand for transport fuels.

Biodiesel production from biorenewable sources has a number of problems. First, most biorenewable sources, such as waste oil, animal fat, and vegetable oil, have a limited supply (Ma and Hanna 1999). Second, many of these sources have competitive uses, such as food or cosmetic production. Extensive use of renewable oils may cause other significant problems such as starvation in poor and developing countries (Demirbas 2007). Third, the resources that were used to create the biomass have competition with other uses, and this includes arable land. Third, because of the limited supply and competition, many sources of biomass have become increasingly expensive (Haag 2007).

Like plants, microalgae use sunlight to produce oils, but they do so more efficiently than crop plants. Oil productivity of many microalgae greatly exceeds the oil productivity of the best producing oil crops. Approaches to making microalgal biodiesel economically competitive with petrodiesel have been discussed (Chisti 2007). Biodiesel derived from green algae biomass has the potential for high-volume, cost-effective production (Campbell 2008).

Laboratory studies exploring methods to maximize both density and oil content have demonstrated that there is yet much unrealized potential. Xu *et al.* (2006) cultivated the algae *Chlorella protothecoids* in a light-deprived, heterotrophic environment with inexpensive hydrolyzed corn starch as the sole food source. The algae were not only able to adapt to this environment, but they reached a high population density of 15.5 g/L.

Biodiesel from microalgae seems to be the only renewable biofuel that has the potential to completely displace petroleum-derived transport fuels without adversely affecting the food supply and other crop products. Most productive oil crops, such as oil palm, do not come close to microalgae in being able to sustainably provide the necessary amounts of biodiesel. Similarly, bioethanol from sugar cane is no match for microalgal biodiesel (Chisti 2008).

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, especially when you realize that oil was originally formed from algae.

In order to have an optimal yield, these algae need to have CO_2 in large quantities in the basins or bioreactors where they grow. Thus, the basins and bioreactors need to be coupled with traditional electricity-producing thermal power centers that produce CO_2 at an average rate of 13% of the total flue gas emissions. The CO_2 is put into the basins and assimilated by the algae. It is thus a technology that recycles CO_2 while also treating used water.

Algae can grow practically anywhere where there is enough sunshine. Some algae can grow in saline water. All algae contain proteins, carbohydrates, lipids, and nucleic acids in varying proportions. While the percentages vary with the type of algae, there are algae types that are comprised of up to 40% of their overall mass by fatty acids (Becker 1994). The most significant distinguishing characteristic of algal oil is its yield and, hence, its biodiesel yield. According to some estimates, the yield (per acre) of oil from algae is over 200 times the yield from the best-performing plant/vegetable oils (Sheehan *et al.* 1998). Microalgae are the fastest growing photosynthesizing organisms. They can complete an entire growing cycle every few days. Approximately 46 tons of oil/ha/year can be produced from diatom algae. Different algae species produce different amounts of oil. Some algae produce up to 50% oil by weight. The production of algae to harvest oil for biodiesel has not been undertaken on a commercial scale, but working feasibility studies have been conducted to arrive at the above number.

Microalgae are very efficient solar energy converters, and they can produce a great variety of metabolites (Chaumont 2005). The culture of algae can yield 30 to 50% oil (Chisti 2007; Dimitrov 2008). Oil supply is based on the theoretical claims that 47,000 to 308,000 L/ha/year of oil could be produced using algae. The calculated cost per barrel would be only $ 20 (Demirbas 2009a). Currently, a barrel of oil in the US market sells for over $ 100. Despite all the claims and research dating from the early 1970s to date, none of the projected algae and oil yields have been achieved (Patil *et al.* 2005). Algae, like all plants, require large quantities of nitrogen fertilizer and water, plus significant fossil energy inputs for the functioning system (Goldman and Ryther 1977). Harvesting the algae from tanks and separating the oil from the algae are difficult and energy-intensive processes (Pimentel *et al.* 2004; Pimentel 2008).

Fatty acids come in two varieties: saturated and unsaturated. Saturated fats come from animal products such as meat and dairy. Most vegetable oils are unsaturated. The properties of the various individual fatty esters that comprise biodiesel determine the overall fuel properties of the biodiesel fuel. Algae generally produce a lot of polyunsaturates, which may present a stability problem since higher levels of polyunsaturated fatty acids tend to decrease the stability of biodiesel. However, polyunsaturates also have much lower melting points than monounsaturates or saturates; thus algal biodiesel should have much better cold-weather properties than many other bio-oils (Demirbas 2009b). Algae are theoretically a very promising source of biodiesel. The lipid and fatty acid contents of microalgae vary in accordance with culture conditions. In some cases, lipid content can be enhanced by the imposition of nitrogen starvation or other stress factors. Which is the best species of algae for biodiesel? There is no one strain or species of algae that can be said to be the best in terms of oil yield for biodiesel. However, diatoms and secondly green algae have shown the most promise. *Scenedesmus dimorphus* is a unicellular alga in the class Chlorophyceae (green algae). While this is one of the preferred species for oil yield for biodiesel, one of the problems with *Scenedesmus* is that it is heavy and forms thick sediments if not kept in constant agitation. The strain known as *Dunaliella tertiolecta* has an oil yield of about 37% (organic basis). *D. tertiolecta* is a fast growing strain, which means it has a high CO_2 sequestration rate as well (Demirbas 2009a,b; Ozkurt 2009). Table 6.5 shows the yield of various plant oils.

Certain algae strains also produce polyunsaturated fatty acids (omega-3s) in the form of eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) generally found in fish oils. Phototrophic microalgae are used to provide polyunsaturated fatty

Table 6.5 Yield of various plant oils

Crop	Oil (L/ha)
Algae	100,000
Castor	1,413
Coconut	2,689
Palm	5,950
Safflower	779
Soy	446
Sunflower	952

acids (omega-3 and omega-6) for aquaculture operations. These additional products greatly enhance the overall marketability and economics of producing algae (Volkman *et al*. 1989; Yaguchi *et al*. 1997; Vazhappilly and Chen 1998).

A selection of algae strains with the potential to be used for the production of oils for biofuel is presented in Table 6.6. A major current problem for the commercial viability of biodiesel production from microalgae is the low selling price of biodiesel (less than US$ 1.38/kg). Microalgal oils can potentially completely replace petroleum as a source of hydrocarbon feedstock for the petrochemical industry.

Table 6.6 Oil content in selected microalgal species

Species	Oil content (% dw)	Reference
Ankistrodesmus TR-87	28–40	Ben-Amotz and Tornabene 1985
Botryococcus braunii	29–75	Sheehan *et al*. 1998; Banerjee *et al*. 2002; Metzger and Largeau 2005
Chlorella spp.	29	Sheehan *et al*. 1998
Chlorella protothecoides (autotrophic/heterothrophic)	15–55	Xu *et al*. 2006
Cyclotella DI-35	42	Sheehan *et al*. 1998
Dunaliella tertiolecta	36–42	Kishimoto *et al*. 1994; Tsukahara and Sawayama 2005
Hantzschia DI-160	66	Sheehan *et al*. 1998
Isochrysis spp.	7–33	Sheehan *et al*. 1998; Valenzuela-Espinoza *et al*. 2002
Nannochloris	31 (6–63)	Ben-Amotz and Tornabene 1985; Negoro *et al*. 1991
Nannochloropsis	46 (31–68)	Hu *et al*. 2008
Nitzschia TR-114	28–50	Kyle and Gladue 1991
Phaeodactylum tricornutum	31	Sheehan *et al*. 1998
Scenedesmus TR-84	45	Sheehan *et al*. 1998
Stichococcus	33 (9–59)	Sheehan *et al*. 1998
Tetraselmis suecica	15–32	Sheehan *et al*. 1998; Zittelli *et al*. 2006; Chisti 2007
Thalassiosira pseudonana	(21–31)	Brown *et al*. 1996

6.4 Acceptability of Microalgal Biodiesel

The idea of producing biodiesel from microalgae that accumulate high amounts of oil was a main focus in the NREL project (Sheehan *et al*. 1998). Many species of algae accumulate large amounts of oils that to a large extent are made up of triacylglycerols consisting of three fatty acids bound to 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 (Chisti 2007). A number of algae strains with good potential for making biodiesel were identified.

Some microalgae appear to be a suitable group of oleaginous microorganisms for lipid production (Chisti 2007). Microalgae have been suggested as potential candidates for fuel production because of a number of advantages including higher photosynthetic efficiency, higher biomass production, and higher growth rate compared to other energy crops (Milne *et al.* 1990; Dote *et al.* 1994; Minowa *et al.* 1995). Moreover, according to the biodiesel standard published by the American Society for Testing Materials (ASTM), biodiesel from microalgal oil is similar in properties to standard biodiesel and is also more stable according to their flash point values. Figure 6.4 shows a biodiesel product obtained from microalgae.

Figure 6.4 Biodiesel product obtained from microalgae

6.5 Economics of Biodiesel Production

There are small numbers of economic feasibility studies on microalgae oil (Richardson *et al.* 2009). Currently, microalgae biofuel has not been deemed economically feasible compared to the conventional agricultural biomass (Carlsson *et al.* 2007).

Critical and controversial issues are the potential biomass yield that can be obtained by cultivating macro- or microalgae and the costs of producing biomass and derived products. The basis of the estimates is usually a discussion of three parameters: photosynthetic efficiency, assumptions on scaleup, and long-term cultivation issues. For microalgae the productivity of raceway ponds and photobioreactors is limited by a range of interacting issues.

Typical productivity for microalgae in open ponds is 30 to 50 t/ha/y (Benemann and Oswald 1996; Sheehan *et al.* 1998). Several possible target areas to improve productivity in large-scale installations have been proposed (Benemann and Oswald 1996; Grobbelaar 2000; Suh and Lee 2003; Torzillo *et al.* 2003; Carvalho *et al.* 2006).

Harvesting costs contribute 20 to 30% to the total cost of algal cultivation, with the majority of the cost attributable to cultivation expenses. Genetic engineering, development of low-cost harvesting processes, improvements in photobioreactor, and integration of coproduction of higher-value products/processes are other alternatives in reducing algal oil production costs (Chisti 2007). The harvested algae then undergo anaerobic digestion, producing methane that could be used to produce electricity.

In commercial photobioreactors, higher productivities may be possible. Typical productivity for a microalga (*Chlorella vulgaris*) in photobioreactors is 13 to 150 (Pulz 2001). Photobioreactors require ten times more capital investment than open-pond systems. The estimated algal production cost for open-pond systems ($ 10/kg) and photobioreactors ($ 30 to $ 70/kg) is, respectively, two orders of magnitude higher and almost three orders of magnitude higher than conventional agricultural biomass (Carlsson *et al.* 2007). Assuming that biomass contains 30% oil by weight and carbon dioxide is available at no cost (flue gas), Chisti (2007) estimated the production cost for photobioreactors and raceway ponds at $ 1.40 and $ 1.81 per liter of oil, respectively. However, for microalgal biodiesel to be competitive with petrodiesel, algal oil should be less than $ 0.48/L (Chisti 2007).

It is useful to compare the potential of microalgal biodiesel with bioethanol from sugar cane, because on an equal energy basis, sugar cane bioethanol can be produced at a price comparable to that of gasoline (Bourne 2007). Bioethanol is well established for use as a transport fuel (Gray *et al.* 2006), and sugar cane is the most productive source of bioethanol (Bourne Jr. 2007). For example, in Brazil, the best bioethanol yield from sugar cane is 7.5 m^3/ha (Bourne Jr. 2007). However, bioethanol has only approx. 64% of the energy content of biodiesel. Therefore, if all the energy associated with 0.53 billion m^3 of biodiesel that the USA needs annually (Chisti 2007) were to be provided by bioethanol, nearly 828 million m^3 of bioethanol would be needed. This would require planting sugar cane over an area of 111 million ha, or 61% of total available US cropland.

Recovery of oil from microalgal biomass and conversion of oil into biodiesel are not affected by whether the biomass is produced in raceways or photobioreactors. Hence, the cost of producing the biomass is the only relevant factor for a comparative assessment of photobioreactors and raceways for producing microalgal biodiesel. If the annual biomass production capacity is increased to 10,000 t, the cost of production per kilogram reduces to roughly $ 0.47 and $ 0.60 for photobioreactors and raceways, respectively, because of economies of scale. Assuming that the biomass contains 30% oil by weight, the cost of biomass for providing a liter of oil would be something like $ 1.40 and $ 1.81 for photobioreactors and raceways, respectively (Chisti 2007).

Biodiesel from palm oil costs roughly $ 0.66/L, or 35% more than petrodiesel. This suggests that the process of converting palm oil into biodiesel adds about $ 0.14/L to the price of oil. For palm-oil-sourced biodiesel to be competitive with petrodiesel, the price of palm oil should not exceed $ 0.48/L, assuming no tax on biodiesel. Using the same analogy, a reasonable target price for microalgal oil is $ 0.48/L for algal diesel to be cost competitive with petrodiesel.

6.6 Improving Economics of Microalgal Biodiesel

Algae are among the fastest growing plants in the world, and about 50% of their weight is oil. That lipid oil can be used to make biodiesel for cars, trucks, and airplanes. Algae will some day be competitive as a source of biofuel.

Only renewable biodiesel can potentially completely displace liquid fuels derived from petroleum. The economics of producing microalgal biodiesel need to improve substantially to make it competitive with petrodiesel, but the level of improvement necessary appears to be attainable (Demirbas 2009b).

Biodiesel has great potential; however, the high cost and limited supply of renewable oils prevent it from becoming a serious competitor with petroleum fuels. As petroleum fuel costs rise and supplies dwindle, biodiesel will become more attractive to both investors and consumers. For biodiesel to become the alternative fuel of choice, it requires an enormous quantity of cheap biomass. Using new and innovative techniques for cultivation, algae may allow biodiesel production to achieve the price and scale of production needed to compete with, or even replace, petroleum (Campbell 2008).

It has been estimated that 0.53 billion m^3 of biodiesel would be needed to replace current US transportation consumption of all petroleum fuels (Chisti 2007). Neither waste oil nor seed oil can come close to meeting the requirement for that much fuel; therefore, if biodiesel is to become a true replacement for petroleum, a more productive source of oil such as algal oil is needed (Scott and Bryner 2006; Chisti 2007).

The cost of producing microalgal biodiesel can be reduced substantially by using a biorefinery-based production strategy, improving capabilities of microalgae through genetic engineering and advances in photobioreactor engineering. Like a petroleum refinery, a biorefinery uses every component of the biomass raw material to produce usable products (Chisti 2007).

6.7 Advantages and Disadvantages of Biodiesel from Algal Oil

Producing biodiesel from algae has been touted as the most efficient way to make biodiesel fuel. Algal oil processes into biodiesel as easily as oil derived from land-based crops. The difficulties in efficient biodiesel production from algae lie not in the extraction of the oil but in finding an algal strain with a high lipid content and fast growth rate that is not too difficult to harvest and a cost-effective cultivation system (i.e., type of photobioreactor) that is best suited to that strain.

Algae are the fastest growing plants in the world. Microalgae have much faster growth rates than terrestrial crops. The per-unit area yield of oil from algae is estimated to be between 18,927 and 75,708 L/acre/year; this is 7 to 31 times greater than the next best crop, palm oil, at 2,404 L/acre/year.

Algae are very important as a biomass source. Different species of algae may be better suited for different types of fuel. Algae can be grown almost anywhere,

Table 6.7 Advantages of biodiesel from algae oil

Rapid growth rates
Grows practically anywhere
A high per-acre yield (7 to 31 times greater than the next best crop, palm oil)
No need to use crops such as palms to produce oil
A certain species of algae can be harvested daily
Algae biofuel contains no sulfur
Algae biofuel is nontoxic
Algae biofuel is highly biodegradable
Algal oil extracts can be used as livestock feed and even processed into ethanol
High levels of polyunsaturates in algal biodiesel are suitable for cold weather climates
Can reduce carbon emissions based on where it's grown

Table 6.8 Disadvantages of biodiesel from algal oil

Produces unstable biodiesel with many polyunsturates
Biodiesel performs poorly compared to its mainstream alternative
Relatively new technology

even on sewage or salt water, and does not require fertile land or food crops, and processing requires less energy than the algae provides. Algae can be a replacement for oil-based fuels, one that is more effective. Algae consume CO_2 as they grow, so they could be used to capture CO_2 from power stations and other industrial plant that would otherwise go into the atmosphere. Tables 6.7 and 6.8 show the advantages and disadvantages of biodiesel from algal oil.

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