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Bıodıesel from Mıcroalgae: A Renewable Energy Source

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Abstract: Due to fact that fossil fuels are consumable and limited, renewable energy sources have growing importance in recent years. Biodiesel is a renewable diesel fuel that consists of simple alkaly esters of fatty acids. This fuel technology is based on the use of agricultural, animal or waste oils. Also researches are focused on to develop new technologies and alternative resources. All microalgae species produce lipid, however some species can contain up to 75% of their dry weight. Biodiesel production by using microalgae is an alternative process in contrast to other procedures not only being degradable and non-toxic but also as a solution to global warming via reducing emission gases. The aim of this study is making feasibility about biodiesel production to supply energy requirement by using microalgae. In this paper, the main advantages of microalgae for biodiesel production were described in comparison with other biodiesel sources.

Key words: Microalgal oils · Biodiesel · Renewable energy sources · Transesterification

INTRODUCTION

Biodiesel is a kind of sustainable energy source, produced from oils. It is known that fossil fuels have drawbacks for environment. The energy has been depleted because of the finite fossil fuel resources. These consumable fuels lead to environmental pollution [1]. Also global warming is important around the world.

Biodiesel is a renewable energy sources that is produced from oil crops such as plants, animals and microalgae. Biodiesel is known as fatty acid methyl esters originating from vegetable oils and animal fats [2]. In biodiesel production, triglycerides are reacted with methanol by a catalyst. This process is known as transesterification.Biodiesel can be produced from any material that contains fatty acids which can be linked to other molecules or present as free fatty acids. Hence various oil such as animal fats, vegetable and microalgal oils can be used for biodiesel production.

Like plants, microalgae use sunlight to produce oils however their production is more efficient than crop plants. Oil productivity of many microalgae is higher than the best oil producing crops. Microalgae have been suggested as very good candidates for biodiesel production, because they have some advantages such as higher photosynthetic efficiency, higher biomass production and faster growth compared to other energy crops [2]. It was found that microalgae are the more sustainable source of biodiesel in terms of food and environmental impact compared to other feedstocks [1]. Additionally, it provides advantage for usage of unfertile lands, inefficient for agriculture, for biodiesel production instead of using productive lands for food production.

Biodiesel: The most common biofuels are biodiesel and bioethanol which can replace diesel and gasoline. They are mainly produced from renewable energy sources such as biomass and contribute to lower combustion emissions than fossil fuels per equivalent power output [3]. Biodiesel is the monoalkyl esters of long-chain fatty acids originating from the chemical reaction (transesterification) of renewable feedstocks, such as animal fats, vegetable and microalgal oils and alcohol with or without a catalyst [1]. Biodiesel has a growing importance because of its advantages of being renewable, biodegredable and non-toxic. It does not emit the detrimental gases such as CO_2, sulfide and it reduce engine emissions and greenhouses gases.

Vegetable oil has too high viscosity for using in most existing diesel engines for direct usage instead of fuel oil. However, there are four basic processes for production of biodiesel; direct usage and blending (blend of 20%

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biodiesel), microemulsions, pyrolysis, transesterification. The most commonly used method is transesterification of vegetable oils and animal fats. The transesterification reaction is effected by molar ratio of glycerides to alcohol, catalysts, reaction temperature, reaction time and free fatty acids and water content of oils or fats [4]. There are three basic processes for biodiesel production from oils and fats by transesterification:

- Base catalyzed transesterification of the oil.
- Direct acid catalyzed transesterification of the oil.
- Conversion of the oil to its fatty acids and then to biodiesel.

Characteristics of Biodiesel: Biodiesel has been shown to give engine performance generally comparable to that conventional diesel fuel while reducing engine emissions of particulates, hydrocarbons and carbon monoxide [5]. The sources for production of biodiesel are sustainable products such as animal fats, vegetable and microalgal oils.

Biodiesel has similar properties with petroleum diesel such as specific gravity as seen in table 1. Biodiesel operates in compression-ignition engines or diesel engines just like petroleum diesel [6]. Biodiesel is used as a fuel in house and industry beside transportation.

Advantages and Disadvantages of Biodiesel: Biodiesel may not require any engine modification in regular diesel motors used in cars without the hassle. It prologs engine life and reduces the need for maintenance (biodiesel has better lubricating qualities than normal diesel), it is safer to handle, being less toxic, biodegradable and having a higher flash point. Biodiesel is an efficient, clean, %100 natural energy resource that is alternative to petroleum diesel [6]. Also it reduces some exhaust gases such as carbonmonoxide (CO) and SO_X. It produces 78% less carbondioxide (CO_2). It is an ecologically friendly fuel because of this emission profile. Biodiesel is better than petroleum diesel in terms of sulfur content, flash point, aromatic content and biodegradability [6]. It provides usage advantage of waste oils. Industrial and fried food waste oils pose a threat to environment. Their usage for biodiesel production could be a solution for this problem too.

Besides its number of advantages, biodiesel has some disadvantages. When it is used in low temperatures, it causes some problems because of its high flow point. So, cold flow additives must be added into biodiesel to solve these troubles. Additionally, freezing of fuel in cold weather causes reducing the energy density and degradation of fuel under storage for prolong period. NO_X emissions are higher than normal diesel. One of the most important disadvantages of biodiesel is production cost because of feedstocks. Feedstock costs account for a large percent of the direct biodiesel production cost, including capital cost and return [6].

The Choice of Feedstock for Biodiesel: Biodiesel can be produced from any biological materials. These are; (i) vegetable oil feedstock; such as rapeseed and soybean; (ii) waste vegetable oil; (iii) animal fats including tallow, lard and yellow grease; (iv) microalgal oils. Cost of raw material significantly effects cost of biodiesel production besause biodiesel production cost includes raw material approximately %70-75 of the total cost. Therefore choice of feedstock is an important parameter in biodiesel production [8].

The standard or specification required by a production facility depends on the process used for making biodiesel as well as company requirements for product yield and purity. Some considerations must be thought for choosing the appropriate feedstock to produce biodiesel:

Table 1: Comparison of biodiesel from microalgal oil and diesel fuel and ASTM biodiesel standart [7]

Comparison of properties of biodiesel from microalgal oil and diesel fuel and ASTM biodiesel Standard			
Properties	Biodiesel from microalgal oil	Diesel fuel	ASTM biodiesel standart
Density (kg L^{-1})	0.864	0.838	0.86-0.90
Viscosity ($mm^2 s^{-1}$, cSt at 40 °C)	5.2	1.9-4.1	3.5-5.0
Flash point (°C)	115	75	Min 100
Solidifying point (°C)	-12	-50-100	-
Cold filter plugging point (°C)	-11	-3.0 (max. -6.7)	Summer max 0 Winter max <-15
Acid value (mg $KOHg^{-1}$)	0.374	Max. 0.5	Max 0.5
Heating value (MJ kg^{-1})	41	40-45	-
H/C ratio	1.81	1.81	-

- Physical and chemical characteristics of the bio-oil,
- Competition for the bio-oil by other end users and markets,
- Cost, consistency and reliability of supply [8].

Key physical and chemical characteristics that affect the ability of oils to be used for biodiesel production include the titre, free fatty acid (FFA) content, moisture content and other impurities and calorific content [8].

Biodiesel from Microalgae: Algae are photosynthetic organisms that found in marine and freshwater environments. They utilize sunlight to convert chemical energy. This chemical energy is used to drive chemical reactions such as the formation of sugars or the fixation of nitrogen into amino acids, the building blocks for protein synthesis. Microalgae are sunlight-driven cell factories that convert carbondioxide to potential biofuels, foods and fine bioactive chemicals [9]. The inefficiency and unsustainability of the use of food crops as a biodiesel source have increased interest in usage of microalgae species as a renewable energy source [1].

Why is Biodiesel Production from Microalgae?

Microalgae contain lipids and fatty acids as membrane components, storage products, metabolites and resources of energy. Algal strains, diatoms and cyanobacteria have been found to contain relatively high levels of lipids. Most of microalgae can produce and accumulate hydrocarbons and oil content of some microalgae exceeds 80% of dry weight of microalgal biomass shown in table 2. Oil productivity, that is the mass of oil production per volume per day, depends on algal growth rate and oil content of the algal biomass [10].

Microalgae are good candidates for biodiesel production besause of the high oil productivity. Also microalgae have several attractive characteristics for biodiesel production:

- Doubling time is shorter than other biomass materials such as trees, animals etc. and microalgae have higher growth rates.
- Higher yield and oil productivity-lower cost
- Costs related with their harvesting, transportation of microalgae are lower than other biomass materials.
- Microalgae are biodegradable and they can be chemically treated easily.
- Their cultivation is not complex; algae can grow practically in every place where there is enough sunshine
- Microalgae are capable of fixing CO_2 in the atmosphere, thus facilitating the reduction of increasing atmospheric CO_2 levels, which are now considered a global problem.
- Microalgae do not compete for land with crops used for food production. The cultivation of microalgae does not require a large area of land compared to other plant sources. In addition, they do not directly affect the human food supply chain, eliminating the food versus fuel dispute.
- Microalgae produce valuable co-products or by-products such as biopolymers, proteins, carbohydrates and residual biomass, which may be used as feed or fertilizer.
- Microalgae are considered to be an efficient biological system for harvesting solar energy to use in the production of organic compounds [9], [1].

Table 2: Oil content of some microalgae

Strain	% Oil content (Dry weight)
Scenedesmus sp.	12-40
Chlamydomonas sp.	21
Chorella sp.	14-22
Spirogyra sp.	11-21
Euglena so.	14-20
Prymnesium sp.	22-38
Porphyridium sp.	9-14
Synechoccus sp.	11
Botryococcus braunii	25-75
Chlorella sp	28-32
Crypthecodinium cohnii	20
Cylindrotheca sp.	16-37
Dunaliella primolecta	23
Isochrysis sp.	25-33
Monallanthus salina	>20
Nannochloris sp.	20-35
Nannochloropsis sp.	31-68
Neochloris oleoabundans	35-54
Nitzschia sp.	45-47
Phaeodactylum tricornutum	20-30
Schizochytrium sp.	50-77

Table 3: Comparison of some sources of biodiesel [9]

Crop	Oil yield (L/ha)	Land area needed (M ha)^a	Percent of existing US cropping area^a
Corn	172	1540	846
Soybean	446	594	326
Canola	1190	223	122
Jatropha	1892	140	77
Coconut	2689	99	54
Oil palm	5950	45	24
Microalgae^b	136,900	2	1.1
Microalgae^c	58,700	4.5	2.5

a For meeting 50% of all transport fuel needs of the United States.
b 70% oil (by wt) in biomass.
c 30% oil (by wt) in biomass.

Agricultural oil crops, such as soybean oil and oil palm, are widely used to produce biodiesel. However their oil content is less compared with microalgae shown in Table 3 [9].

For example, U.S. 's biodiesel requirement is nearly $0.53*10^9$ m^3. Oil palm is one of the most oil producing plants which oil yield is ~ (nearly) 5950 L/ha. Biodiesel yield is ~ 80% of the oil yield per hectar [10]. Thus;

$$A= \frac{0.53*10^{12} L}{5950 L/ha} * 0.80 \cong 111*10^6 ha$$

A: Area for oil palm to production of biodiesel

This is nearly 61% of all agricultural land in U.S. based on these calculations, biodiesel replacement petroleum diesel is not realistic and reasonable. On the other hand microalgae have potential because of their growth rate. Their doubling times commonly are 24 h and during exponential phase this can be as short as 3.5 h. In addition oil levels reach up to %20-50.

Additionally, it is worthwhile to compare other bioenergy sources such as bioethanol. Bioethanol has only 64% of energy content of biodiesel. Hence, if $0.53*10^9$ m^3 biodiesel requirements substitute with bioethanol, $828*10^6$ m^3 bioethanol will be needed. Starvation becomes an important problem around the world. To cope with this problem it is important that use of productive and cultivated land for food instead of fuel production.

Fuels from Algae: Several types of renewable biofuels can be produced from microalgae:

- Methane production by anaerobic digestion of algal biomass
- Biodiesel production by transestrification of algal oils
- Photobiologically produced biohydrogen [10].

Also biofuels can be produced by thermal liquefaction or pyrolizis of microalgae. Certain microalgae can accumulate 70% and more of dry weight of microalgal biomass as hydrocarbons. Therefore microalgae are potential sources of biofuels [9].

Oil Yield from Algae: Microalgae are single cell organisms which has high level lipid content (Table 4). Under the environmental stres conditions such as nutrient deficiency lipid accumulation can be triggered. The lipid and fatty acid contents of microalgae can vary with culture conditions.

Table 4: Biochemical composition of some microalgae [11]

Strain	Protein	Carbohydrate	Lipid	Nucleic Asid
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	-

In some cases, lipid content can be enhanced by nitrogen starvation or other stress factors.

Nitrogen deficiency in microalgae and silicon deficiency in diatoms triggers the lipid accumulation. Also Si depletion is increased the oil levels in diatoms. Si is a component of the diatom's cell wall. For that reason when Si was spent up, cell division slowed down. In the diatom C. cryptica, the rate of oil production remained constant once Si depletion occurred, while growth rate of the cells dropped. Further studies identified two factors that seemed to be at play in this species:

- Si-depleted cells direct newly assimilated carbon more toward lipid production and less toward carbohydrate production.
- Si-depleted cells slowly convert non-lipid cell components to lipids [11]. Diatoms store carbon in lipid or carbohydrate form. The results of these experiments suggested that it might be possible to alter which route the cells used for storage [11].

While the rate of production of all cell components and growth rate is lower under nutrient deficiency, oil production and accumulation is higher. For the high rate oil production from microalgae, initially biomass should be produced in optimum conditions, then oil productivity should be increased under stres conditions. Also, heterotrophic growth of microalgae Chlorella protothecoides increased the accumulation of lipid content up to 55% in the cells. Large amount of microalgal oil was efficiently extracted from these heterotrophic cells by using n-hexane. C.protothecoides can be photoautotrophically or heterotrophically grown under

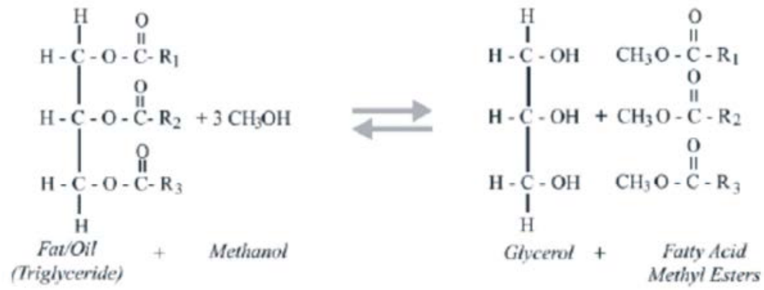

Fig. 1: Transesterification of oil to biodiesel [14].

different culture conditions. Heterotrophic growth of C. protothecoides results in high production of biomass and accumulation of high lipid content in cells. When glucose was added in the culture medium and glycine was reduced for heterotrophic growth lipid content of cells reached up to 55.20%. The heterotrophic cells were full of lipid vesicles,which could be easily observed under differential interference microscopy [2].

Algae Production Systems for Biodiesel: Photosynthetic growth requires light, carbon dioxide, water and inorganic salts. Also temperature must remain generally within 20-30°C [9]. Several methods can be used to grow large scale of phototrophic algae. These systems include outdoor systems such as open ponds and tanks where the light source is sunlight and closed systems such as photobioreactors [12].

Growth medium must provide the inorganic elements. Essential elements include nitrogen (N), phosphorus (P), iron and in some cases silicon especially diatoms [9]. Although sunlight is used as a light source in outdoor systems, electric lights are used for illumination in closed systems. Photobioreactors are defined as closed systems and these systems provide the control and optimization of culture parameters. Also photobioreactors prevent contamination. But in outdoor systems, algal culture can be contaminated by the other algal species or microorganisms. Therefore outdoor systems are only used for algae that grow in extreme conditions such as pH, temperature [13].

Biodiesel Production Process

Transesterification: Biodiesel is produced using a process referred to as "transesterification". In making biodiesel, triglycerides are reacted with methanol in a reaction known as transesterification or alcoholysis. Transestrification produces methyl esters of fatty acids, that are biodiesel and glycerol (Figure 1). The reaction occurs stepwise: triglycerides are first converted to diglycerides, then to monoglycerides and finally to glycerol [9]. During transesterification, the glycerin molecule is replaced by three alcohol molecules which form three alcohol esters and release one glycerin molecule [8].

The process consists of three key steps: transesterification, ester and glycerin separation and ester purification. Overall, the process employs a relatively simple chemical reaction. Animal, vegetable or algal oils consist of triglycerides, meaning they are comprised of three fatty acid molecules connected by a glycerin molecule.

When the feedstock characteristics, transesterification temperature, reaction time, amount of excess alcohol and amount of catalyst are optimum, nearly all of the triglycerides in animal and vegetable oils are converted to alcohol esters [9].

Process Parameters:

- Molar ratio of alcohol to oil
- Moisture and water content on yield of biodiesel
- Effect of free fatty acids
- Raw material (feedstock)
- Reaction temperature
- Effect of stirring (Mixing intensity)
- Amunt of catalyst
- Type of catalyst [14], [15].

CONCLUSION

Biodiesel produced from microalgae is a new sustainable energy source substituted for petroleum diesel. Microalgal biodiesel is technically feasible because of the possibility of using the same engines and equipments used for petroleum diesel. Large scale microalgal production is needed for microalgal biodiesel to be used instead of petroleum diesel. These large amount of algal biomass could be cultivated in photobioreactors but a favorable assessment of the economics of production is necessary to establish. Cultivation of microalgal biomass in open ponds, especially in sunny and temperate region, could be very economic. Additionally, open ponds in hectars of area, could remove excess CO_2 in atmosphere with photosynthesis. This could be not only a solution for renewable energy production but also a solution for CO_2 problem causing global warming. Microalgae with their high doubling time and photosynthetic activity, could be the only quick solution for solving global warming problem in short term.

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