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Biodiesel an Alternative Motor Fuel-An Overview

M.Sakunthala[1], V.Sridevi[2*], M.V.V.CH.Lakshmi[3] ,K. Vijay Kumar[4]
[1]M.Tech, Centre for Biotechnology, Dept of Chemical Engineering, Andhra University, A.P, India,
[2*]Associate professor, Dept of Chemical Engineering, Andhra University, A.P, India
[3]M.Tech, Centre for Biotechnology, Department of Chemical Engineering, Andhra University, Visakhapatnam-03, Andhra Pradesh, India
[4]M.Tech, Centre for Biotechnology, Dept of Chemical Engineering, Andhra University, A.P, India

Abstract:* Bio fuels play a vital role in mitigating CO_2 emission, reducing global warming and bringing down the hike in oil prices. Bio diesel has become a recent attraction since it is biodegradable, renewable and non toxic. "In any case, they make it certain that motor-power can still be produced from the heat of the sun, which is always available for agricultural purposes, even when all our natural stores of solid and liquid fuels are exhausted.." Sustainable and renewable energy resources are highly essential to replace the vanishing petroleum fossil fuels. The objective of the paper is to study the potential of micro algae as an alternative raw material for bio diesel generation. Bio diesel is a fuel comprised of monoalkyl esters of long chain fatty acids traditionally derived from vegetable oils or animal fats. The world is witnessing an unprecedented increase in interest and demand for bio diesel and other fuels derived from renewable biomass due to rising petroleum fuel costs, increasing concern for the environmental impact of emissions from the combustion of conventional fossil fuels, increasing reliance on foreign oil sources, and decline in domestic oil production. Bio diesel production from micro algae is being widely developed at different scales as a potential source of renewable energy with both economic and environmental benefits.

***Keywords:* Bio diesel; free fatty acid (FFA); micro algae; transesterification; triacylglycerides (TAG); viscosity.**

I. INTRODUCTION

Majority of the world energy need are supplied through petrochemical sources, coal, and natural gases, with the exception of hydroelectricity and nuclear energy, of all, these sources are finite in the current usage rates will be consumed shortly. Non-renewable energy sources such as petroleum are related to several drawbacks including; increase green house emission, high cost of processing the crude petrol and energy demand during the process, non-renewable etc. This has provided incentives to seek for alternative sources for petroleum-based fuels.[1, 2]

An alternative fuel must be technically feasible, economically competitive, environmentally acceptable and readily available. One possible alternative to fossil fuel is the use of oils of plant origin like vegetable oils and tree borne oil seeds. The alternative diesel fuel can be termed as biodiesel. The fuel is biodegradable, non-toxic and has low emission profiles as compared to petroleum-based diesel. Usage of biodiesel will allow balance to be sought between agriculture, economic development and the environment.[3] Various edible and non edible vegetable oils, like rice bran oil, coconut oil, Jatropha caucus oil, castor oil, cottonseed oil, mahua, karanja which are either surplus and are non-edible type, can be used for the preparation of biodiesel.[4-6] Chemically, the oils/fats consist of triglyceride molecules of three long chain fatty acids that are ester bounded to a single glycerol molecule. These fatty acids differ by length of carbon chains, the number, orientation and position of the double bounds in these chains. Thus the biodiesel refers to as lower alkyl esters of long chain fatty acids, which are synthesized either by transesterification with lower alcohols or by esterification of fatty acid.[3]

Biodiesel is liquid which varies in color between golden and dark brown depending upon the production feedstock. It is immiscible with water, has a high boiling point and low vapor pressure. A biodegradable transportation fuel that contributes no net carbon dioxide or sulfur emission to the atmosphere and is low in particulate emission. Biodiesel has very good lubricating properties, significantly better than standard diesel which can prolong engine's life. Table 1, shows comparison of characteristics between diesel and biodiesel.

Table 1: Comparative study between diesel and biodiesel

Characteristics	Diesel	Biodiesel
Color	Golden	Golden and dark brown
Density, kg/m^3	0.84	0.88
Flash point, ºC	60 to 80	130
Fire point, ºC	78	138
Viscosity, mm^2/s @40ºC	1.3-4.1	1.5-4.0
Aniline Point, ºC	42	54
Pour point, ºC (summer)	18	10
Calorific Value, MJ/L	38.3	36
Boiling Point, ºC	180 to 340	315 to 350

II. THE FUTURE OF BIODIESEL FUEL

Biodiesel is diesel made from animate source (using plant oil and animal fats). Biodiesel is basically comprised of short-alkyl esters, made from animal fats and plant seeds. The possibility of obtaining oil from plant resources has aroused a great interest and in several countries, vegetable oil after esterification being used as 'Biodiesel'. Biodiesel is a nontoxic, biodegradable replacement of the petroleum diesel. The vegetable oils are treated with alcohol ethanol or methanol and alkali. The products of the reaction are Biodiesel and glycerol.

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Chemically biodiesel is monoalkyl esters of long chain fatty acid and its properties are similar to petro-diesel. The biodiesel can be used as 20% blend with petro-diesel in existing engines without any modification. Both the edible and non edible vegetable oils can be used as the raw materials for the biodiesel. Considering the cost and demand of the edible oils the non edible oils may be preferred for the preparation of biodiesel in India. Biodiesel is a substance that preserves air quality. This type of fuel is designed to enhance the richness of a diesel automobile. Biodiesel fuel also has its own advantages and disadvantages. The biggest advantage of biodiesel is that it can play a significant role in reducing the harmful carbon dioxide emissions. Biggest advantage of biodiesel fuel is that it is non toxic and biodegradable, which makes it one of the most environment friendly alternatives of power generation.

III. RAW MATERIALS FOR BIODIESEL PRODUCTION

The raw materials for biodiesel production are vegetable oils, animal fats and short chain alcohols. The oils most used for worldwide biodiesel production are rapeseed (mainly in the European Union countries), soybean (Argentina and the United States of America), palm (Asian and Central American countries) and sunflower, although other oils are also used, including peanut, linseed, safflower, used vegetable oils, and also animal fats. Methanol is the most frequently used alcohol although ethanol can also be used. Biodiesel can also be produced using non-edible oils such as castor oil, tung, cotton, jojoba and jatropha. Animal fats are also an interesting option, especially in countries with plenty of livestock resources, although it is necessary to carry out preliminary treatment since they are solid; furthermore, highly acidic grease from cattle, pork, poultry, and fish can be used. Micro algae appear to be a very important alternative for future biodiesel production due to their very high oil yield; however, it must be taken into account that only some species are useful for bio fuel production. Although the properties of oils and fats used as raw materials may differ, the properties of biodiesel must be the same, complying with the requirements set by international standards.

A. Rapeseed and Canola

Rapeseed adapts well to low fertility soils, but with high sulphur content. It has high oil yield of 40–50%. Rapeseed flour has high nutritional value, in comparison to soybean; it is used as a protein supplement in cattle rations. Canola oil is highly appreciated due to its high quality, and with olive oil, it is considered as one of the best for cooking as it helps to reduce blood cholesterol levels.

B. Soybean

Biodiesel production form soybean yields other valuable sub-products in addition to glycerin: soybean meal and pellets (used as food for livestock) and flour (which have a high content of lecithin, a protein). Grain yield varies between 2,000 and 4,000 kg/hectare. Since the seeds are very rich in protein, oil content is around 18%.

C. Oil Palm

Oil palm[7] is a tropical plant that reaches a height of 20–25 m with a life cycle of about 25 years. Full production is reached 8 years after planting. Two kinds of oil are obtained from the fruit: palm oil proper, from the pulp, and palm kernel oil, from the nut of the fruit (after oil extraction, palm kernel cake is used as livestock food). International demand for palm oil has increased steadily during the past years, the oil being used for cooking, and as a raw material for margarine production and as an additive for butter and bakery products. It is important to remark that pure palm oil is semisolid at room temperature (20–22ºC), and in many applications is mixed with other vegetable oils, sometimes partially hydrogenated.

D. Sunflower

Sunflower ‘‘seeds’’ are really a fruit, the inedible wall (husk) surrounding the seed that is in the kernel. The great importance of sunflower lies in the excellent quality of the edible oil extracted from its seeds. It is highly regarded from the point of view of nutritional quality, taste and flavour. Moreover, after oil extraction, the remaining cake is used as a livestock feed. Oil yield of current hybrids is in the range 48–52%.

E. Peanut

The quality of peanut is strongly affected by weather conditions during the harvest. Peanuts are mainly used for human consumption, in the manufacture of peanut butter, and as an ingredient for confectionery and other processed foods. Peanut oil is used in blends for cooking and as a flavoring agent in the confectionery industry. The flour left over, following oil extraction, is of high quality with high protein content; in pellet form, it is used as a livestock feed.

F. Flax

Flax[8] is a plant of temperate climates, with blue flowers. Linen is made with the threads from the stem of the plant and the oil from the seeds is called linseed oil, used in paint manufacture. The plant adapts well to a wide range of temperature and humidity; however, high temperatures and plentiful rain do not favour high yields of seed and fiber. Flax seeds contain between 30 and 48% of oil, and protein content is between 20 and 30%.

G. Safflower

Safflower adapts well to dry environments. The oil content of the seed is high, from 30 to 40%. Currently, safflower is used in oil and flour production and as bird feed. There are two varieties, one rich in mono-unsaturated fatty acids (oleic acid) and the other with a high percentage of polyunsaturated fatty acids (linoleic acid). Both varieties have a low content of saturated fatty

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acids. The oil from safflower is of high quality and low in cholesterol content, and is used in the manufacture of paints and other coating compounds, lacquers and soaps. Safflower oil is extracted by means of hydraulic presses, without the use of solvents, and refined by conventional methods, without anti-oxidant additives.

H. Castor Seed

The castor oil plant grows in tropical climates, with temperatures in the range 20–30ºC.It is important to note that once the seeds start germinating, the temperature must not fall below 12ºC.Athough it is resistant to drought, the castor oil plant needs at least 5 months of rain during the year. Castor oil is a triglyceride, ricinolenic acid being the main constituent (about 90%). The oil is non-edible and toxic owing to the presence of 1–5% of ricin, a toxic protein that can be removed by cold pressing and filtering. The presence of hydroxyl groups in its molecules makes it unusually polar as compared to other vegetable oils.

I. Tung

Tung[8] is a tree that adapts well to tropical and sub-tropical climates. The optimum temperature for Tung is between 18 and 26 ºC, with low yearly rainfall. During the harvest season, the dry nuts fall off from the tung tree and are collected from the ground. Nut production starts 3 years after the planting. The oil from tung nuts is non-edible and used in the manufacture of paints and varnishes, especially for marine use.

J. Cotton

Among non-foodstuffs, cotton is the most widely traded commodity. After the harvest, it may be traded as raw cotton, fiber or seeds. In cotton mills, fiber and seeds are separated from raw cotton. Cotton fiber is processed to produce fabric and thread, for use in the textile industry. In addition, cotton oil and flour are obtained from the seed; the latter is rich in protein and is used in livestock feed and after further processing, for human consumption.

K. Jojoba

Jojoba needs a warm climate, but a cold spell is necessary for the flowers to mature. The plant reaches its full productivity 10 years after planting. The oil from jojoba is mainly used in the cosmetics industry; therefore, its market is quickly saturated.

L. Jatropha

Jatropha is a shrub that adapts well to arid environments. Yield depends on climate, soil, rainfall and treatment during sowing and harvesting. Jatropha plants become productive after 3 or 4 years, and their lifespan is about 50 years. Oil yield depends on the method of extraction; it is 28–32% using presses and up to 52% by solvent extraction. Since the seeds are toxic, jatropha oil is non-edible. The toxicity is due to the presence of curcasin (a globulin) and jatrophic acid (as toxic as ricin).

M. Avocado

Avocado is a tree between 5 and 15 m in height. The weight of the fruit is between 120 and 2.5 kg and the harvesting period varies from 5 to 15 months. The avocado fruit matures after picking and not on the tree. Oil may be obtained from the fruit pulp and pit. It has a high nutritional value, since it contains essential fatty acids, minerals, protein and vitamins A, B6, C, D, and E. The oil content of the fruit is in the range 12–30%.

N. Microalgae

Microalgae have great potential for biodiesel production, since the oil yield (in litres per hectare) could be one to two orders of magnitude higher than that of other raw materials. Oil content is usually from 20 to 50%, although in some species it can be higher than 70%.[9] High levels of CO_2, water, light, nutrients and mineral salts are necessary for the growth of microalgae. Production processes take place in raceway ponds and photobiological reactors.[9]

IV. TRANSESTERIFICATION

Transesterification also called alcoholysis is the displacement of alcohol from an ester by another alcohol in a process similar to hydrolysis except that an alcohol is used instead of water. [10] This has been widely used to reduce the viscosity of the triglycerides. The transesterification is represented as

$$\underset{\text{Ester}}{RCOOR'} + \underset{\text{Alcohol}}{R''OH} \rightleftharpoons \underset{\text{Ester}}{R'COOR''} + \underset{\text{Alcohol}}{ROH}$$

If methanol is used in this process then it is called methanolysis. Methanolysis of triglycerides is represented as

$$\underset{\text{Triglyceride}}{\begin{array}{l} CH_2COOR^1 \\ | \\ CHCOOR^2 \\ | \\ CH_2COOR^3 \end{array}} + \underset{\text{Methanol}}{3CH_3OH} \xrightarrow{\text{Catalyst}} \underset{\text{Glycerine}}{\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}} + \underset{\text{Methyl ester}}{\begin{array}{l} R^1COOCH_3 \\ R^2COOCH_3 \\ R^3COOCH_3 \end{array}}$$

Triglycerides are readily trans-esterified in the presence of alkaline catalyst at atmospheric pressure and at a temperature of approximately 60 to 70°C with an excess of methanol. The mixture at the end of reaction is allowed to settle. The lower glycerol layer is drawn off while the upper methyl ester layer is washed to remove entrained glycerol and is then processed further. The

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excess methanol is recovered by distillation and sent to a rectifying column for purification and recycled. The transesterification works well when the starting oil is of high quality. However, quite often low quality oils are used as raw materials for bio-diesel preparation. In cases where the free fatty acid content of the oil is above 1%, difficulties arise due to the formation of soap which promotes emulsification during the water washing stage and at FFA content above 2% the process becomes unworkable.[11]

V. BIODIESEL CONVERSION FROM MICROALGAE

The process of isolation and selection of algae strains needs to consider the requirements of algal oil suitable for biodiesel production. Algal lipids occur in cells predominantly as either polar lipids (mostly in membranes) or lipid bodies, typically in the form of triacylglycerides. The latter are accumulated in large amounts during photosynthesis as a mechanism to endure adverse environmental conditions. Polar lipids usually contain polyunsaturated fatty acids which are long-chained, but have good fluidity properties. TAG in lipid storage bodies typically contain mostly saturated fatty acids which have a high energy contents, but, depending on the fatty acid profile of the algae strain, may lack fluidity under cold conditions. Provided the algal oil is low enough in moisture and free fatty acids, biodiesel is typically produced from TAG with methanol using base-catalyzed transesterification.[12] Most current feedstock for biodiesel production is based on plant oils produced from oil palm, soybean, cottonseed and canola, recycled cooking greases or animal fats from beef tallow or pork lard.[13] According to Fukuda, transesterification using base catalysts is 4,000 times faster than using acid catalysts.[14] Some common base catalysts used by industry are sodium hydroxide and potassium hydroxide. Use of lipase enzymes as a catalyst is efficient; however their use is limited because of the high costs.[14] The best temperature for the reaction is typically 60 °C under normal atmospheric pressure. If the temperature is higher, methanol will boil, lowering then efficiency.[14] during the transesterification process, saponification reactions can occur, forming soap. Thus, oil and alcohol must be dried. Finally, biodiesel is recovered by washing rapidly with water to remove glycerol and methanol.[9] The high potential of oil production from microalgae has attracted several companies to commercialize biodiesel from microalgae (e.g., MBD Energy Pty and Muradel Pty Ltd in Australia). Basically, algal biodiesel is produced after algae cultivation and harvesting, followed by oil extraction and its conversion by transesterification. Principally, microalgal oil can be directly used as fuel feedstock, based on the conventional process of biodiesel production, provided the fatty acid profile is favourable. But even algal oils with a high degree of saturation (e.g., similar as tallow) can be considered as a drop-in fuel (e.g., for B20 blends).

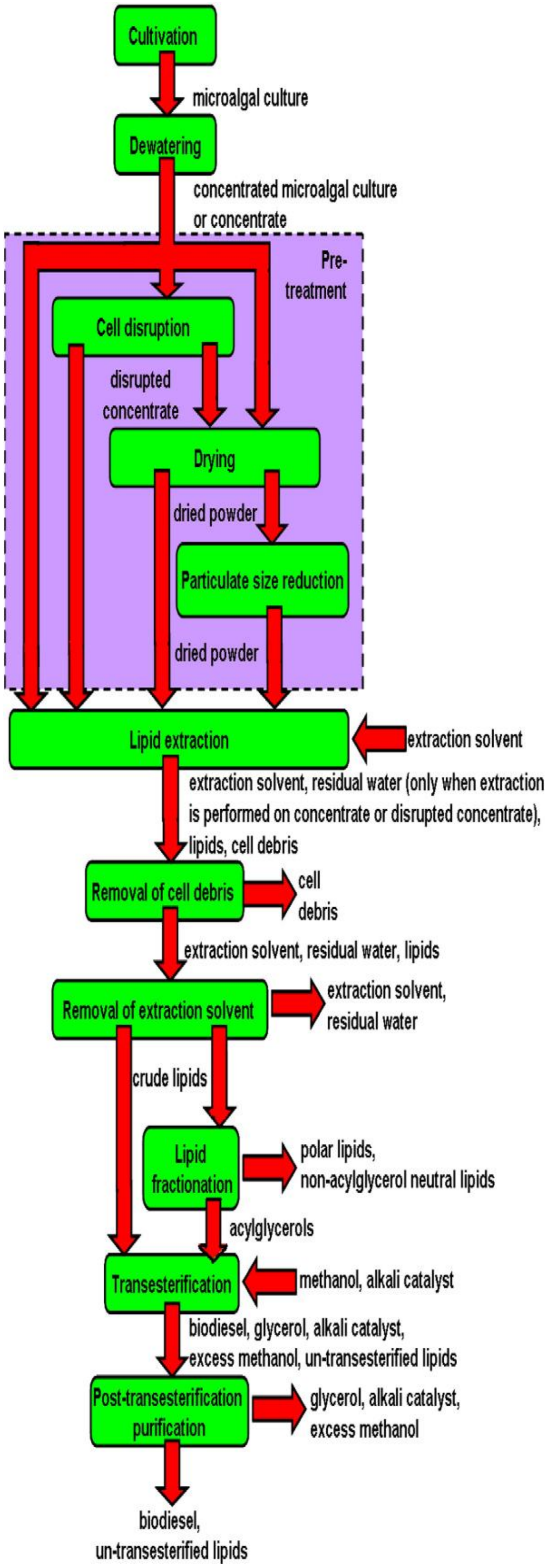

Fig 1 Process flow diagram showing the downstream processing steps needed to produce biodiesel from microalgal biomass.

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In addition, scientists are also focusing on the conversion to higher value products. For example, thermal cracking is used for decomposition of triglycerides into hydrocarbons such as alkans, alkenes, and aromatic compounds.[15, 16]

Figure 1. Shows the downstream processing steps required to produce biodiesel from microalgal biomass.[17] After the microalgal culture is harvested from the bioreactor, it is concentrated in a dewatering step. The concentrated microalgal culture is then processed in a pre-treatment step to prepare it for lipid extraction. During lipid extraction, lipids are extracted out of the cellular matrices with an extraction solvent. The lipids are then separated from the cellular debris, isolated from the extraction solvent and any residual water, and finally converted to biodiesel in the transesterification step.

VI. ADVANTAGES OF USING MICROALGAE FOR BIODIESEL PRODUCTION

Microalgae are easy to cultivate, can grow with little or even no attention, using water unsuitable for human consumption and easy to obtain nutrients. Microalgae reproduce themselves using photosynthesis to convert sun energy into chemical energy, completing an entire growth cycle every few days.[18] They have much higher growth rates and productivity when compared to conventional forestry, agricultural crops, and other aquatic plants, requiring much less land area than other biodiesel feed stocks. Microalgae can provide feedstock for several different types of renewable fuels such as biodiesel, methane, hydrogen, ethanol, among others. Algae biodiesel contains no sulphur and performs as well as petroleum diesel, while reducing emissions of particulate matter, CO, hydrocarbons, and SOx. However emissions of NOx may be higher in some engine types.[19] The utilization of microalgae for bio fuels production can also serve other purposes. They are: Removal of CO_2 from industrial flue gases by algae bio-fixation,[20] reducing the GHG emissions of a company or process while producing biodiesel.[21] Wastewater treatment by removal of NH_4^+, NO_3^-, PO_4^{3-}, was making algae to grow using these water contaminants as nutrients.[20] After oil extraction the resulting algae biomass can be processed into ethanol, methane, livestock feed, used as organic fertilizer due to its high N:P ratio, or simply burned for energy cogeneration (electricity and heat) .[20] Combined with their ability to grow under harsher conditions, and their reduced needs for nutrients, they can be grown in areas unsuitable for agricultural purposes independently of the seasonal weather changes, thus not competing for arable land use, and can use wastewaters as the culture medium, not requiring the use of freshwater. Depending on the microalgae species other compounds may also be extracted, with valuable applications in different industrial sectors, including a large range of fine chemicals and bulk products, such as fats, polyunsaturated fatty acids, oil, natural dyes, sugars, pigments, antioxidants, high-value bioactive compounds, and other fine chemicals and biomass.[22,23,24] Because of this variety of high-value biological derivatives, with many possible commercial applications, microalgae can potentially revolutionize a large number of biotechnology areas including bio fuels, cosmetics, pharmaceuticals, nutrition and food additives, aquaculture, and pollution prevention.[24, 25]

VII. CONCLUSION

Alternative fuel is currently an important issue all over the world due to the efforts on reducing global warming which is contributed by the combustion of petroleum or petrol diesel. Biodiesel is non-toxic, biodegradable, produced from renewable sources and contributes a minimal amount of net green house gases, such as CO_2, SO_2 and NO emissions to the atmosphere. With the increase in global human population, more land may be needed to produce food for human consumption (indirectly via animal feed). The problem already exists in Asia. Vegetable oil prices are relatively high there. The same trend will eventually happen in the rest of the world. This is the potential challenge to biodiesel. From this point of view, biodiesel can be used most effectively as a supplement to other energy forms, not as a primary source. Biodiesel is particularly useful in mining and marine situations where lower pollution levels are important. The vegetable oils used as raw materials can be obtained from different oil crops that may be grown in a wide variety of environments, some of which are not adequate for traditional agricultural production. Microalgae grown in ponds and photobiological reactors have also great potential for the production of oils for biodiesel production. Moreover, used cooking oils and fat residues from the meat processing industry may also be employed in biodiesel production. Transesterification is a chemical reaction between triglyceride and alcohol in the presence of catalyst. The purpose of the transesterification process is to lower the viscosity of the oil. Methanol being cheaper is the commonly used alcohol during transesterification reaction. The biodiesel high flash point makes it possible for its easy storage and transportation. A Biodiesel fuel as alternative to petro diesel is technically feasible, economically competitive, environmentally acceptable, and easily available; since it is renewable, biodegradable, nontoxic, and essentially free of sulphur and aromatics; thus, Biodiesel seems to be a realistic fuel for future.

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