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***Review Article***

# BIODIESEL: SOURCE MATERIALS AND FUTURE PROSPECTS

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**ABSTRACT**
Biodiesel has become more attractive recently because of its environmental benefits and the facts that it is made from renewable resources. These concerns have increased the interest in developing second generation biofuels produced from non-food feedstocks such as no edible oils which potentially offer greatest opportunities in the longer term.
Production of biodiesel have four primary ways, direct use and blending, microemulsion, thermal cracking (pyrolysis) and transesterification. Algae for biodiesel production can grow on fuel gas; it gives opportunities in consuming greenhouse gas feedstock. In future, biofuels should ideally create the environmental, economic and social benefits to the communities and reflect energy efficiency so as to plan a road map for the industry to produce third generation biofuels.

***Key Words*:** *Biodiesel, Non-Edible Sources, Microalgae Based Biodiesel, Production Procedure, Production and Demand in India*

## INTRODUCTION

Biodiesel is an alternative fuel for diesel engines that is produced by chemically reacting a vegetable oil or animal fat with an alcohol such as methanol. The reaction of biodiesel require catalyst as a strong base, such as sodium or potassium hydroxide ,it produces new chemical compounds called methyl esters, this esters are known as biodiesel (Vangerpen, 2005). Dr. Rudolph diesel designed the original diesel engine to run on vegetable oil. He used peanut oil to fuel one of his engines at the Paris exposition of 1900 (Demirbas, 2003).

Biodiesel made from different vegetable oils (e.g. soyabean oil, sunflower oil, rapeseed oil) using alkali catalyst. The most of the biodiesel produced by alkali-catalyzed like NAOH and KOH transesterification with methanol, because it takes short reaction time. Biodiesel operates in compression ignition engines. It can also be used as pure biodiesel. Biodiesel fuels used in regular diesel vehicles without making any changes to the engines, and also older vehicles may require replacement of fuel lines and other rubber components. It can be stored and equipments so it is better lubricant than diesel fuel and also it will increasing the life of engines and combusted more completely.

Many countries are introducing biodiesel blends to enhance the lubricity of low-sulfur diesel fuels. Biodiesel’s higher flash point make it safer fuel to use, handle and store and its low emission profile It is an ideal fuel for use in sensitive environments such as heavily polluted cities.(Freedman *et al.,* 1984).

### *Biodiesel characteristics*

Biodisel is a cleaner-buring diesel replacement fuel made from natural renewable sources such as new and used vegetable oils and animal fats. The biodiesel was characterized by determining its density, viscocity, high heating value, cetane index, clod and pour points, characteristics of distillation and flash and combustion points according to Iso norms.

**Table 1: Physical characteristics of biodiesel and no.2 diesel fuels**

| Property | Biodiesel | NO.2 diesel |
|---|---|---|
| Specific gravity(kg/l) | 0.87-0.89 | 0.84-0.86 |
| Cetane number | 46-70 | 47-55 |
| Cloud point(k) | 262-289 | 256-265 |
| Pour point(k) | 258-286 | 237-243 |
| Flasf point(k) | 408-423 | 325-350 |
| Sulfur (wt %) | 0.0000-0.0024 | 0.04-0.01 |
| Ash (wt %) | 0.002-0.01 | 0.06-0.01 |
| Iodine number | 60-135 | - |
| Kinematic viscosity,313k | 3.7-5.8 | 1.9-3.8 |
| Higher heating value,MJ/Kg | 39.3-39.8 | 45.3-46.7 |

*Data source: A comprehensive review on biodiesel as an alternative energy resource and its characteristics by Atabani et al., (Balat, 2005; Demiras, 2003)*

In the biodiesel production transesterification reaction is the most efficient process today for sevral reasons which including.
1. Low temp (65c) and pressure (20 psi) of the process.
2. High conversion (98%) with minimal side reaction and reaction time.
3. Direct conversion to methyl ester with no intermediate steps.
4. No need of special construction materials. (IPTS, JRC (2002)

**Table 2: Top 10 countries in terms of biodiesels potential**

| Rank | Country | Potential biodiesel(ml) | Production($/l) |
|---|---|---|---|
| 1 | Malaysia | 14,540 | 0.53 |
| 2 | Indonesia | 7,595 | 0.49 |
| 3 | Argentina | 5,255 | 0.62 |
| 4 | USA | 3,212 | 0.70 |
| 5 | Brazil | 2,567 | 0.62 |
| 6 | Netherlands | 2,496 | 0.75 |
| 7 | Germany | 2,024 | 0.79 |
| 8 | Philippines | 1,234 | 0.53 |
| 9 | Belgium | 1,213 | 0.78 |
| 10 | Spain | 1,073 | 0.71 |

*Data source: A comprehensive review on biodiesel as an alternative energy resource and its characteristics by Atabani et al. (Sharma, 2009; Balat et al., 2010; Johnston et al., 2007; Atadashi 2011)*

***Advantages of biodiesel***

A number of technical advantages of biodiesel fuel.
1. It prolongs engine life and reduced the need for maintenance (biodiesel has better lubricating qualities than fossil diesel)
2. It is safe to handle, being less toxic more biodegradable and having a higher flash point.
3. It reduces some exhaust emission. (Warale, 2003)

Biodiesel is safe for use in all conventional diesel engines, offers the same performance and engine non-flammable and non-toxic and reduces tailpipe emissions, visible smoke and noxious fumes and ordors. (Jadhav, 2009)

***Disadvantages of biodiesel***

Biodiesel/fossil diesel blends include problem with fuel freezing in cold weather, reduced energy density and degradation of fuel under storage for prolonged periods. On additional problem is encountered when blends are frist introduced into equipment that has a long history of pure hydrocarbon usage. Hydrocarbon fuels typically from a layer of deposits on block fuel filters. However,this is a minor problem, easily remedied by proper filter maintenance during the period following introduction of the biodiesel blend (Warale, 2003).

Direct use of vegetable oils and/or the use of blends of the oils have generally been considered to be not satisfactory and impractical for both direct and diesel engines. The high viscosity, acid composition, free acid content, as well as gum formation due to oxidation and polymerization during storage and combustion, carbon deposits and lubrication oil thickening are obvious problem.

***Global market scenario***

The fuel-grade ethanol production in 2007 in China and Thailand was 1.8 and 0.3 billion litres respectively (Jadhav, 2009). For now, the energy use has already increased by about 30% in Latin America, 40% in Africa and 50% in Asia (Jadhav, 2009). The European Union produces 4.84 million tonnes/year of biodiesel with m share from Germany (2.18 million tonnes) (Jadhav, 2009) while current production is about 100 million litres in Australia and 200, 000 tonnes in Malaysia. In the USA, the ethanol production may reach a target of 136.38 billion litres by 2016. Overall, the global demand of biofuels is expected to rise by 50 to 60% in coming 20 years.

***Major non-edible tree borne oil seeds (Chand, 2002)***

1. SOAPNUT –Soapnut is a fruit of the soapnut tree generally found in tropical and subtropical climate areas including Asia, America and Europe. Two varieties *S. mukorossi* and *S. trifoliatus* found in India, Nepal, Bangladesh, Pakistan. Soapnut tree have many application in medicinal treatment to soap and surfactants. Its fruits use as natural laundry detergents for washing fabrics ,bathing and traditional medicines.Soapnut seeds are mostly used as a biodiesel source, it is called as “waste to enrgy”scheme.so,planting of soapnut trees in community forestry and I barren lands provides sink for carbon sequestration as well as feedstock for biodiesel production.
2. MAHUA- Mahua is mostly found in tribal areas, In India it is found Orissa, chatisgada, Jharkhand, Bihar, Madhya Pradesh, Tamil nadu. From mahua seeds high amount of biodiesel are extracted. Mahvua is an important plant having vital socioeconomic value.
3. JATROPHA- *Jatropha curcus* is a drought resistant perennial, growing well in marginal/poor soil. It is a major source of biodiesel. Its seed contain around 37% oil, which is used for combustion as fuel without being refined. It burns with clear smoke –free flame, tested successfully as fuel for simple diesel engine. It’s by products are used as good organic fertilizer, oil contain also insecticide, it is also used for disease like cancer, piles, snakebite, paralysis, dropsy etc.
4. KARANJ (*Pongomia pinnta*) - Karanj is widely found in tropical Asia and it is nonedible oil of Indian origin. Pongomia’s seeds are major sources of biodiesel. The oil content extracted by various aurthors ranges between 30.0 to 33%.
5. NEEM- Neem is from Meliaceae family. Neem oil used as soaps, medicinal and insecticides. The seed kernels, which weight 0.2g, constitutes some 50-60% of the seed weight and 25% of fruit.

***Biodiesel from microalgae***

More recently, microalgae have emerged to be the third generation of biodiesel feedstock. Microalgae are photosynthetic microorganisms that convert sunlight, water and CO2 to algal biomass but they do it more efficiently than conventional crop plants. It represents a very promising feedstock because of its high photosynthetic efficiency to produce biomass, higher growth rates and productivity and high oil content compared to edible and non-edible feedstocks.

Microalgae have the potential to produce an oil yield that is up to 25 times higher than the yield of oil palm and 250 times the amount of soybeans as can be seen in Table 3. This is because microalgae can be grown in farm or bioreactor. Moreover, they are easier to cultivate than many other plants**.** It is believed that microalgae can play an important role in solving the problem between the production of food and that of biodiesel in the near future. Moreover, among other generations of biodiesel feedstocks, microalgae appear to be the only source of renewable biodiesel that is capable of meeting the global demand for transport fuels and can be sustainably developed in the future. The main obstacle for the commercialization of microalgae is its high production cost from requiring high-oil-yielding algae strains and effective large-scale bioreactors. Recent studies indicate that algae for biodiesel production can grow on flue gas, giving opportunities in consuming greenhouse gas as feedstock.(Ahmad *et al.*, 2011; Janaun *et al.*,2010; Demiras, 2008; Karmee *et al.*, 2005; Singh, 2010; Lin *et al.*,2011; Kumar *et al.*, 2011; Balat, 2011; Basha *et al.*, 2009; Demiras, 2007; Parawira, 2010; Hossain *et al.*, 2008) Table 3 shows the comparison of biodiesel production from algae and oil plants. Knothe (Sharma *et al.*, 2008) reported that the use of the terms first, second and third generation are sometimes misleading and should not be used to imply that biodiesel derived from second or third generation feedstock may have superior fuel properties over first generation. For instance, biodiesel from Jatropha oil possesses poorer cold flow properties than biodiesel derived from soybean, palm or rapeseed oil. Recently, there have been several publications which highlighted the positive effects of blending different oils on the basic properties of biodiesel (Knothe, 2010; Sarin *et al.*, 2009, Sarin *et al.*, 2007).

**Table 3: Comparison of biodiesel production from algae and oil plants**

| **Biodiesel produced from algae** | | **Biodiesel produced from plants** |
|---|---|---|
| **Technology** | **Cell bioengineering, automatically produced in pilot plant** | **Agriculture in farm** |
| Production period | 5–7 days for a batch cultivation | Several months or years |
| Oil content | 30% (low oil content), 50% (medium oil content), 70% (high oil content) | Less than 20% in seeds or fruits |
| Land occupied | 0.010–0.013 hectare for producing 1x103 L oila | 2.24 ha for producing 1x103 L oilb |
| Cost performance | $2.4 per liter microalgal oil | $0.6–0.8 per liter plant oil |
| Development potential | Unlimited (work just beginning) | Limited (many works have been done) |

*Data source: A comprehensive review on biodiesel as an alternative energy resource and its characteristics by Atabani et al., (Janaun et al., 2007)*

***Production of biodiesel***

Natural vegetable oils and animal fats are pressed to obtain crude oil which contains free fatty acids, phospholipids, impurities (Openshaw, 2000). These compounds have high viscosity, low volatility and polyunsaturated character so; they cannot be directly used in compression engines (Banpurmath *et al.*, 2008). The processing techniques that are mainly used to convert vegetable oil into fuel are direct blending, pyrolysis, micro-emulsification and transesterification (Demirbas, 2000).

***1. Direct use and blending***

In 1900 Dr Diesel demonstrated his engine running on 100% peanut oil at world exibition in Paris. In 1981 Bartholomew give the concept of using food for fuel indicating that petroleum should be the alternative fuel rather than vegetable oil and alcohol being the alternatives and some form of renewable energy must being to take place of nonrenewable resources (Bartholomew, 1981).

Caterpillar from brazil use pre-combustion chamber engines with a mixture of 10% vegetable oil to maintain total power without any alteration or adjustment to the engine 1980. From these points we can conclude that 100% vegetable oil for diesel fuel is not used, but a blend of 20% vegetable oil and 80% diesel fuel was successfully used. It means that it was used up to 50/50 ratio.

Mixtures of degummed soybean oil and no.2 diesel fuel in the ratios of 1:2 and 1:1 were tested for engine performance and crankcase lubricant viscosity in a John Deere-6-cylinder,6,6 l displacement, direct injection, turbochared engine for a total of 600h.(Adams *et al.*, 1983)The lubricating oil thickening and potential gelling existed with the 1:1 blend, but it did not occur with the 1:2 blend should be suitable as a fuel for agricultural equipment during periods of diesel fuel shortages or allocations.

***2. Micro –emulsion***

The problem of the high viscosity of vegetable oils was solved by micro-emulsion with solved such as methanol, ethanol and 1-butanol (Agarwal, 2007)˙A micro –emulsion is defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimensions generally in the 1-150 nm formed spontaneously from two normally immiscible liquids and one or more ionic or non-ionic amphiphiles (Ma and Hanna, 1999).

Ziejewski *et al*., (1984) prepared an emulsion of 53%(vol)alkali-refined and winterized sunflower oil,13.3%(vol)190-proof ethanol and 33.4%(vol)1-butanol (Ziejewski *et al*.,1983)

Micro emulsion can improve spray properties by explosive vaporization of the low boiling constituents in the micelles.Micro emulsion result in reduction in viscosity increase in cetane number and good spray characters in the biodiesel.

Continuous use of micro-emulsified diesel in engines causes problems like injector needle sticking, carbon deposit formation and incomplete combustion (Wilson parawaira).

***3. Pyrolysis***

Pyrolysis can be defined as the conversion of one subtance into another by means of heat in the absence of air or by heat in presence of a catalyst which results in cleavage of bonds and formation of a variety of small molecules.

In 1947, a large scale of thermal cracking of tung oil calcium soaps was reported (Chang and Wan, 1947).Tung oil was first saponified with lime and then thermally cracked to yield a crude oil, which was refined to produce diesel fuel and small amounts of gasoline and kerosene.

Pioch *et al.,* in 1933 studied that catalytic cracking of vegetable oils to produce biofuel. Another disadvantage of pyrolysis is the need for separate distillation equipment for separation of the various fractions. Also the product obtained was similar to gasoline containing sulphur which makes it less eco-friendly (Ranganathan *et al.*, 2007).

**4. *Transesterification:*** *(*Wilson parawira)

Transeterification of vegetable oils is the most popular method of producing biodiesel. Transesterification is the reaction of fat or oil with an alcohol to form fatty acid alkyl esters, methyl and ethyl esters.

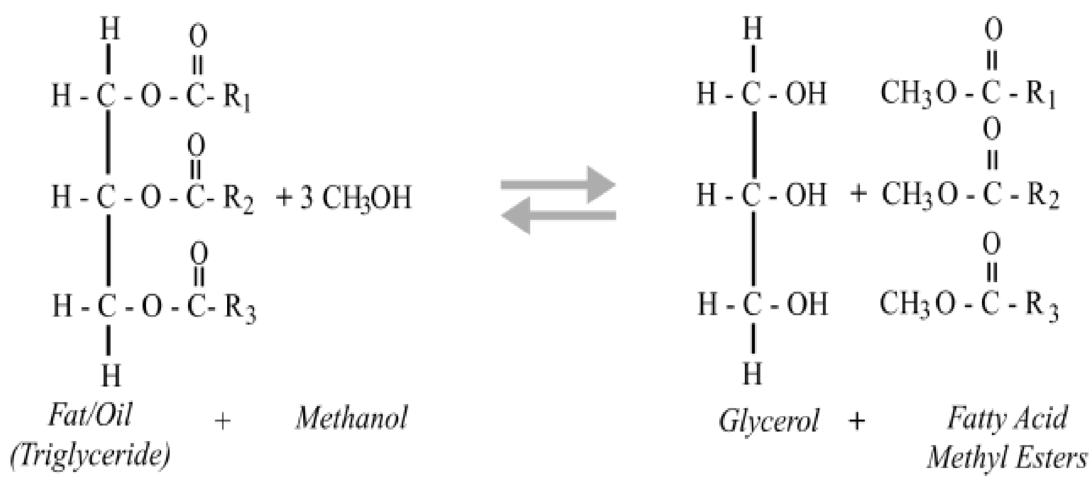


**Figure 1: Transesterification reaction**

***Variables affecting the transesterification reaction***

Transesterification reaction is affected by various parameters depending upon the reaction conditions. The reaction is either incomplete or the yield is reduced to a significant extent if the parameters are not

optimized. Each parameter is equally important to achieve a high quality biodiesel which meets the regulatory standards. The most important parameters that affect the transesterification process are mentioned below (Sharma, 2009; Ranganthan *et al.*, 2008; Shahid *et al.*, 2011; Balat *et al.*, 2010; Srivastava *et al.*, 2000; Jain *et al.*, 2010; Sharma *et al.*, 2008; Agarwal, 2007; Ma *et al.*, 1999; Jain *et al.*, 2010; Fukuda *et al.*, 2001; Meher *et al.*, 2006; Attantho *et al.*, 2004; Ehimen *et al.*,2010; Encinar *et al.*, 2005; Freegman *et al.*, 1984; May, 2004; Parlak *et al.*, 2008; Murugesan *et al.*, 2009).
1- Free fatty acids, moisture and water content.
2- Type of alcohol and molar ratio employed.
3- Type and concentration of catalysts.
4- Reaction temperature and time.
5- Rate and mode of stirring.
6- Purification of the final product.
7- Mixing intensity.
8- Effect of using organic co-solvents.
9- Specific gravity.

***Current situation of biofuels demand and production in India***

India is the sixth largest energy consumer and there is enormous scope for developing production and marketing of biofuels. At present, the supply of bioenergy looms as one of the important challenges, because India produces 30% of its annual crude oil and petroleum products requirement of 105 million tonnes and meets 70% of its requirement through import (Jadhav, 2009) with 150 to 200 tonnes of ethanol used annually for fuel blending. This demand (annual rate of 4.8%) is estimated to grow to 5.8% till 2030 (Jadhav, 2009). Nevertheless, the importance of biofuels will depend upon petroleum price, progress in bioscience and technology, and awareness among people about natural resources. In recent years, there had been steep rise in prices of the petroleum products. Although, the 100% foreign direct investment (FDI) in technologies provided the fuel for domestic use, it is speculated that biofuel production on large scale will result in non-availability of foods, rise in food prices, deforestation, diminution in biodiversity and undesirable impact on local land and water resources. Public and private firms are therefore working on technologies for the biofuel production from agricultural residues and energy crops. Likewise, the government has plans to execute greening of countryside by providing green fuels for rural electrification programmes along with employment opportunities expecting that the production will trigger huge growth in domestic plantation and processing (Jadhav, 2009). This venture is welcome since availability of land and the low cost of production have made India as one of the most favoured and potential country for biofuel production. In this sector, major activities include community development through afforestation, incentivizing the operations across the value chain, regulating the markets by curtailing import of free fatty acids, restricting handling and distribution within and outside the states and revising periodically the purchase prices of biofuel crops for the benefit of farmers. For this purpose, biofuel manufacturing has been taken by several private companies. At government level, the Ministry of New and Renewable Energy has announced the National Policy on Biofuels on December 23, 2009. The goal of this policy is to ensure a minimum level of biofuels and meet the public demand. For this purpose, 20% blending of biofuels, both for biodiesel and is proposed by 2017 instead of current mandatory 5% blending of ethanol and optional 10% mixing. To achieve this target, the biodiesel production has to be increased to 11.38 million tonnes by the end of the year 2012 (Jadhav, 2009).Although, statistics on use of biodiesel is not available as it is mostly distributed through unorganized means, the National Mission on Biodiesel forecasted blending of biodiesel/bioethanol with high speed diesel and about 11.19 million hectares of land, from a total 185 million hectares of cultivable land have to be converted into plantations of which 7.98% ha under jatropha (*Jatropha curcas*) alone. The policy also encourages industry with subsidies to boost biofuel processing.

**Table 4: Estimated oil content and yields of different biodiesel feedstocks**

| Feedstocks | Oil content (%) | Oil yield (L/ha/year) |
|---|---|---|
| **Castor** | **53** | **1413** |
| Jatropha | Seed: 35-40, kernel: 50-60 | 1892 |
| Linseed | 40-44 | - |
| Neem | 20-30 | - |
| Pongamia pinnata (Karanja) | 27-39 | 225-2250a |
| Soybean | 15-20 | 446 |
| Sunflower | 25–35 | 952 |
| Calophyllum inophyllum L. | 65 | 4680 |
| Moringa oleifera | 40 | - |
| Euphorbia lathyris L. | 48 | 1500-2500a |
| Sapium sebiferum L. | Kernel 12-29 | - |
| Rapeseed | 38-46 | 1190 |
| Tung | 16-18 | 940 |
| Pachira Glabra | 40-50 | - |
| Palm oil | 30-60 | 5950 |
| Peanut oil | 45-55 | 1059 |
| Olive oil | 45-70 | 1212 |
| Corn (Germ) | 48 | 172 |
| Coconut | 63-65 | 2689 |
| Cottonseed | 18-25 | 325 |
| Rice bran | 15-23 | 828 |
| Sesame | - | 696 |
| Jojoba | 45-50 | 1818 |
| Rubber seed | 40-50 | 80-120a |
| Sea mango | 54 | - |
| Microalgae (low oil content) | 30 | 58,700 |
| Microalgae (medium oil content) | 50 | 97,800 |
| Microalgae (high oil content | 70 | 136,900 |

*Data source: A comprehensive review on biodiesel as an alternative energy resource and its characteristics by Atabani et al., (Wilson parawaria and Rangangathan, 2008; Shahid, 2011; Balat, 2010; Srivastava 2000; Jain et al., 2010)*

### *Future of biodiesel*

Acceptance of Kyoto protocol and clean development mechanism (CDM) will lead to more biodiesel production around the world. With the increase in global human population, more land will be needed to produce food for human consumption. Thus, the insufficient lands could increase the production cost of biodiesel plants. This problem already exists in Asia where vegetable oil prices are relatively high. The same trend will eventually happen in the rest of the world. This is the potential challenge to biodiesel production. Therefore, non-edible oil, genetically engineered plants and microalgae feedstocks can be proper solutions for this problem and can ensure the sustainability of biodiesel production in the future the world (Karmee *et al.*, 2005, Mekhilef *et al.*, 2011)

## CONCLUSION

Energy is an indispensable factor for human to preserve economic growth and maintain standard of living. Globally, the transportation sector is the second largest energy consuming sector after the industrial sector and accounts for 30% of the world's total delivered energy. This sector has experienced a steady growth in the past 30 years. It has been estimated that the global transportation energy use is expected to increase by an average of 1.8% per year from 2005 to 2035. Nearly all fossil fuel energy consumption in the transportation sector is from oil (97.6%). However, the expected depletion of fossil fuels and the environmental problems associated with burning them has encouraged many researchers to investigate the possibility of using alternative fuels. Among them, biodiesel seems a very promising resource

The wide range of available feedstock for biodiesel production represents one of the most important advantages of producing biodiesel. From literature, it has been found that feedstock alone represents more than 75% of the overall biodiesel production cost. Therefore, selecting the best feedstock is vital to ensure low production cost of biodiesel.

Biodiesel is currently not economically feasible, and more research and technological development are needed. As a recommendation, supporting policies are important to promote biodiesel research and make their prices competitive with other conventional sources of energy

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