

# Biodiesel as an Alternative Fuel for Diesel Engines

F. Halek, A. Kavousi, and M. Banifatemi

**Abstract**—There is growing interest in biodiesel (fatty acid methyl ester or FAME) because of the similarity in its properties when compared to those of diesel fuels. Diesel engines operated on biodiesel have lower emissions of carbon monoxide, unburned hydrocarbons, particulate matter, and air toxics than when operated on petroleum-based diesel fuel. Production of fatty acid methyl ester (FAME) from rapeseed (nonedible oil) fatty acid distillate having high free fatty acids (FFA) was investigated in this work. Conditions for esterification process of rapeseed oil were 1.8 %  $H_2SO_4$  as catalyst, MeOH/oil of molar ratio 2 : 0.1 and reaction temperature 65 °C, for a period of 3h. The yield of methyl ester was > 90 % in 1 h.

The amount of FFA was reduced from 93 wt % to less than 2 wt % at the end of the esterification process. The FAME was pureed by neutralization with 1 M sodium hydroxide in water solution at a reaction temperature of 62 °C. The final FAME product met with the biodiesel quality standard, and ASTM D 6751.

**Keywords**—Alternative Fuels, Biodiesel, Fatty Acid, Methyl Ester, Seed Oil, Transesterification.

## I. INTRODUCTION

**B**IODIESEL 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 requires a catalyst, usually a strong acid or base such as sulphuric acid sodium or potassium hydroxide, and produces new chemical compounds called methyl esters. It is these esters that have come to be known as biodiesel. A possible association has been shown between the intake of trans fatty acids and the risk of coronary heart disease. They are proven to produce adverse effects on blood lipids, including increasing LDL-cholesterol concentration and decreasing HDL-cholesterol concentration. Dietary trans fats not only include mono- and poly unsaturated fatty acids, but also conjugated linoleic acids [1], [2].

Biodiesel, produced from different vegetable oils (soybean, rapeseed and sunflower, for example), seems very interesting for several reasons: it can replace diesel oil in boilers and internal combustion engines without major adjustments; only a small decrease in performances is reported; almost zero

emissions of sulfates; a small net contribution of carbon dioxide ( $CO_2$ ) when the whole life-cycle is considered (including cultivation, production of oil and conversion to biodiesel); emission of pollutants comparable with that of diesel oil. Criteria pollutants are reduced with biodiesel use. Tests show the use of biodiesel in diesel engines results in substantial reductions of unburned hydrocarbons, carbon monoxide, and particulate matter. The exhaust emissions of total hydrocarbons (a contributing factor in the localized formation of smog and ozone) are on average 67 percent lower for biodiesel than diesel fuel. The exhaust emissions of carbon monoxide (a poisonous gas) from biodiesel are on average 48 percent lower than carbon monoxide emissions from diesel. Breathing particulate has been shown to be a human health hazard. The exhaust emissions of particulate matter from biodiesel are about 47 percent lower than overall particulate matter emissions from diesel. Emissions of nitrogen oxides stay the same or are slightly increased. However, some companies have successfully developed additives to reduce  $NO_x$  emissions in biodiesel blends.

The ozone (smog) forming potential of biodiesel hydrocarbons is less than diesel fuel. Sulfur emissions are essentially eliminated with pure biodiesel. The exhaust emissions of sulfur oxides and sulfates (major components of acid rain) from biodiesel are essentially eliminated compared to diesel.

Biodiesel reduces the health risks associated with petroleum diesel. Biodiesel emissions show decreased levels of polycyclic aromatic hydrocarbons (PAH) and nitrated polycyclic aromatic hydrocarbons (nPAH), which have been identified as potential cancer causing compounds. Biodiesel is the first and only alternative fuel to have a complete evaluation of emission results and potential health effects submitted to the U.S. Environmental Protection Agency (EPA) under the Clean Air Act Section 211(b). For these reasons, several campaigns have been planned in many countries to introduce and promote the use of biodiesel [3]-[6].

In general, vegetable oil contains of triglycerides and monoglycerides and fatty acids. However production cost of the biodiesel is not economically, competitive with petroleum-based fuel according to relatively high cost of the lipid feedstocks, which are usually edible-grade refined oils. The process of removal of all glycerol and the fatty acids from the vegetable oil in the presence of a catalyst is called

F. Halek (corresponding author) is with the *Materials and Energy Research Center (merc)*, P. O. Box 14155-4777, Tehran, Iran (phone: +98-261-6280036; fax: +98-261-6280030; e-mail: f-halek@merc.ac.ir).

A. Kavousi is with the *Materials and Energy Research Center (merc)*, P. O. Box 14155-4777, Tehran, Iran (e-mail: kavousi@merc.ac.ir).

M. Banifatemi is with the *Materials and Energy Research Center (merc)*, P. O. Box 14155-4777, Tehran, Iran (e-mail: mbbani@yahoo.com).

transesterification. With low-cost lipid feedstocks containing high amount of free fatty acids (FFA), conventional biodiesel production by transesterification with alcohol using base catalyst is not appropriated. A two-step process is then proposed [7]-[9]. The first step of the process is to reduce FFA content in vegetable oil by esterification with methanol and acid catalyst. The second step is transesterification process, in which triglyceride (TG) portion of the oil reacts with methanol and base catalyst to form ester and glycerol. The acid catalyst is generally sulfuric acid [10], [11], while the base catalyst is usually sodium or potassium hydroxide. Product from the reaction is separated into two phases by gravity [12], [13].

## II. TRANSESTERIFICATION

Fuels derived from chemical and thermal processes are termed as biodiesels [14]. While thermal process had some limitations, the chemical process, i.e. transesterification, proved to be a better method. Simple process, easy operation and the by-products obtained in the form of glycerol make the process attractive and widely accepted. Transesterification has been described as a chemical reaction between triglycerides and alcohol in the presence of catalyst to produce mono-esters that are termed as biodiesel [15], [16]. Fig. 1 depicts the transesterification reaction [17]. An ideal transesterification reaction differs on the basis of variables such as fatty acid composition and the free fatty acid content of the oil. Other variables include the type of catalyst, alcohol, water content in oil and the rate of stirring. Zheng et al. [13] and Hofman [18] emphasized that mode of stirring is equally important, where better yield was obtained with mechanical stirring than with magnetic stirring. Depending on the fatty acid composition of the oil, its Saponification number (SN), Iodine value (IV) and Cetane number (CN); it can be determined at the starting stage, whether the oil is suitable for transesterification reaction or not. Vicente et al. [19] thus chose 75 plant oils available in India and found their fatty acid composition, SN, IV and CN. On the basis of these parameters, 37 species showed the potential for development of biodiesel [19], [20]. An inverse relationship exists between the oxidation stability and cold temperature properties of the biodiesel. Better stability of biodiesel is achieved with oil having more content of saturated.

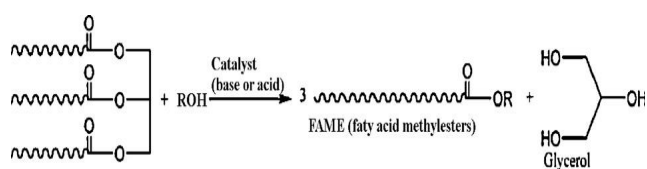


Fig. 1 Transesterification reaction of triglycerides

## III. MATERIALS AND METHODS

Fatty acid oil obtained from Fraco oil Industry. It consists of 90 w % of FFA (59.8 % Linoleic, 24.96 % Oleic, 4.87 % Palmitic) and the rest are methyl ester, vitamin, sitosterol and

traces impurities. The esterification process was carried out in 1000 ml screw-capped bottles. Preheated oil was firstly poured into the bottles following by MeOH and H<sub>2</sub>SO<sub>4</sub>. The bottles were immersed in mantel at designed temperature, stirrer and time. Operating parameters for esterification process for methanolysis of rapeseed oil were 1.8 % H<sub>2</sub>SO<sub>4</sub> as catalyst, MeOH/oil of molar ratio 2: 0.1 and reaction temperature 62 °C, for a period of 3h. The yield of methyl ester was > 90 % in 1 h (Fig. 2).



Fig. 2 Biodiesel production in the laboratory

Production mixture was poured into the separating funnel and then allowed to settle into two phases. A bottom FAME-layer was separated and purified by water washing process before being analyzed for its compositions by GC mass.

## IV. PURIFICATION PROCESSES AND ANALYSIS OF FAME

The reaction product was transferred to cooling water unit and then to a separator. It was separated into two phases for 70-100 min (a good separating time). The top phase contained excess MeOH and water formed during the reaction, while the FAME phase was at the bottom. The FAME phase was taken off at the bottom and passed into evaporator to remove traces of methanol. The purification was performed with sodium hydroxide NaOH (0.1 M) solution at a reaction temperature of 62 °C. The mixture was heated to its reaction temperature and let the reaction to carry out for 15 min. The product obtained from the purification step was settled in a separator. The FAME phase was separated and washed with water at temperatures of 50-60 °C to remove impurities. The solution was settled for water separation and finally the residual water was evaporated. The compositions of the reaction mixture samples were determined by a GC-mass.

## V. RESULTS AND CONCLUSION

Biodiesel, derived from vegetable oil or animal fats, is recommended for use as a substitute for petroleum-based diesel mainly because biodiesel is a renewable, domestic resource with an environmentally friendly emission profile and is readily biodegradable. The use of biodiesel has grown dramatically during the last few years. Feedstock costs account for a large percent of the direct biodiesel production costs, including capital cost and return.

The amount of FFA was reduced from 93 wt % to less than 2 wt % at the end of the esterification process. The FAME was purified by neutralization with 0.1 M sodium hydroxide in water solution at a reaction temperature of 62 °C.

Condition parameters for esterification process for methanolysis of rapeseed oil were 1.8 % H<sub>2</sub>SO<sub>4</sub> as catalyst, MeOH/oil of molar ratio 2: 0.1 and reaction temperature 62 °C, for a period of 3h. The yield of methyl ester was > 90 % in 1 h. Biodiesel has a viscosity much closer to diesel fuel than vegetable oil. The cost of biodiesel is higher than diesel fuel.

In general as discussed, biodiesel has some benefits such as:

- Cheaper fuel for consumers,
- More energy security & diversified sources,
- Higher farm incomes & rural employment,
- Significant carbon emission reduction,
- Lower Imports & energy prices.

## VI. RECOMMENDATION

As the stock of fossil fuel is getting depleted emphasis should be given to renewable sources of fuel such as biofuel in some cases such as:

- Design, develop and popularize appliances and equipments specifically for rural application.
- Prime facie, biodiesel seems to have significant potential to contribute to Iran's energy security, the need of the hour is to undertake R&D on sustainable plantation management, oil extraction and use environmental and social impact assessment and build institutional models.
- Contact training programs to sanitize media personnel on latest technologies and developments related to rural development.
- Creating awareness regarding loan, insurance facilities subsidies.

Although almost all types of vegetable oils can be used to replace the diesel oil, however the rapeseed oil can be the most suitable oil which can be used as diesel fuel extender. Vegetable oils alone can be used only for small engines for a short-term period. For long-term use and for heavy and big engines, blend of diesel and vegetable oils is recommended.

## REFERENCES

- [1] A. S. Ramadhas, S. Jayaraj, and C. Muraleedharan, "Use of vegetable oils as I.C. engine fuel - A Review." *Renewable Energy*, vol. 29, pp. 727-742, 2004.
- [2] H. Fukuda, A. Kondo, and H. Noda, "Biodiesel fuel production by transesterification of oils." *Journal of Bioscience and Bioengineering*, vol. 92, pp. 405-416, 2001.
- [3] C. Carraretto, A. Macor, A. Mirandola, A. Stoppato, and S. Tonon, "Biodiesel as alternative fuel: experimental analysis and energetic evaluations." *Energy*, vol. 29, pp. 2195-2211, 2004.
- [4] P. E. Dick Talley, (2004, February). "Biodiesel." *Biosource Fuels Inc.*, Available: <http://www.rendermagazine.com>.
- [5] G. S. Peace, *Taguchi methods*. 2nd ed. The United States of America: Addison-Wesley Publishing Company, 1993.
- [6] A. Demirbas, "Current advances in alternative motor fuels." *Energy Explor Exploit*; vol. 21, pp. 475-487, 2003.
- [7] A. Demirbas, "Biodiesel fuels from vegetable oils via catalytic and non-catalytic supercritical alcohol transesterifications and other methods: a survey." *Energy Convers Manage*, vol. 44, pp. 2093-3109, 2003.
- [8] Y. Wan, S. Ou, P. Liu, F. Xue, and S. Tang, "Comparison of two different processes to synthesize biodiesel by waste cooking oil." *Journal of Molecular Catalysis A: Chemical*, vol. 252, pp. 107-112, 2006.
- [9] P. K. Srivastava, and M. Verma, "Methyl ester of karanja oil as an alternative renewable source energy." *Fuel*, vol. 87, pp. 1673-1677, 2008.
- [10] V. G. Shashikant, and H. Raheman, "Process optimization for biodiesel production from mahua (*Madhuca indica*) oil using response surface methodology." *Bioresource Technology*, vol. 97, pp. 379-384, 2006.
- [11] V. G. Shashikant, and H. Raheman, "Biodiesel production from mahua oil having high free fatty acids." *Biomass and Bioenergy*, vol. 28, pp. 601-605, 2005.
- [12] M. Di Serio, R. Tesser, M. Dimiccoli, F. Cammarota, M. Nastasi, and E. Santacesaria, "Synthesis of biodiesel via homogeneous Lewis acid catalyst." *Journal of Molecular Catalysis A: Chemical*, vol. 239, pp. 111-115, 2005.
- [13] S. Zheng, M. Kates, M. A. Dube, and D. D. McLean, "Acid-catalyzed production of biodiesel from waste frying oil." *Biomass and Bioenergy*, vol. 30, pp. 267-272, 2006.
- [14] V. B. Veljkovic, S. H. Lakicevic, O. S. Stamenkovic, Z. B. Todorovi, and M. L. Lazic, "Biodiesel production from tobacco seed oil with a high content of free fatty acids." *Fuel*, vol. 85, pp. 2671-2675, 2006.
- [15] L. C. Meher, V. S. S. Dharmagadda, and S. N. Naik, "Optimization of alkali-catalyzed transesterification of *Pongamia pinnata* oil for production of biodiesel." *Bioresource Technology*; vol. 97, pp. 1392-1397, 2003.
- [16] Y. M. Choo and A. N. Ma, "Production technology of methyl esters from palm and palm kernel oils." PORIM Technology 18. Malaysia: Palm Oil Research Institute of Malaysia, 1996.
- [17] R. Brand, "Greening of policies-policy integration and interlinkages" Networks in renewable energy policies in Germany and France Berlin conference on the human dimension of global environmental change, Berlin, 3-4 December, 2004.
- [18] V. Hofman, *Biodiesel Fuel*, NDSU Extension Service, North Dakota State University of Agriculture, Applied Science and US Department of Agriculture cooperating, Fargo, North Dakota, 2003.
- [19] G. Vicente, M. Martinez and J. Aracil, "Integrated biodiesel production: a comparison of different homogeneous catalysts systems." *Bioresource Technology*, vol. 92, pp. 297-305, 2004.
- [20] A. S. Ramadhas, S. Jayaraj and C. Muraleedharan, "Biodiesel production from high FFA rubber seed oil." *Fuel*, vol. 84, pp. 335-340, 2004.