

PREPARATION AND CHARACTERIZATION OF BIODIESEL FROM NON-EDIBLE VEGETABLE OILS**Dr. M. Harinatha Reddy*, A. Rajkumar*, Dr. S. Sreenatha Reddy** & Dr. M. Ramalinga Reddy***

* Department of Mechanical Engineering, Guru Nanak Institutions Technical Campus, Hyderabad, Telangana

** Department of Mechanical Engineering, Guru Nanak Institute of Technology, Hyderabad, Telangana

Cite This Article: Dr. M. Harinatha Reddy, A. Rajkumar, Dr. S. Sreenatha Reddy & Dr. M. Ramalinga Reddy, "Preparation and Characterization of Biodiesel from Non-Edible Vegetable Oils", International Journal of Advanced Trends in Engineering and Technology, Special Issue, January, Page Number 1-5, 2018**Abstract:**

Biodiesel is the name for a variety of ester-based oxygenated fuels derived from natural, renewable biological sources such as vegetable oils which conform to ASTM D6751 specifications for use in diesel engines. Biodiesel refers to the pure fuel before blending with the diesel fuel. In this study vegetable oils mahua and karanja oils are selected as biodiesel fuels. One of the problems of using vegetable oils in diesel engine relates to their higher viscosity and poor volatility compared to conventional diesel. The different methods to reduce the viscosity are blending with diesel, emulsification, pyrolysis and transesterification. Among these, the transesterification is commonly used to produce clean and environment friendly fuels. Over the last few years, extensive research was carried out using methyl esters of various vegetable oils as Compression Ignition (CI) engine fuel. In this study, transesterification method is employed to convert the vegetable oil (mahua and karanja oils) into biodiesel, which result in a fuel closer to diesel fuel. Transesterification is a chemical reaction that aims at substituting the glycerol of the glycerides with three molecules of monoalcohols such as methanol thus leading to three molecules of methyl ester of vegetable oil known as biodiesel.

Introduction:

Fossil fuels are non-renewable energy resources. Although, these fuels are contributing largely to the world energy supply, their production and use have raised environmental concerns and political debates. It has been shown that 98% of carbon emissions are resulted from fossil fuel combustion. The need of energy is increasing continuously due to rapid increase in the number of industries and vehicles owing to population explosion. [1] The sources of this energy are petroleum, natural gas coal, hydrocarbon and nuclear. The major disadvantages of using

Petroleum based fuels are atmospheric pollution created by the use of petroleum diesel. The petroleum diesel combustion emits several greenhouse gases. Apart from these emissions, petroleum diesel is also major source of these air containments including NO_x, SO_x, CO, particulate matter and volatile organic compounds. [2] Several alternative fuels have been studied to either substitute diesel fuel partially or completely. Vegetable oils are proposed to be promising alternatives to diesel, as they are produced in rural areas. The oil produced from seeds can provide self employment opportunities. The concept of bio-fuel is not new. Rudolph Diesel was the first to use a vegetable oil (peanut oil) in a diesel engine in [3]. The use of bio-fuels in place of conventional fuels would slow the progression of global warming by reducing sulfur and carbon oxides and hydrocarbon emissions. Biodiesel is defined as monoalkyl esters of long chain fatty acids originated from natural oils and fats of plants and animals, is a kind of alternative for fossil fuels. Biodiesel has attracted wide attention in the world due to its renewability, biodegradability, nontoxicity and environmentally friendly benefits. Manufacturing biodiesel from used vegetable oil is relatively easy and possesses many environmental benefits. [5-7] Vegetable oil from plant sources is the best starting material to produce biodiesel because the conversion of pure triglyceride to fatty acid methyl ester is high and the reaction time is relatively short.

Over the last few years, methyl ester has been considered important as research has been intensified on the utilization of vegetable oils and animals fat derivatives for liquid fuel known as biodiesel. Two of such vegetable oils are considered in this research work.

The vegetable oil from trees such as Tung tree, Neem tree, Wood tree, Bale tree, Custard tree, Orchid tree, Geranium tree and other oils such as Dhak oil, Desert date oil, Phulwara oil, Kapok oil, Kokum butter oil etc., take longer time to produce and do not yield requisite quantity. Mahua and karanja are typical oils. They can withstand drought for three consecutive years. The non-edible mahua and karanja oils are promising sources of oil and can be used for preparation of biodiesel to run the compression ignition engines.

Biodiesel Production:

Biodiesel can be produced from straight vegetable oil, animal oil/fats, tallow and waste oils. There are three basic routes to biodiesel production from oils and fats:

- ✓ 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.

Almost all biodiesel is produced using base catalyzed transesterification as it is the most economical process requiring only low temperatures and pressures and producing a 98% conversion yield. For this reason only this process will be described in this report. The transesterification process is the reaction of a triglyceride (fat/oil) with an alcohol to form esters and glycerol. A triglyceride has a glycerine molecule as its base with three long chain fatty acids attached. The characteristics of the fat are determined by the nature of the fatty acids attached to the glycerine. [7] The nature of the fatty acids can in turn affect the

characteristics of the biodiesel. During the esterification process, the triglyceride is reacted with alcohol in the presence of a catalyst, usually a strong alkaline like sodium hydroxide or potassium hydroxide.

The alcohol reacts with the fatty acids to form the mono-alkyl ester, or biodiesel and crude glycerol. In most production methanol or ethanol is the alcohol used (methanol produces methyl esters while ethanol produces ethyl esters) and is base catalysed by either potassium or sodium hydroxide. Potassium hydroxide has been found to be more suitable for the ethyl ester biodiesel production, while either base can be used for the methyl ester. A common product of the transesterification process is the Oil Methyl Ester (OME) produced from raw oil reacted with methanol.

The figure below shows the chemical process for methyl ester biodiesel. The reaction between the fat or oil and the alcohol is a reversible reaction and so the alcohol must be added in excess to drive the reaction towards the right and ensure complete conversion.

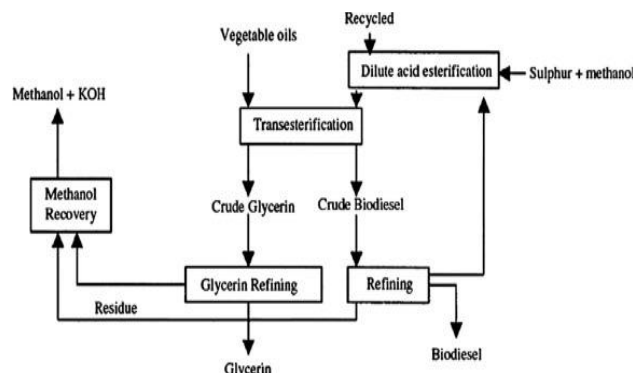


Figure 1: Basic technology process variables

Effect of Different Parameters on the Production of Biodiesel:

The most important parameters that influence transesterification reaction time and conversion are described below.

Oil Temperature:

The temperature to which oil is heated before mixing with catalyst and methanol, affects the reaction. It is observed that increase in oil temperature marginally increases the percentage oil to biodiesel conversion as well as the biodiesel recovery. However, the tests are conducted up to only 60°C, as higher temperatures will result in loss of methanol in the transesterification process.

Reaction Temperature:

The rate of reaction is strongly influenced by the reaction temperature. Generally, the transesterification process is conducted close to the boiling point of methanol (60 to 70°C) at atmospheric pressure. The maximum yield of esters occurs at temperatures ranging from 60°C to 80°C at a molar ratio (alcohol to oil) of 6:1. Further increase in temperature is reported to have a negative effect on the conversion.

Alcohol Type:

Methanol is most commonly used for transesterification of vegetable oils and fats. It has been reported that yield of esters is more for methanol, as methanol is the shortest-chain alcohol. The methanol is more reactive to oil with the added advantage of alkali catalysts being easily soluble in it.

Ratio of Alcohol to Oil:

Another important variable affecting the yield of ester is the molar ratio of alcohol to vegetable oil. Higher molar ratio of alcohol to vegetable oil interferes in the separation of glycerol. It is observed that lower molar ratio requires more reaction time. With higher molar ratios, conversion is increased but recovery is decreased due to poor separation of glycerol. [8, 9] It is found that optimum molar ratios depend upon the type and quality of oil. The stoichiometric of the transesterification reaction requires three mole of alcohol per mole of triglyceride to yield three moles of fatty esters and one mole of glycerol. The reaction being reversible in nature, it is necessary to use either excess of alcohol or to remove one of the products from the reaction mixture to favourably shift reaction to the product side. The second option is preferred wherever feasible, since in this way, the reaction can be driven to completion. When 100% excess methanol is used, the reaction rate is at its highest. A molar ratio of 6:1 is normally used in industrial processes to obtain methyl ester which yields greater than 98% on weight basis.

Type of Catalyst and Concentration:

Alkali metal alkoxides are the most effective transesterification catalyst compared to the acidic catalyst. Sodium alkoxides are among the most efficient catalysts used for this purpose. Trans-methylation occur many folds faster in the presence of an alkaline catalyst than those catalyzed by the same amount of acidic catalyst. Most commercial transesterification is conducted with alkaline catalysts. [10] Further, increase in catalyst concentration does not increase the conversion and it adds to extra costs because it is necessary to remove it from the reaction medium at the end. It is observed that higher amounts of sodium hydroxide catalyst are required for higher free fatty acid oil.

Intensity of Mixing:

The mixing effect is most significant during the slow rate region of the transesterification reaction. As the single phase is established, mixing becomes insignificant. It is observed that after adding methanol and catalyst to the oil, 5 to 10 minutes stirring helps in higher rate of conversion and recovery.

Purity of Reactants:

Impurities present in the oil also affect conversion levels. For alkali catalyzed transesterification, the glycerides and alcohol must be substantially anhydrous as water causes partial reaction change to saponification, which produces soap [1, 3]. Under the same conditions, 67 to 84% conversion of neat sea lemon oil into esters can be obtained, using crude vegetable oils, compared with 94 to 97% when using refined oils. The free fatty acids in the vegetable oils interfere with the catalyst. However, under conditions of high temperature and pressure this problem can be resolved. It is observed that crude oils are equally good compared to refined oils for production of biodiesel. However, the oils should be properly filtered. Oil quality is very important in this regard. The oil settled at the bottom during storage may give lesser biodiesel recovery because of accumulation of impurities like wax etc.

Vegetable Oils for Present Investigation:**Mahua Oil:**

Scientific name of Mahua oil is “*Madhuca indica*”, botanical name is “*Madura long folia*” The annual production of non edible seed was greater than 2 MT of which mahua is nearly 181 KT. The major component fatty acids of mahua oil are Palmitic (16-28.2%), Stearic (20-25.1%), Arachidic (0-3.3%), Oleic (41-51%) and Linoleic (8.9-13.7%). Mahua is a non-traditional and non-edible oil. Mahua tree is also known as Indian butter tree. Mahua is a medium to large tree, which may attain a height of up to 20 meters. It is a tree of deciduous nature, of the dry tropical and sub-tropical climate. The tree grows on a wide variety of soils, but prefers sandy soils. As a plantation tree, Mahua is an important plant having vital socio-economic value. This species can be planted on roadside, canal banks etc. on commercial scale and in social forestry programme, particularly in tribal areas. [11,12] Its flowers and fruits are eaten traditionally by tribal people. Mahua oil seed cake can be used as manure.



Figure 2: Mahua seed crop and seeds

Karanja Oil:

Figure 3: Karanja seed crop and seeds

Karanja is a medium sized tree that is found almost throughout India. Karanja tree is almost like neem tree. Karanja is widely distributed in tropical Asia. Karanja Oil is a non-edible oil of Indian origin. The plant is also said to be highly tolerant to salinity and is reported to be grown in various soil textures viz. stony, sandy and clayey. Major countries that produce karanja oil are East Indies, Philippines, and India. Karanja can grow in humid as well as subtropical environments with annual rainfall

ranging between 500 and 2500 mm. This is one of the reasons for wide availability of this plant species. The oil content extracted by various authors ranges between 30 to 33%. The cake after oil extraction may be used as manure. Karanja oil has been widely tested for insecticidal and bactericidal activity. In south part of the Indian peninsula the karanja oil/cake are also used same like neem oil and neem cake. The seed oil has been used by the natives of India for hundreds of years. It can be regenerated through direct sowing, transplanting and root or shoot cutting. Its maturity comes after 4–7 years. The oil expelled from the seeds is also burned during the festival of lighting to purify the environment. All these applications are at local or regional level and 94% of the oil from plant is still underutilized.

Biodiesel is the name for a variety of ester-based oxygenated fuels derived from natural, renewable biological sources such as vegetable oils which conform to ASTM D6751 specifications for use in diesel engines. Biodiesel refers to the pure fuel before blending with the diesel fuel. Biodiesel operates in compression ignition engines like petroleum diesel, thereby requiring no essential engine modifications. Biodiesel can be made from new or used vegetable oils and animal fats. Unlike fossil diesel, pure biodiesel is biodegradable, non-toxic and essentially free of sulphur and aromatics. Biodiesel blends are denoted as, Bxx with “xx” representing the percentage of biodiesel contained in the blend (i.e. B10 is 10% biodiesel and 90% diesel). The concept of using vegetable oil as a fuel, date back to 1895, when Dr. Rudolf diesel developed the first diesel engine to run on vegetable oil.

In this study, transesterification method is employed to convert the vegetable oil (mahua and karanja oils) into biodiesel, which result in a fuel closer to diesel fuel. Transesterification is a chemical reaction that aims at substituting the glycerol of the glycerides with three molecules of monoalcohols such as methanol thus leading to three molecules of methyl ester of vegetable oil known as biodiesel.

Fuel Characterisation:

The important physical and chemical properties of Methyl Ester of Mahua and Methyl Ester of karanja oils are determined as per Indian standard instrumentation in the fuels and lubricants laboratory. Determination of density, calorific value, viscosity, flash point and fire point are conducted using Hygrometer, Bomb calorimeter, Red wood viscometer and Able's apparatus respectively. The properties of methyl esters of mahua and karanja oils used are compared to diesel and neat oils.

Characterization of Mahua oil and Mahua Oil Methyl Ester:

A comparison of fuel properties are made between mahua oil, mahua oil methyl ester and Diesel in table 1. and it is found that the reduction of viscosity is about 80-85%. mahua oil methyl ester has calorific value 7.94% lower than diesel fuel. Kinematic viscosity is slightly higher than diesel. This is favorable for combustion. Flash point and Fire point are high, which is an advantage for fuel transportation. The various properties of mahua oil methyl ester (MOME) are found to be comparable with that of the Diesel fuel. Properties of biodiesel depend on the nature of the vegetable oil to be used for preparation of biodiesel by transesterification.

Table 1: Comparison of Fuel properties of Mahua oil, Mahua Oil Methyl Ester and diesel

Property	Diesel	Mahua Oil	MOME
Specific gravity	0.85	0.924	0.916
Kinematic viscosity at 40 ^o C (Cst)	3.54	39.45	5.8
Calorific Value (KJ/kg)	42800	37614	39400
Flash point (^o C)	56	230	129
Fire point (^o C)	63	246	141
Cetane number	47	45	50

Characterization of Karanja Oil and Karanja Oil Methyl Ester:

The measured values of properties of karanja oil methyl esters are given in Table 2. It is observed that the quality of biodiesel produced here are comparable with that of diesel fuel. It is also observed that the specific gravities of karanja oil methyl esters are slightly higher than that of diesel fuel. As they are slightly heavier than diesel fuel hence their viscosities are also little higher than that of diesel fuel. The heating values of these Karanja oil methyl ester is 35.87 MJ/kg, which is lower as compared to diesel fuel (42.8 MJ/kg). The fuel properties of Karanja oil methyl esters were also within biodiesel specifications.

Table 2: Comparison of fuel properties of Karanja oil, Karanja Oil Methyl Ester and diesel

Property	Diesel	Raw Karanja	KOME
Specific gravity	0.85	0.912	0.882
Kinematic viscosity at 40 ^o C (Cst)	3.54	29.65	8.73
Calorific Value (KJ/kg)	42800	34128	35870
Flash point (^o C)	56	241	217
Fire point (^o C)	63	253	223
Cetane number	47	38	56

Conclusion:

In this study, transesterification method is employed to convert the vegetable oil (mahua and karanja oils) into biodiesel, which result in a fuel closer to diesel fuel. The important physical and chemical properties of Methyl Ester of Mahua and Methyl Ester of karanja oils are determined as per Indian standard instrumentation in the fuels and lubricants laboratory. The properties of methyl esters of mahua and karanja oils used are compared to diesel and neat oils. A comparison of fuel properties are made between mahua oil, mahua oil methyl ester and Diesel and it is found that the reduction of viscosity is about 80-85%. mahua oil methyl ester has calorific value 7.94% lower than diesel fuel. Kinematic viscosity is slightly higher than diesel. This is favorable for combustion. Flash point and Fire point are high, which is an advantage for fuel transportation. The various properties of mahua oil methyl ester (MOME) are found to be comparable with that of the Diesel fuel. The measured values of properties of karanja oil

methyl esters are observed that the quality of biodiesel produced here are comparable with that of diesel fuel. It is also observed that the specific gravities of karanja oil methyl esters are slightly higher than that of diesel fuel. As they are slightly heavier than diesel fuel hence their viscosities are also little higher than that of diesel fuel. The heating values of these Karanja oil methyl ester is 35.87 MJ/kg, which is lower as compared to diesel fuel (42.8 MJ/kg). The fuel properties of Karanja oil methyl esters were also within biodiesel specifications.

References:

1. Aransiola, E. F, Betiku, E. Ikhuomogbe, D.I.O., Ojumu T.V. (2012) Production of biodiesel from crude neem oil feedstock and its emissions from internal combustion engines. *African Journal of Biotechnology*, 11(22): 6178-6186.
2. Kannahi, P.M., Arulmozhi, R. (2013) Production of biodiesel from edible and non-edible oils using *Rhizopus oryzae* and *Aspergillus niger*. *Asian Journal of Plant Science and Research*, 3(5): 60-64.
3. Mulimani, H., Hebbal, O. D., Navindgi, M. C. (2012) Extraction of Biodiesel from Vegetable Oils and Their Comparisons, *International Journal of Advanced Scientific Research and Technology*, 2(2), 242-250
4. Ghaly, A.E., Dave, D., Brooks, M.S., Budge, S. (2010) Production of Biodiesel by Enzymatic Transesterification: Review. *American Journal of Biochemistry and Biotechnology* 6 (2): 54-76.
5. Zhen-xing, L., Xiao-an, N., Yi-gang, W. (2013) Study on Technology of Comprehensive Utilization of Biodiesel and Dimers from Rapeseed Oil. *Journal of forest products & industries*, 2(4): 5-8.
6. Thirumarimurugan, M., Sivakumar, V. M., Merly Xavier, A., Prabhakaran, D., Kannadasan, T. (2012) Preparation of Biodiesel from Sunflower Oil by Transesterification, *International Journal of Bioscience, Biochemistry and Bioinformatics*, 2(6), 441-444.
7. e –book on biodiesel and jatropha planitation by satishlale.
8. Divya Bajpai., Tyagi.V.K. (2006) Biodiesel: source, production composition, properties and its benefits. *Journal of oleo science*, 55(10): 487-502.
9. Guoqing Guan, Katsuki Kusakabe, Nozomi Sakurai, Kimiko Moriyama. (2009) Transesterification of vegetable oil to biodiesel fuel using acid catalysts in the presence of dimethyl ether. *Fuel*, 88: 81-86.
10. Sharma Y.C., Singh B. (2009) Development of biodiesel: Current scenario. *Renewable and Sustainable Energy Reviews*, 13:1646-1651.
11. Subramanian K.A., Singal S.K., Mukesh Saxena, Sudhir Singhal. (2005) Utilization of liquid biofuels in automotive diesel engines: An Indian perspective, *J. Biomass and Bioenergy*, 29: 65-72.
12. Kegl B. (2008) Biodiesel usage at low temperature. *Fuel*, 87: 1306-1317.
13. Kapilan N., Ashok Babu T.P., Reddy R.P. (2009) Technical aspects of biodiesel and its oxidation stability. *International Journal of Chem Tech Research*, 1(2): 278-282.