PREPARATION OF BIODIESEL FROM KARANJA OIL

**Venkata Ramesh Mamilla[1], M.V.Mallikarjun[2],
Dr. G. Lakshmi Narayana Rao[3]
[1,2] Research Scholar, [3] Principal**
Department of Mechanical Engineering
[1,2] St.Peter's University,Chennai
[3] QIS Institute of Technology
Ongole,Andhra Pradesh
Email: maa_ram@yahoo.co.in, mvmsharma@yahoo.co.in
glnrao_68@yahoo.o.in
phone No: 09885183268,09885029816,09441887405

ABSTRACT

Biodiesel was prepared from the non-edible oil of Karanja by transesterification of the crude oil with methanol in the presence of NaOH as catalyst. A maximum conversion of 92% (oil to ester) was achieved at 60^0c. Important fuel properties of methyl esters of biodiesel produced from karanja oil like viscosity, flash point ,fire point ,calorific value etc., was found out and compared to the properties of Indian standard biodiesel.

Keywords: Karanja oil, Biodiesel, Transesterification.

1. INTRODUCTION

Karanja is a medium sized tree is found almost throughout India. Karanja tree is wonderful tree almost like neem tree. The common name of the oil is Karanja Seed Oil and the botanical name is Pongamia glabra of Leguminaceae family. Pongamia is widely distributed in tropical Asia and it is nonedible oil of Indian origin . It is found mainly in the Western Ghats in India, northern Australia, Fiji and in some regions of Eastern Asia. .The plant is also said to be highly tolerant to salinity and can be grown in various soil textures viz. stony, sandy and clayey. 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 tree bears green pods which after some 10 months change to a tan colour. The pods are flat to elliptic, 5-7 cm long and contain 1 or 2 kidney shaped brownish red kernels. The yield of kernels per tree is reported between 8 and 24 kg. .The kernels are white and covered by a thin reddish skin. The composition of typical air dried kernels is: Moisture 19%, Oil 27.5%, and Protein 17.4%. The present production of karanja oil approximately is 200 million tons per annum. The time needed by the tree to mature ranges from 4 to 7 years and depending on the size of the tree the yield of kernels per tree is between 8 and 24 kg.

India is a tropical country and offers most suitable climate for the growth of karanja tree. It is found in abundance in rural areas and forests of entire India, especially in eastern India and Western Ghats. Fig.1 shows the close view of seeds of karanja. The seeds are crushed in expeller to get the oil. A view of raw oil obtained by crushing the seeds has been given in Fig.2 As the tree of karanja is naturally found in forests, there are so far no reports on adverse effects of karanja on fauna, flora, humans or even on environment but that is a different area of research. Karanja oil has been reported to contain furanoflavones, furanoflavonols, chromenoflavones, flavones and furanodiketones which make the oil non-edible and hence further encourages its application for biodiesel production.

Fatty acids composition of Karanja Palmitic (C16:0)11.6%, Stearic (C18:0) 7.5%, Oleic (C18:1) 51.5%, Linoleic (C18:2) 16.0%, Linolenic(C18:3) 2.6%, Arachidic (C20:0) 1.7%, Eicosenoic (C20:1) 1.1%,Behenic(C22:0) 4.3% Lignoceric (C24:0)1.0%.

Fig 1. Seeds of karanja   **Fig. 2 Oil expelled from seeds of karanja**

2. TRANSESTERIFICATION

Transesterification of a vegetable oil was conducted as early as 1853, by scientists E. Duffy and J. Patrick, many years before the first diesel engine became functional. Rudolf diesel's prime model, a single 10 ft (3 m) iron cylinder with a flywheel at its base, ran on its own power for the first time in Augsburg, Germany. This engine stood as an example of Diesel's vision because it was powered by peanut oil a bio-fuel, though not strictly bio-diesel, since it was not Tran esterifies. He believed that the utilization of a biomass fuel was the real future of his engine.
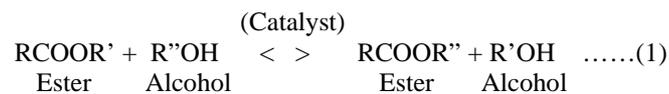
During the 1920s, diesel engine manufacturers altered the engines to utilize the lower viscosity of the fossil fuel (petro-diesel) rather than vegetable oil, a biomass fuel. The petroleum industries were able to make inroads in fuel markets because their fuel was much cheaper to produce than the biomass alternatives. The result was, for many years, a nearer elimination of the biomass fuel production infrastructure. Only recently have environmental impact concerns and a decreasing cost differential made biomass fuels such as bio-diesel a growing alternative.

In the 1900s, France launched the local production of biodiesel fuel (known locally as diester) obtained by the TRANSESTERIFICATION of rapeseed oil. It is mixed to proportion of 5% into regular diesel fuel, and to the proportion of

30% into the diesel fuel used by some captive fleets (public transportation). Renault, Peugeot and other manufacturers have certified truck engines for use with up to this partial bio-diesel. Experiments with 50% bio-diesel are underway.

From 1978 to 1996, the U.S. National Renewable Energy Laboratory experimented with using algae as a bio-fuel source in the "Aquatic Species Program".

Transesterification, also called alcoholysis, is the displacement of alcohol from an ester by another alcohol in a process similar to hydrolysis, except than a alcohol is used instead of water. This process has been widely used to reduce the viscosity of triglycerides. equation:

$$\begin{array}{cc} & \text{(Catalyst)} \\ \underset{\text{Ester}}{\text{RCOOR'}} + \underset{\text{Alcohol}}{\text{R''OH}} & < \quad > \quad \underset{\text{Ester}}{\text{RCOOR''}} + \underset{\text{Alcohol}}{\text{R'OH}} \quad \ldots\ldots(1) \end{array}$$

If methanol is used in the above reaction, it is termed methanolysis. The reaction of triglyceride with methanol is represented by the general equation:
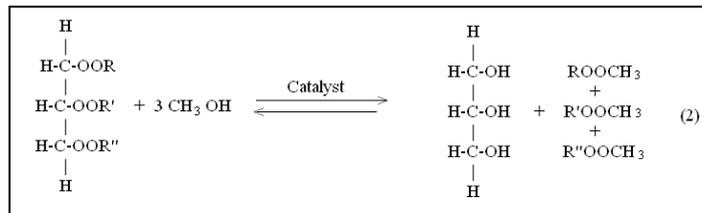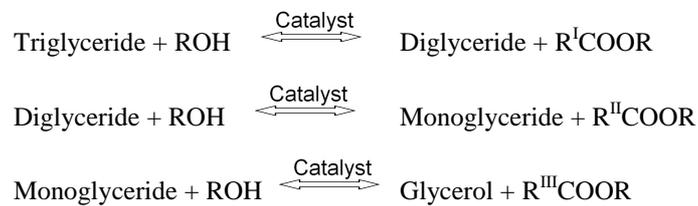

Fig. 3

$$\text{Triglyceride} + \text{ROH} \underset{}{\overset{\text{Catalyst}}{\rightleftharpoons}} \text{Diglyceride} + \text{R}^{I}\text{COOR}$$

$$\text{Diglyceride} + \text{ROH} \underset{}{\overset{\text{Catalyst}}{\rightleftharpoons}} \text{Monoglyceride} + \text{R}^{II}\text{COOR}$$

$$\text{Monoglyceride} + \text{ROH} \underset{}{\overset{\text{Catalyst}}{\rightleftharpoons}} \text{Glycerol} + \text{R}^{III}\text{COOR}$$

3. PROCESS VARIABLES

The most important variables that influence transesterification reaction time and conversion are:

- Reaction temperature

- Ratio of alcohol to oil

- Catalyst type and concentration

- Mixing intensity

- Purity of reactants

3.1 Reaction Temperature

The rate of reaction is strongly influenced by the reaction temperature. However, given enough time, the reaction will proceed to near completion even at room temperature. Generally, the reaction is conducted close to the boiling point of methanol (60° to 70°C) at atmospheric pressure. These mild reaction conditions, however, require the removal of free fatty acids from the oil by refining or pre-esterification. The pretreatment is not required if the reaction is carried out under high pressure (9000kpa) and high temperature (2408°C). Under these conditions, simultaneous esterification and transesterification take place. The maximum yield of esters occurs at temperatures ranging from 60° 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.

3.2 Ratio of Alcohol to Oil

Another important variable affecting the yield of ester is the molar ratio of alcohol to vegetable oil. The stoichiometry of the transesterification reaction requires 3mol of alcohol per mole of triglyceride to yield 3mol of fatty esters and 1 mol of glycerol. To shift the transesterification reaction to the right, it is

necessary to use either a large excess of alcohol or to remove one of the products from the reaction mixture. 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 yields higher than 98% by weight. Higher molar ratio of alcohol to vegetable oil interferes in the separation of glycol.

3.3 Catalyst Type 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, although NAOH and KOH can also be used. Transmethylations occurs approximately 4000 times faster in the presence of an alkaline catalyst than those catalyzed by the same amount of acidic catalyst. Partly for this reason and partly because alkaline catalysts are less corrosive to industrial equipment than acidic catalysts, most commercial transesterifications are conducted with alkaline catalysts. The alkaline catalyst concentration in the range of 0.5 to 1% by weight yields 94 to 99% conversion of vegetable oil into esters. 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.

3.4 Mixing Intensity

In the transesterification reaction, the reactants initially from a two phase liquid system. The reaction is diffusion controlled and poor diffusion between the phases results in a slow rate. As methyl esters are formed, they act as a mutual solvent for the reactants and a single phase system is formed. The mixing effect is most significant during the slow rate region of the reaction. As the single phase is established, mixing becomes insignificant. The understanding of

the mixing effects on the kinetics of the transesterification process is a valuable tool in the process scale up and design.

3.5 Purity of Reactants

Impurities present in the oil also affect conversion levels. Under the same conditions, 67 to 84% conversion into esters using crude vegetable oils can be obtained, compared with 94 to 97% when using refined oils. The free fatty acids in the original oils interfere with the catalyst. However, under conditions of high temperature and pressure this problem can be overcome.

4. PROCEDURE FOR PRODUCTION OF BIODIESEL

Raw materials required:

- Used or fresh vegetable oil (strained with a coffee filter or cloth)

- Lye (Catalyst)

- Methanol

- Isopropyl Alcohol (for tests. Use 99% IPA)

4.1 Titration Process to Determine Lye Quantity

Free fatty acids will increase with the amount of time vegetable oil has been heated. Oil which has been used for cooking will require more of the reactive agents (lye and methanol) than fresh oil. The presence of too many free fatty acids will retard or stop the reaction which produces biodiesel, so it is necessary to detect the exact amount of LYE (Sodium Hydroxide or NaOH) needed to neutralize. Adding too much or too little NaOH will just make excessive amounts of bi-products (soap).

4.2 To Determine Reaction Proportion

To find the total amount of NaOH to be added we add the number of drops of NaOH needed for the wasted vegetable oil solution to reach a ph of 8-9 and 3.5 grams NaOH to catalyze the oil (stoichiometric).

An example formula used with one particular batch of wasted vegetable oil: 1ml of oil was titrated with a 1gm NaOH/1000ml H_2O solution. It required 6.0ml to raise the ph level to 8. Hence 6.0gm/1000ml to neutralize the free fatty acids + 3.5g NaOH as catalyst = 9.5g per 1000ml oil.

4.3 Vegetable Oil

Diesel has a chain of 11-13 carbons and new vegetable oil has a chain of about 18, but waste vegetable oil, which has been heated, has chain of up to 32 carbons. To burn in an engine the chain needs to be broken down to be similar in length to diesel.

4.4 Lye (Catalyst)

Lye is the catalyst used for transesterification. It works by "cracking" the vegetable oil molecules, splitting the triglycerides from the hydrocarbons and shortening the carbon chain of 3.5gm or 0.35% is the standard amount of lye necessary to create a reaction, when using fresh vegetable oil. Due to the presence of a very small quantity of FFA we add an additional 0.3 to 0.4 grams in order to neutralize completely.

4.5 Methanol

The amount of methanol needed will also vary, but the ideal is to use the least amount of methanol necessary in order to get the highest yield. The yield is related to completion so if you get 90% yield that means that 90% of the fatty acids have been eliminated from the vegetable oil. We have found that the best is to use 15% to 20% methanol, based upon the total weight of batch of oil.

A hydrometer can also be used to check the amount of completion according to density.

5.   STEPS FOR PRODUCTION OF BIODIESEL

- Weight 6 kg of vegetable oil (refined sunflower oil) and pour it into the reactor for preliminary heating to temperature of about 60-70°C.

- In separate container, dissolve 22.8grams of NaOH (3.8grams per liter of oil, got by 3.5grams stoichiometric equivalent and 0.3grams for neutralizing FFA) in 1.2L methanol (200ml per liter of oil) add the NaOH slowly. This combined mixture makes sodium methoxide.

- Add this to the vegetable oil. Provide rigorous mixing with the use of a stirrer.

- The cloudy looking free fatty acids, called glycerine, will sink to the bottom and the methyl ester- a translucent liquid, will remain on top.

- When the separation appears not to be advancing any more, stop mixing.

- Let the mixture settle overnight. Meanwhile another batch can be started as the reactor is not being used.

- The liquid on top is methyl ester, but before using it any remaining soaps or salts which could cause engine damage have to be removed.

- The glycerin which has sunk to the bottom can be used in production of cosmetics

5.1 Rinsing Methyl Ester

- Methyl ester was poured off into a separate clean container, where it was washed free of any remaining soaps, salts or free fatty acids.

- Warm water was added to the methyl ester. It was stirred lightly and

then allowed to settle. The warm water was heated in the main reactor itself.

- When the water had cleanly separated from the methyl esters, the water was drained out from the bottom.

- The process was repeated until the discarded rinse water reached ph level of 6-7 and no soap bubbles appeared in it.

- If the liquid remaining is cloudy, there is water being retained in the fuel, and it will need to be reheated slowly to evaporate out the water. Any white substances forming at the bottom or any bubbles forming at the surface is a sign of soaps and should be removed or the liquid should be re-washed. The cleaned methyl ester is a version of biodiesel.

5.2 Observation for Production of Biodiesel

- The optimum condition for the reaction was found to be the following: for every liter of oil used, 200ml of methanol needed to be used.

- The optimum temperature for the reaction was identified to be in the range of 53°C to 58°C for methanol.

- Vigorous stirring and heating is of paramount importance for better conversion efficiency.

- The ideal time for the completion of reaction is around 3-4hrs.

- Reaction with ethanol is difficult unless 2 conditions are met – a) Requirement of anhydrous ethanol and b) Requirement of closed system to prevent ethanol from absorbing water.

- The FFA content of oil needs to be determined and appropriate quantity of Lye needs to be added in order to neutralize excess acid. This excess acid is present when the oil gets heated.

- Care must be taken to prevent the process of saponification from occurring. This can be ensured by proper heating and stirring.

- About 4.5 Liters of Biodiesel has been obtained for an input quantity of 6L oil.

6. ESTERIFICATION SETUP

The design and fabrication of esterification equipment for methyl ester preparation are discussed in this section.

6.1 Components of the System

The following are the major components of the batch equipment:

1. Main reactor
2. Settling (Separation) vessels
3. Washing unit and diffuser unit
4. Storage unit
5. Heating system
6. Stirring system and baffles

Fig: 4 Esterification setup

6.2 Main Reactor

The first aspect with respect to the design of the reactor was the total volume of the reactor. As was decided that a maximum output of 8 liters of bio-diesel was required from a single batch, the total required volume of the reactor was estimated to 10 liters. This volume is required to accommodate all the reactants vise versa vegetable oils, methanol and the lye in the recommended ratios.

Hence with the required volume in consideration a cylindrical shape was sought to be appropriate. Since it was decided that the flow of liquid contents from one vessel to the other would be assisted by gravity, use of a tapered conical section at the bottom of the viscous fluid. Glycerol is highly viscous and the formation of this would result in sluggish flow of the reacted mixture from the reactor.

Fig. 5

The system requires to be closed system and hence a flange was designed to prevent any leakage of the methanol which could vaporize due to heating and potentially be health hazard. Hence the whole system was designed to be air tight with the use of a flange and a rubber bush to prevent any leakage. Since it was observed that methanol has tendency to vaporize and to allay a fear of

explosion due to increase in pressures, use of pressure relief valve (PRV) was envisaged.

As the reaction requires vigorous stirring and heating, the design was involved to integrate the stirring and the heating systems into the main reactor. The main reactor was designed to include baffles to provide for higher mixing sufficiency and more uniform temperature during the reactions.

6.3 Separating and Washing Vessels

From the literature study and the preliminary laboratory experiment it was observed that immediately after the reaction period, i.e. the length of time for which the reaction occurs and during which both stirring and heating of time for which the reaction mixture should be allowed to cool and settle. The settling period allows for the reaction mixture to separate into the two products namely glycerol and the biodiesel. The separation occurs over a period of about 6 or more hours.

Fig. 6

It was decided to separate the reaction contents from the main reactor into two separate vessels to facilitate washing of the bio-fuel. Once the reaction contents are transferred the two settling vessels, they are allowed to separate. To enable viewing of the settling between the lower glycerol layer and the upper

bio-fuel layer, a glass tube was designed to be accommodated into the separating vessel and in turn facilitates easier removal of the glycerol from the bio-fuel.

The separating vessels are designed to be cylindrical in shape with a capacity to accommodate more than 10 liters to hold water necessary for bubble washing. The quantity of water is estimated in the ratio of 2:1 i.e. for every one part of bio fuel two parts if warm water is required.

The biofuel separated in this stage still impure and needs to be cleansed in a process known as bubble washing. This process involves cleaning the fuel with water by using agitation which is provided by pumping air through the water and biodiesel mixture.

The washing system was designed using a pump to deliver air through a pipe to a diffuser inside the washing/separating vessel. The diffuser used for this purpose is to be integrated into the tank with the help of the appropriate piping from the pump.

The design involves the pump to be positioned at a height greater than the position of the diffuser in the tank. This is necessary to prevent reverse flow of fluid from the tank into the pipe providing the compressed air. A one way check valve is also provided at the diffuser attachment in the tank to prevent flow of liquid into the Same Pipe.

6.4 Heating System

The optimum temperature for efficient conversion of vegetable oil to biodiesel was identified to be about 51°C-55°C. The heating system required for this purpose was required to maintain a constant temperature in the above mentioned range. The heating system was designed to be a closed loop feedback system which could maintain a required temperature so that the reaction conditions can be maintained as needed. A thermostat control is used to maintain constant temperature.

The system was designed with an electric heating coil, a temperature controller and a sensor. The ideal location for the sensor was identified to be on the flange of the closed reactor. This would allow for the measurement of temperature near the liquid surface so that temperature gradient does not affect the temperature reading. The heating coil is placed ideally to provide uniform heating.

The heating coil is connected to the temperature controller through a relay. The temperature sensor provides feed back to the controller and allows a present temperature to be maintained.

7. PROPERTIES OF METHYL ESTERS

The properties of methyl esters produced were measured using respective standard techniques. It was found that the properties of the methyl esters satisfy Indian standards (IS 15607:2005) for Biodiesels. The Properties of oil ,methyl esters, diesel and Indian Standards for biodiesel are listed in Table .1 & 2

The photographs of neat oil and the corresponding methyl esters (biodiesel) are shown in Figures.7 & 8

Table 1. Properties of oil before esterification

Property	Karanja oil
Density (Kg/m^2)	991
Kinematic viscosity c.stokes	69.6
Flash point(^{0}c)	241
Fire point (^{0}c)	253
Heating Value KJ/Kg	34000
Specific gravity	0.912

Table 2. Properties of oil After esterification

Property	Karanja Methyl Esters	Diesel	IS for Biodiesel
Density (Kg/m^2)	885	836	860-900
Kinematic viscosity c.stokes	5.60	3.8	2.5-6
Flash point(^{0}c)	217	56	120
Fire point (^{0}c)	223	63	130
Heating Value KJ/Kg	36120	42800	37270
Specific gravity	0.876	0.85	0.86-0.90

Fig: 7 Karanja oil   **Fig:8 Biodiesel from karanja oil**

8. ADVANTAGES OF BIO-DIESEL

There are numerous advantages of bio-diesels. Some of the most important are listed:

- Biodiesel runs in any conventional, unmodified diesel engine. No engine modifications are necessary to use b

- Bio-diesel and there is no "engine conversion." In other words, "you just pour it into the fuel tank."

- Biodiesel can be stored anywhere that petroleum diesel fuel is stored. All diesel fuelling infrastructure including pumps, tanks and transport trucks can use bio-diesel without any major modifications.

- Biodiesel reduces carbon dioxide emissions, the primary cause of the greenhouse effect, by up to 100%. Since bio-diesel comes from plants and plants breathe carbon dioxide, there is no net gain in carbon dioxide from using bio-diesel.

- Biodiesel can be used alone or mixed in any amount with petroleum diesel fuel. A 20% blend of bio-diesel with diesel fuel is called "B20"; a 5% blend is called "B5" and so on.

- Biodiesel is more lubricating than diesel fuel, it increases the engine life and it can be used to replace sulfur, a lubricating agent that, when burned, produces sulfur dioxide. The primary component in acid rain. Instead of sulphur, all diesel fuel sold in France contains 5% bio-diesel.

- Biodiesel is safe to handle because it is biodegradable and non-toxic. According to the national bio-diesel board, "neat diesel is as biodegradable as sugar and less toxic than salt."

- Biodiesel is safe to transport. Bio-diesel has a high flash point, or ignition temperature, of about 150°C compared to petroleum diesel fuel, which has a flash point of 52°C.

- Engines running on bio-diesel run normally and have similar fuel mileage to engines running on diesel fuel. Auto ignition, fuel consumption, power output, and engine torque are relatively unaffected by biodiesel.

9. CONCLUSIONS

Crude Karanaja oil was transesterified using NaOH as catalyst and methanol to form biodiesel .The conversion was 92% at 60^0c. The fuel properties like viscosity,density,flash point ,fire point and calorific value of the the transesterified product(biodiesel) compare well with accepted biodiesel standards i.e ASTM and German biodiesel standards.

REFERENCES

1. A.S. Ramadhas, S. Jayaraj and C. Muraleedharan, Use of vegetable oils as I.C.engine fuels—a review, Renewable Energy 29 (2004), pp. 727–742.

2. A. Srivastava and R. Prasad, Triglycerides-based diesel fuels, Renew Sust Energ Rev 4 (2000), pp. 111–133.

3. Barnwal B.K. and Sharma M.P. (2005), "Prospects of biodiesel production from vegetable oils in India", Journal of Renewable and Sustainable Energy Reviews, 9, 363-378.

4. Houfang Lu, Yingying Liu, Hui Zhou, Ying Yang, Mingyan Chen and Bin Liang. (2009), "Production of biodiesel from jatropha curcas L. oil", Journal of Computers and Chemical Engineering, 33, 1091–1096.

5. Sanjib Kumar Karmee and Anju Chadha.,"Preparation of biodiesel from crude oil of pongamia pinnata", Bioresource Technology Vol.96, 2005 pp.1425–1429.

6. Shashikant Vilas Ghadge and Hifjur Raheman, , "Biodiesel production from mahua (Madhuca indica) oil having high free fatty acids", Biomass and Bioenergy Vol.28, 2005 pp 601–605.

7. Siti Zullaikah, Chao-Chin Lai, Shaik Ramjan Vali and Yi-Hsu Ju., "A two-step acid-catalyzed process for the production of biodiesel from rice bran oil", Bioresource Technology, Vol. 96, 2005 pp 1889–1896.

8. Raheman, H. and Phadatare, A.G., "Diesel engine Emissions and performance from blends of karanja methyl ester and diesel", Biomass and Bioenergy Vol. 27 , 2004 pp 393-397.