

Biodiesel production from Karanja oil

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Received: 09 July 2003; accepted: 12 November 2003

Import dependence for oil in India, which is about 70 per cent, is likely to increase further. The study is initiated to investigate the potential of Karanja oil as a source of biodiesel. Biodiesel is an alternative fuel made from renewable biological resources such as, vegetable oil and animal fat. It is completely biodegradable and non-toxic. Main objectives of the study are feasibility of Karanja oil for the production of biodiesel, optimization of different parameters for high yield/conversion of Karanja oil to biodiesel. Optimum conditions were found to be: Pressure 1 atm, Temperature 68-70 °C, Reactant ratio 8-10 (Moles of MeOH: Moles of oil), Reaction time 30-40 min, Catalyst (KOH) 1.5 per cent w/w. Tests were also conducted to compare the biodiesel with diesel fuel in terms of engine performance and emissions.

Keywords: Biodiesel, Karanja oil, Alternate fuel, Fuel

1 Introduction

During last decade, India maintained a high growth rate, which has also led to increased energy demand/ consumption. The share of hydrocarbons in the primary energy consumption of the country has been increasing over the years and is presently estimated at 44.9 per cent (36 per cent for oil and 8.9 per cent for natural gas). The demand for oil in India is expected to grow at an average rate of 3.6 per cent over the next 5 y, which will be higher than the average growth rate of around 2 per cent in the world. Import dependence of oil in India, which is presently about 70 per cent, is likely to increase further during the next 10 y (Tenth Five Year Plan, Government of India). Drive for alternative fuels gathered momentum with the introduction of auto LPG and setting up of an ethanol-petrol blending projects in selected states in India. Alternative source for diesel is also being explored.

Biodiesel is an alternative diesel fuel made from vegetable oil and animal fats. It can act both as substitute and an additive to diesel fuel. European Union has set an objective to replace its 5 per cent of total motor fuel consumption with biodiesel by 2005. Similarly the US department of energy estimated that up to 50 per cent of the diesel fuel could be replaced with biodiesel. Importance of biodiesel increases due to (i) Increasing petroleum prices, (ii) Limited fossil fuel reserves, and (iii) Environmental benefits of biodiesel.

Different methodologies used for production of biodiesel are:

- (i) Direct use/blending,
- (ii) Micro-emulsion,
- (iii) Pyrolysis, and
- (iv) Transesterification.

1.1 Direct Use/Blending

Vegetable oil can be directly used as diesel fuel without any changes to engine. The very first engine (by Rudolf Diesel) was tested using vegetable oil as fuel. The primary concern with vegetable oil as fuel is its high viscosity (atomization of vegetable oil is difficult), which leads to problems in the long run:

Advantages of vegetable oil as diesel fuel are¹:

- (i) Liquid nature and portability,
- (ii) High heat content (80 per cent of diesel fuel),
- (iii) Ready availability, and
- (iv) Renewability.

The problems appear only after long period. Some of common problems are:

- (i) Coking and trumpet formation on the injectors to such an extent that fuel atomization becomes difficult,
- (ii) Carbon deposits,
- (iii) Oil ring sticking, and
- (iv) Thickening and gelling.

1.2 Micro-emulsions

Micro emulsion is defined as colloidal dispersion of fluid microstructures (1-150 nm) in solvent forming two immiscible phases. The common solvents used are methanol and ethanol. Micro-emulsions is the probable solution to high viscosity of vegetable oil. Their atomization is relatively easy because of lower viscosity.

1.3 Pyrolysis

Pyrolysis means conversion of one substance to another by application of heat. Catalysts are used to speed up the process. Different products can be obtained from the same material depending on different path of reaction and this makes pyrolytic chemistry difficult. Pyrolysis of vegetable oil gives different lower hydrocarbons that can be used as fuel.

1.4 Transesterification

Transesterification is a kind of organic reaction where alcohol group in ester is substituted. It can also be reaction of vegetable oil/fat with alcohol to give ester and glycerol. The applicability of transesterification is not restricted to laboratory. Several relevant industrial processes use this reaction to produce different types of compounds. An example is the production of PET (polyethyleneterephthalate),

which involves a step where dimethylterephthalate is transesterified with ethylene glycol in the presence of zinc acetate as catalyst. Furthermore, a large number of acrylic acid derivatives are produced by transesterification of methyl acrylate with different alcohols, in the presence of acid catalysts.

1.5 Transesterification of Vegetable Oils

In transesterification of vegetable oils, a triglyceride reacts with three molecules of alcohol in the presence of catalyst, producing a mixture of fatty acids alkyl esters and glycerol (Figure 1). The overall process is a sequence of three consecutive reactions, in which di- and monoglycerides are formed as intermediates. Transesterification is a reversible reaction thus; excess alcohol is used to increase the yields of the alkyl esters and to allow its phase separation from the glycerol formed.

Conversion of vegetable oil to biodiesel is effected by several parameters namely

- (i) Time of reaction,
- (ii) Reactant ratio (Molar ratio of alcohol to vegetable oil),
- (iii) Type of catalyst,
- (iv) Amount of catalyst, and
- (v) Temperature of reaction.

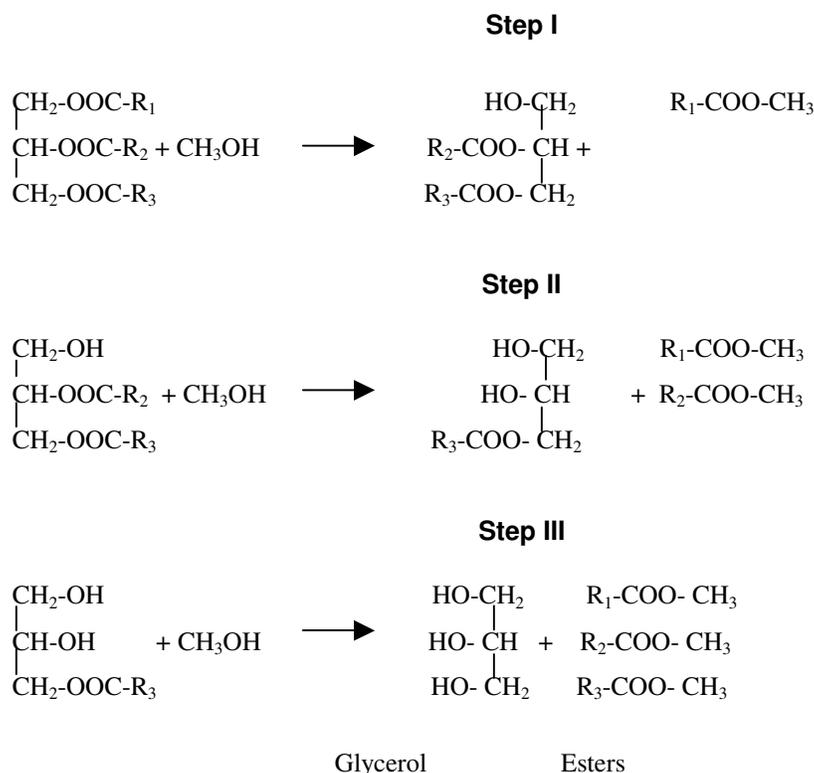


Figure 1 — Transesterification reaction of a triglyceride

1.5.1 Acid Catalyzed Transesterification

Transesterification is catalyzed by Bronsted acids. These catalysts give very high yields in alkyl esters, but the rate of reaction is slow, requiring, typically, temperatures above 100 °C and more than 3h to reach complete conversion. H₂SO₄ is a commonly used acid catalyst. Figure 2 gives the mechanism of an acid catalyzed process.

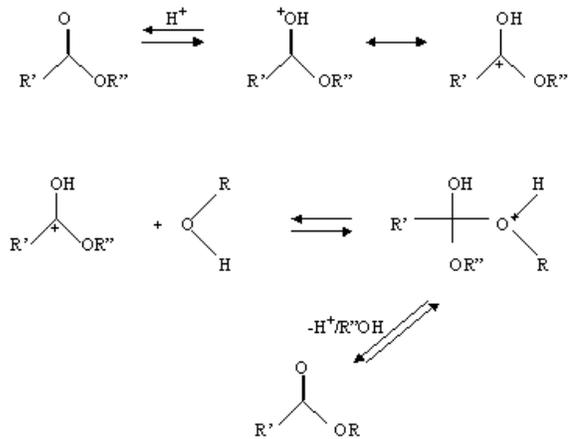


Figure 2 — Mechanism of an acid catalyzed process

1.5.2 Base Catalyzed Transesterification

The base-catalyzed transesterification of vegetable oils proceeds faster than the acid-catalyzed reaction. Because of above reason, together with fact that the bases are less corrosive than acidic catalyst, industrial processes usually use base catalysts such as, alkaline metal alkoxides and hydroxides as well as sodium or potassium carbonates.

The mechanism of the base-catalyzed transesterification² of vegetable oils is shown in Figure 3. Alkaline metal alkoxides (for the transesterification) are the most active catalysts, since they give very high yields in short reaction times even if they are applied at low molar concentrations. However, they require absence of water, which makes them inappropriate for typical industrial processes. Alkaline metal hydroxides (KOH and NaOH) are cheaper than metal alkoxides, but less active.

Undesirable side reaction (saponification) reduces the ester yields and makes the recovery of the glycerol difficult due to the formation of emulsions. For this study, base (KOH, Base catalyzed process) has been used as catalyst.

1.6 Non Edible Oil Resources in India

India has rich and abundant forest resources with a wide range of plants and oilseeds. Economics of the biodiesel production process can be improved if non-edible oils are used. Table 1 gives various non-edible oil sources available in India.

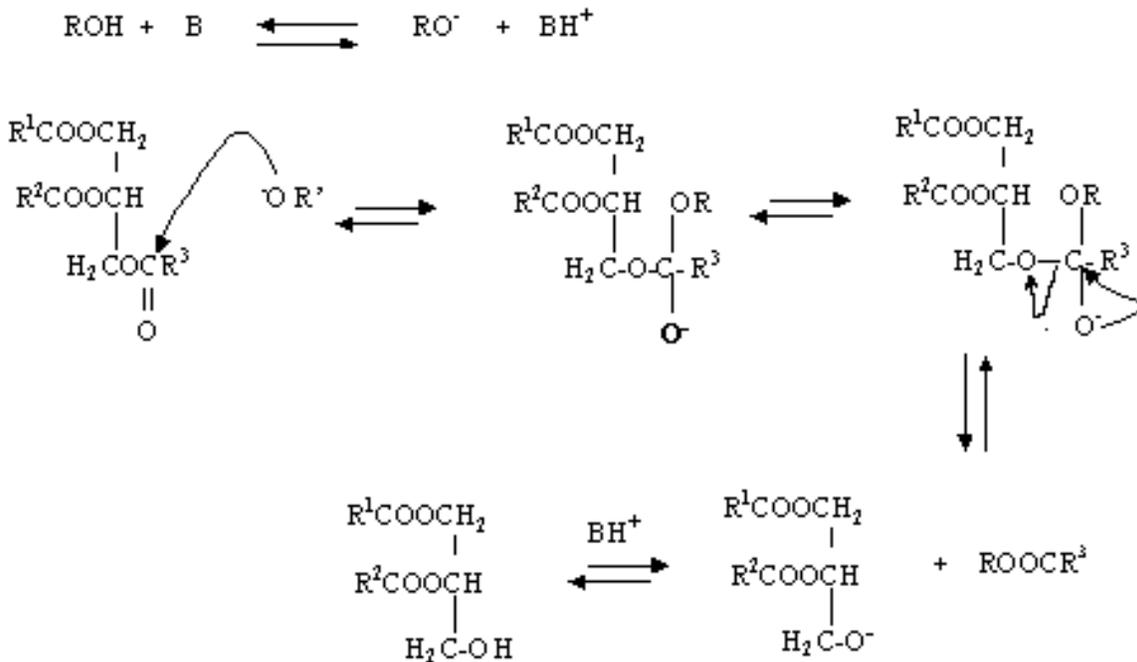


Figure 3 — Mechanism of a base catalyzed process

Karanja (*Pongamia Pinnata*) is (a tree) grown in parts of India and Australia. The seed kernels contain 27-39 per cent of oil. The potential availability of the oil is estimated to be 55,000 t/y. The seed oil is extracted and sold for non-edible commercial purposes. Currently it is used in soap making and in the leather industry (Table 2).

Table 1— Non- edible oil potential in India by National Oilseeds and Vegetable Oil Development (NOVOD) Board, India

Oil	Botanical name	Oil potential, t
Neem	<i>Azadirachta indica</i>	100 000
Karanja	<i>Pongamia pinnata</i>	55 000
Kusum	<i>Schleichera oleosa</i>	25 000
Ratanjyot	<i>Jatropha curcus</i>	15 000
Pilu	<i>Salvadora oleoides</i>	17 000
Tumba	<i>Citrullus collocynthis</i>	21 000
Sal	<i>Shorea robusta</i>	180 000
Mahua	<i>Madhuca indica</i>	180 000
Mango	<i>Mangifera indica</i>	45000
Phulware	<i>Cheura</i>	3000
Kokum	<i>Garcinia indica</i>	500
Simarouba	<i>Simaruba glauca</i>	—
Jjoba	<i>Simmondsia chinensis</i>	—
Chullu	<i>Prunus armeniaca</i>	110
Rice bran	<i>Oryza sativa</i>	474000

Table 2 — Fatty acid composition (per cent) of raw and extracted Karanja oil (GLC analysis) (Cherian 2000)

Fatty acid	Raw Karanja oil	Extracted Karanja oil
C16	9.6	9.6
C18	6.5	6.6
C18:1	50.0	50.0
C18:2	16.0	15.9
C18:3	3.1	3.0
C20	1.7	1.7
C20:1	1.3	1.3
C22	5.7	5.7
C24	2.1	2.3
Unidentified	4.0	3.9

2 Materials and Method

2.1 Experimental Setup

Reaction or transesterification was carried out in a system, as shown in Figure 4. Reactor consisted of spherical flask, which was put inside the heat jacket. Oil was used as medium of heat transfer from heat jacket to the reactor. Thermostat was a part of heat jacket, which maintained the temperature of oil and in turn the temperature of the reactants at a desired value. The reaction was carried out at around 65-70 °C. Spherical flask consisted of four openings. The center one was used for putting stirrer in the reactor. The motor propelled the stirrer. Thermometer was put inside the second opening to continuously monitor the temperature of the reaction. Alcohol being volatile vaporized during the reaction so the condenser was put in the third opening to reflux the vapors back to the reactor to prevent any reactant loss. Fourth opening was used for filling reactants to the reactor.

2.2 Experimental Procedure

A known quantity of Karanja oil (100 mL for each run) was taken inside the reactor and heated at about 70 °C. This temperature was maintained throughout the reaction by the thermostat inside the heat jacket. Preheating was used to remove unwanted moisture present in the oil. The transesterification was carried out in basic medium and to achieve it, KOH was used as catalyst. Catalyst was dissolved in

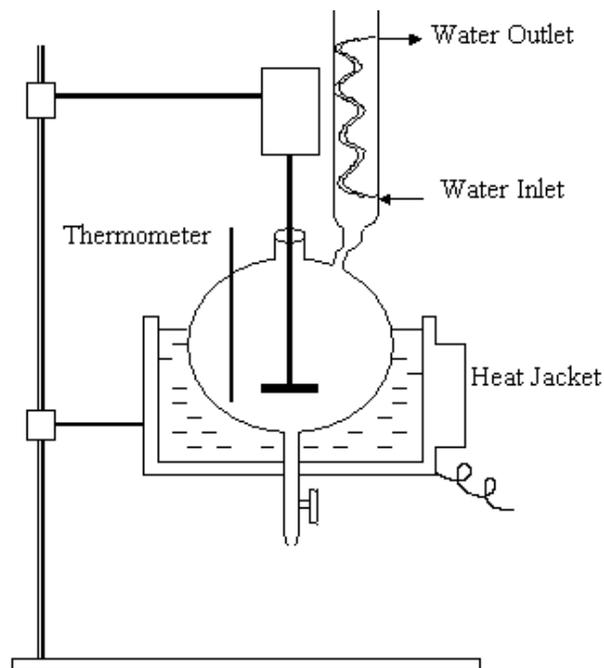


Figure 4 — Experimental setup

alcohol (MeOH). Once the oil temperature reached 70 °C, alcohol solution (containing dissolved catalyst) was added to the reactor and an equilibrium temperature was maintained. During the reaction alcohol gets vaporized. To prevent any reactant loss condenser was used to condense the alcohol vapor and reflux it back into the reactor. Condenser was also helpful in maintaining atmospheric pressure inside the reactor (Figure 5).

Once reaction was over the products were taken out through the outlet in the lower side of the reactor and put in the separating funnel.

Two phases (having different density) are formed as a result of transesterification. Separation was done using a separating funnel (separation took around two hours). Upper layer consisted of biodiesel, alcohol, and some soap (formed as a result of side reaction saponification – free fatty acids get converted to soap). Lower layer consisted of glycerin, excess alcohol, catalyst, impurities, and traces of unreacted oil.

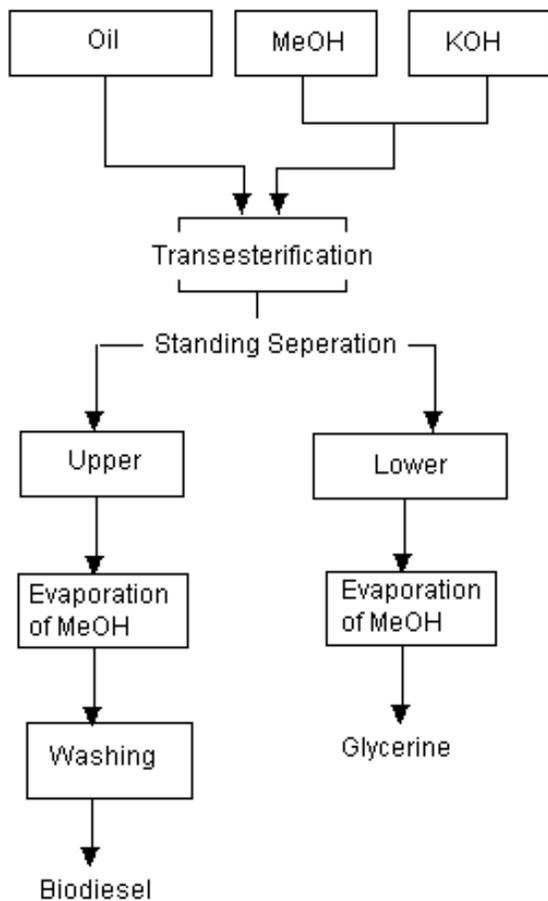


Figure 5 — Experimental process

Purification of upper layer (to obtain biodiesel) was done in two steps.

- (i) Removal of alcohol - by keeping mixture at elevated temperature ~80 oC
- (ii) Removal saponified products - by washing with warm water. Water is immiscible with biodiesel, hence can be easily separated from biodiesel.

2.3 Effect of Temperature on Conversion

It is well known from the chemical kinetics, rate of reaction increases with temperature. Transesterification was carried out at boiling point of mixture, as that is the highest temperature achievable at normal conditions.

Vegetable oil and alcohol mixture forms two different phases when put in the reactor. Reaction takes place at the contact surface of the two phases. To increase the contact surface area reactants are agitated using stirrer. Hence stirring rate also affects the rate of reaction.

3 Result and Discussions

3.1 Effect of Reaction Time on Conversion

Reaction time is one of the most important parameters. Conversion of vegetable oil increases with the increase in reaction time as the reaction progress toward completion. The result of the experiments could be seen from the graph (Figure 6).

Effect of time on conversion decreases with reaction time. After a certain time of reaction there is no further increase in the conversion with increase in reaction time because of the following factors:

Sl No	1	2	3	4	5	6	7	8
Time (min)	5	10	15	20	30	40	60	120
Conversion	0.8	0.8531	0.873	0.884	0.89	0.893	0.901	0.899

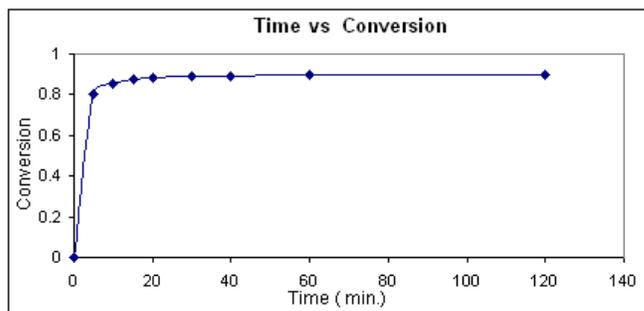


Figure 6 — Plot of Time vs conversion

- (i) Rate of reaction is directly proportional to the concentration of oil in the reaction mixture and as the reaction proceeds the concentration of oil keeps on decreasing and hence the rate of reaction.
- (ii) Transesterification is a reversible reaction and has an equilibrium conversion, which is independent of reaction time.

Optimum reaction time to obtain high conversion is 30-40 min.

3.2 Effect of Reactant Ratio on Conversion

Conversion of vegetable oil to biodiesel increases with reactant ratio (Moles of MeOH: Moles of oil). This can be seen from the graph of reactant ratio vs conversion.

As molar ratio increases, its effect on conversion decreases. It can be seen that conversion nearly saturates at 0.9. The reasons for low conversion are:

- (i) Presence of impurities;
- (ii) Presence of free fatty acid in karanja oil (Acid number – 6 mg KOH/g oil)
- (iii) Side reaction saponification, also limits the conversion by consuming the catalyst and also the saponification products leads to difficulty in separation of the transesterification products.

Conversion keeps on increasing with the molar ratio. Optimum reactant ratio is around 8-10 moles of methanol per mole of vegetable oil. This could be explained as follows:

- (i) No major increase in conversion takes place after molar ratio of 8-10. Conversion at molar ratio of 10 is .885 and conversion at molar ratio of 28 is .887, or we can say a difference of just .002.
- (ii) As we go on increasing the molar ratio the density difference between upper and lower layer (the two phase obtained after transesterification) keeps decreasing and hence leads to problems in separating the two. As we further increase the molar ratio a third separate layer containing pure excess alcohol is formed, which again leads to problems in separating the transesterification products.
- (iii) At higher molar ratio a large amount of alcohol is present in the transesterified products, i.e., biodiesel and glycerin. A large amount of energy is spent in distilling the products.

4 Proposed Industrial Production Process

Based on the experimental findings (optimum conditions) a process for large-scale production has been designed (Figure 7). Following are the different steps to be followed:

Purification — Crushing of oilseed is common method of extracting oil. Raw Karanja oil contains a lot of impurities that cannot be transesterified to alkyl esters. These impurities hinder in the reaction, hence need to be removed. Filtration is used for purification (removal of unwanted particles and gums) of karanja oil.

Neutralization — The presence of large quantity of free fatty acids makes karanja oil inappropriate for industrial biodiesel production. Neutralization converts free fatty acids present in alkyl esters. Acid (such as H_2SO_4) can be used for this purpose. After purification and neutralization a conversion of .95-.98 is achievable.

Mixing Alcohol and Catalyst — The catalyst used is typically sodium hydroxide (caustic soda) or potassium hydroxide (potash). It is dissolved in the alcohol using a standard agitator or mixer.

Reaction — The mixture of alcohol and catalyst is then charged to a closed reaction vessel containing Karanja oil at about 70 °C. Reaction temperature is maintained at boiling point of the mixture, as rate of reaction is directly proportional to temperature. To prevent any loss of alcohol, condenser is attached to the reactor, which condenses the vapors of alcohol and refluxes it back to the reactor. Recommended reaction time vary from 30-45 min. Excess alcohol is normally used to ensure total conversion of the vegetable oil to its esters.

Sl No	1	2	3	4	5	6	7
Reactant ratio	3.00	5.36	8.02	10.91	13.41	18.77	26.95
Conversion	0.75	0.84	0.88	0.88	0.89	0.89	0.89

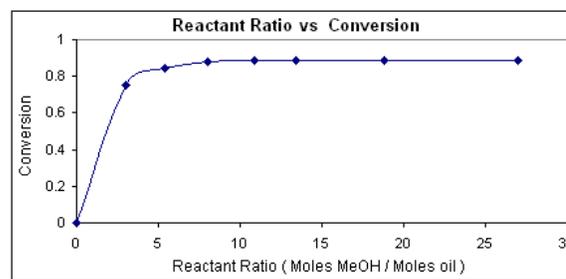


Figure 7 — Plot of reactant ratio vs. conversion

Amount of free fatty acid and water in the incoming oil should be controlled. If the free fatty acid level or water level is too high, it may cause problems with soap formation (saponification of free fatty acid) and the separation of the glycerin by-product.

Separation — Once the reaction is complete, the mixture gets divided into two separate layers one constituting of biodiesel while other constitutes of glycerin. The biodiesel layer is less dense and thus can be separated out using centrifuge or bubbling air method.

Alcohol Recovery/Removal — Both the phases obtained contain excess alcohol. It is removed with a flash evaporation process or by distillation. The alcohol recovered is reused in the process. Every care must be taken to ensure no water accumulates in the recovered alcohol stream.

Glycerin Neutralization — The lower layer contains glycerin, unused catalyst, alcohol and soaps. Removal of water and alcohol gives 80-85 per cent glycerin, which can be sold as crude glycerin. For further purification distillation of crude glycerin can be done. The salts obtained could be used for fertilizers.

Methyl Ester Wash — Biodiesel obtained from the upper layer contains traces of catalyst and soap. These can be removed by gently washing it with warm water.

Important aspects of biodiesel production to ensure trouble-free operation in diesel engines are (Table 3):

- Complete reaction.
- Removal of glycerin.
- Removal of catalyst.
- Removal of alcohol.
- Absence of free fatty acids.

5 Engine Performance

5.1 Calorific Value

Calorific value is one of the most important parameter while selecting a fuel.

Calorific value of biodiesel – 39656 kJ/kg

Calorific value of diesel – 43405 kJ/kg

Heat content of the biodiesel obtained from Karanja oil is nearly 90 per cent that of diesel. All the experiments were conducted with the help of colleague at Mechanical Engineering Department of Indian Institute of Technology, Delhi.

5.2 Brake Thermal Efficiency

Brake thermal efficiency is the ratio of energy in brake power to the input fuel energy in appropriate unit.

$BTPH = bp / \text{mass of fuel} * \text{calorific value.}$

In modern engines thermal efficiency of almost 28 per cent is obtainable with gas and gasoline spark ignition engine.

Table 3 — Standard for biodiesel.

Fuel properties	Unit	DIN 51606 specification	US ASTM specification
Flash point	°C	100 min	100 min
Density at 15 °C	kg/m ³	—	860-900
Water and sediment	Vol per cent	—	0.050 max
Carbon residue	Wt per cent	0.30 max	0.05 max
Sulphated ash	Wt per cent	—	0.020 max
Viscosity @ 40°C	cSt	3.5 – 5.0	1.9 – 6.5
Kinematic viscosity @ 40°C	m ² /s	—	(3.5-5.0)*10 ⁻⁶
Sulfur	Wt. per cent	0.01 max	0.05 max
Cetane	—	49 min	40 min
Cloud point	°C	—	3°C
Copper corrosion	—	1 max	3B max
Total acid number	Mg KOH/g	0.50 max	0.80 max
Free glycerin	Wt per cent	0.02 max	0.02 max
Total glycerin	Wt per cent	0.25 max	0.24 max
Cold filter plugging point	°C	—	Summer max 0 Winter max < -15

Figure 8 gives comparison of BTPH for IC engines when diesel and biodiesel are used as fuel.

5.3 Exhaust Emissions

In this section the emission of carbon monoxide (CO), unburnt hydrocarbon (HC), nitrogen compound (NOx), oxygen in exhaust and smoke opacity for biodiesel and diesel are shown (Figures 9-15). In general the biodiesel is found superior to diesel fuel (for IC engines). Opacity of the smoke emitted, with biodiesel as fuel was lesser than diesel fuel.

5.4 Smoke Number

Smoke number, also called the Bosch or Bacharach smoke number, is the number obtained by comparing the soot (the black carbon portion of diesel

exhaust particulate matter) spot on a filter paper to a gray scale that ranges from white to black in unit steps. The Bosch smoke number was significantly reduced when diesel engine was fueled with biodiesel.

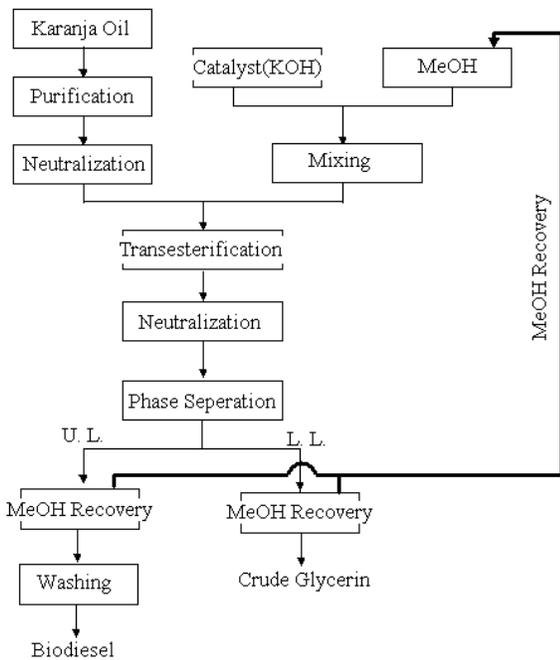


Figure 8 — Industrial process for production of biodiesel from karanja oil.

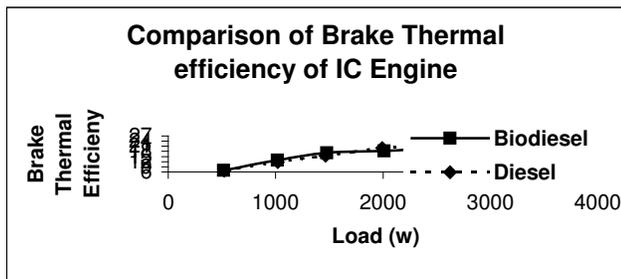


Figure 9 — Brake thermal efficiency vs load (W) for biodiesel and diesel

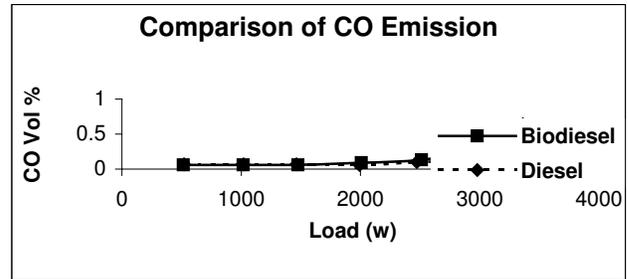


Figure 10 — Carbon monoxide emission (ppm) vs load (W) for biodiesel and diesel

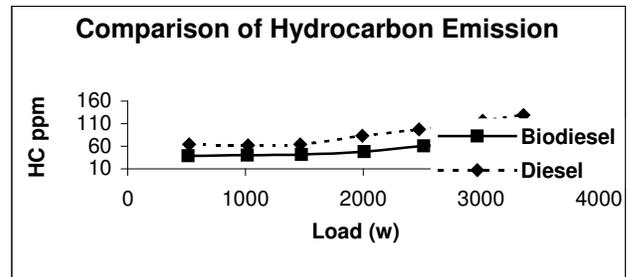


Figure 11 — Hydrocarbon emission (ppm) vs. load (W) for biodiesel and diesel

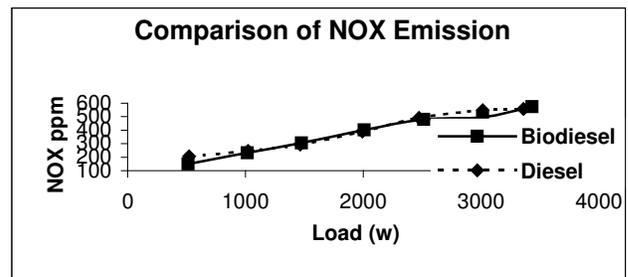


Figure 12 — Sulphur oxide compounds (SOx) emission (ppm) vs load (W) for biodiesel and diesel

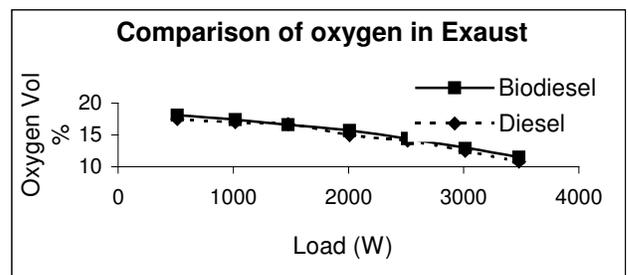


Figure 13 — Oxygen in exhaust vol per cent vs load (W) for biodiesel and diesel

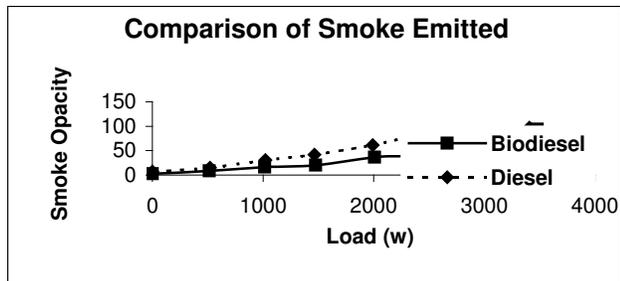


Figure 14 — Smoke opacity vs load (W) for biodiesel and diesel

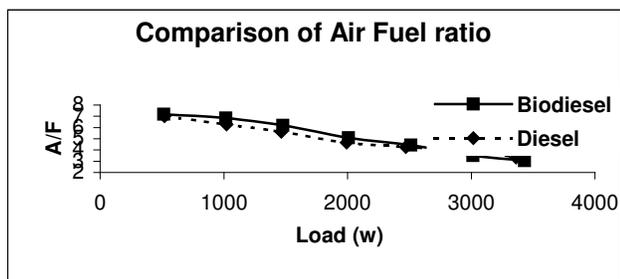


Figure 15 — Air fuel ratio vs. load (W) for biodiesel and diesel

5.5 Conclusions of the Engine Performance (Biodiesel vs Diesel)

- (i) The engine performance for biodiesel is similar to that of diesel with nearly same thermal efficiency, but with higher fuel consumption due to lower energy content/calorific value.
- (ii) Biodiesel produces lower CO emissions. It reduces CO emission 20 – 30 per cent that of diesel fuel all load engine conditions. Also the unburnt hydrocarbon and NO_x emissions are reduced.

6 Conclusions

The study has enabled us to confirm that Karanja oil can be used as a raw material to obtain

biodiesel, which can be used as fuel in diesel engine. The engine performance with biodiesel is similar to that of diesel, while emissions are less in the case of biodiesel.

Optimum parameters for high conversion are:

Pressure 1 atmos, Temperature 68-70 °C, Reactant ratio 8-10 (Moles of MeOH: Moles of oil), Reaction time 30-40 min; Catalyst (KOH) 1.5 per cent w/w.

There are two aspects of the cost of biodiesel (i) Cost of raw material (vegetable oil) and (ii) Cost of processing. The cost of raw material (vegetable oil) accounts to 60-70 per cent of the cost of biodiesel fuel. Using non-edible oil like Karanja oil (in place of vegetable oil) will surely improve the economics of the process (Biodiesel production)

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