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# Optimization of Karanja oil transesterification

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Production of biodiesel through transesterification of Karanja (*Pongamia pinnata*) oil was studied. The Karanja oil was treated with a lower alcohol (methanol) in the presence of a base catalyst (KOH) to yield methyl esters of fatty acids (biodiesel) and glycerin. The influences of reaction temperature, molar ratio of alcohol to oil, amount of catalyst and reaction time on the product yield were studied. The optimal combination of operating parameters for maximum yield was found out using Taguchi's method. The performance and emission tests were carried out in a four stroke single cylinder, Kirloskar AV1 D.I.Engine. Different blends of biodiesel with conventional diesel were tested. The results show an appreciable reduction in emission level and marginal increase in performance when compared with sole fuel. The results concluded that the biodiesel from Karanja oil can be used as an effective alternate in existing diesel engines without any engine hardware modifications.

**Keywords:** Biodiesel, Karanja oil, Transesterification
**IPC Code:** C11C3/02

Increased environmental concerns, tougher clean air act standards and depletion of fossil fuels, necessitate the search for a viable alternative fuel, which is more environment-friendly. Vegetable oils are by far the largest group of exploitable renewable biomass resource for liquid fuels and energy generation. Given the potential of vegetable oils as an alternative fuel, different nations, depending on their unique climate and soil conditions, are exploring variety of vegetable oils for diesel fuel applications.

Vegetable oils are usually triglycerides with number of branched chains of different length. They have nearly 10% lower heating value and several times higher viscosity compared to diesel oil. The high viscosity of vegetable oils (35-200 cSt at 40°C) as compared to diesel oil (4 cSt at 40°C) leads to unfavourable pumping and spray characteristics (atomization and jet penetration etc.). The inefficient mixing of fuel with air contributes to incomplete combustion. The polyunsaturated nature of the vegetable oils causes high viscosity, the combination of high viscosity and high flash point due to lower volatility results in increased carbon deposit formation, injector coking, piston ring sticking, longer ignition delay, lubrication oil dilution and degradation[1]. Because of these problems, vegetable oils need to be converted to more compatible fuels for existing engines. Transesterification has emerged as the most viable and effective method for the purpose.

Transesterification is the reversible reaction of a fat or oil (mainly glycerides) with an alcohol to form esters and glycerol. The reaction yields esters with viscosity and volatility characteristics similar to diesel. The biodiesel thus produced is biodegradable, non-toxic and free from sulphur. The biodiesel is quite similar to conventional diesel fuel in most characteristics and can be blended in any proportion with petroleum diesel to create a biodiesel blend.

A catalyst is usually used to improve the transesterification reaction rate and yield. Alkalis, acids, or enzymes[2] can catalyze the reaction. Recently several heterogeneous catalysts such as synthesized microporus zirconia, sulphated zirconia, titania based zeolite were also tested as potential catalysts[3]. For transesterification, alkali catalysts are preferred due to their faster esterification action and less corrosive nature. Commercially alkaline catalyst is used in the concentration range of 0.4 to 1% by weight for 94 to 99% conversion of vegetable oil into esters. To shift the transesterification reaction in forward direction, it is preferred to remove one of the products from the reaction mixture. Excess alcohol is used to shift the equilibrium to the product side. A molar ratio of 6:1 (alcohol to oil) is normally used[4] in industrial processes to obtain methyl ester yields higher than

98% by weight. The maximum yield of esters occurs at temperatures ranging from 60-80°C.

The conversion rate has been observed to increase with reaction time. Freedman and Pryde[5] transesterified peanut, cottonseed, sunflower and soybean oils using methanol, oil ratio of 6:1 and 0.5% of sodium methoxide catalyst at 60°C. An approximate yield of 80% was observed after 1 min for soybean and sunflower oils. After 1 h, the conversions were almost the same for all four oils (93-98%). Since, for an alkali catalyzed transesterification, as the presence of water may lead to saponification reaction[6], the triglycerides and alcohol must be substantially anhydrous. The soap formation lowers the yield of esters and renders the separation of ester and glycerol and the water washing of esters difficult. After transesterification, glycerol is removed from esters by gravity separation. Hot water washing is employed for separation of catalyst from the esters. Moisture can then be removed using silica gel.

Starting materials used for alkali catalyzed transesterification must meet certain specifications. The glyceride should have an acid value less than 1 and should be substantially anhydrous. If the acid value is greater than 1, more NaOH is required to neutralize the free fatty acid. Presence of water causes soap formation, which consumes the catalyst and reduces catalyst efficiency. The resulting soap causes an increase in viscosity, formation of gels and makes the separation of glycerol difficult.

Due to the relatively high costs of edible oils, the cost of producing methyl or ethyl esters from edible oils is currently more expensive than hydrocarbon-based diesel fuels. The cost of biodiesel can be reduced if one can consider non-edible oils, spent vegetable oils[7] and used-frying oils instead of edible oils. Non-edible oils from plants such as Neem, Mahua, Karanja, Babassu, Jatropha, etc. are easily available in many parts of the world and are less expensive as compared to edible oils. Among these plants, Karanja[8] can be considered as one of the less exploited and highly potent biodiesel source.

The ornamental, fire wood and non-edible oil source Karanja is a medium sized glabrous tree. It belongs to the family *Leguminoceae*. It is a hard tree borne oil seed. It grows under a wide range of agro climatic conditions. These trees reach adult height in 4 to 5 years. The yield of Karanja seeds is up to 90 kg. Presently Karanja oil is used in the manufacture of soaps, treatment of skin diseases, veterinary medicines, fuel for lamps, lubricant, water paint binder, pesticide, in leather industries for tanning and finishing. Karanja oil has the following characteristics: density, 0.92 g/cc; acid value, 5.06 mg KOH/g; saponification value, 187 mg KOH/g; iodine value, 86.5 $I_2$/100g and unsaponifiable matter, 2.6% (*w/w*).

The present work discusses the feasibility of transesterification of Karanja oil, from the point of view of the process technology and its use in diesel engines. The influence of process variables on product yield of the transesterification process has also been studied.

## Experimental Procedure

Taguchi's Design of experiments[9] were carried out in 9 tests, in order to determine the operating conditions that maximize the biodiesel yield. For this experimental study, the following were identified as independent variables, and the numbers of levels were set which are- Low (1), Medium (2), and High (3):

- Amount of catalyst (A): 1-1.5-2.0 g
- Volume of methanol (B): 15-30-45 mL
- Temperature (C): 60-70-80°C
- Time (D): 45-60-75 min

As presence of moisture and free fatty acids always pose difficulties in transesterification and product separation, removal of these impurities from starting materials prior to transesterification process is necessary. So, this factor was excluded as variable and imparted as standard.

Transesterification was carried out in a batch stirred tank reactor with controlled heating and constant mixing. The ester or biodiesel produced during the reaction was separated from the fatty acid layer formed using gravity separation. Washing the esters with distilled water thrice, made the traces of soap and glycerin to get removed. Washing was done by adding approximately 15% by volume of distilled water to the methyl ester and shaking the contents slightly in the first two washings and shaking the contents vigorously in the third washing. After each washing, the contents were allowed to settle at least for 12 h and then separated. The methyl esters were little foggy and a clear liquid was obtained by slightly heating the ester layer. The clear methyl esters were then collected in beaker for further analysis.

Chemitto model GC-8610, with one packed column and one capillary column provision, with WICHROM software with data collector was used. The capillary glass column BPX-70 (equivalent to FFAP) was 30 mm long and 0.2 mm in internal diameter, the inner surface of which was coated with a layer of 50% cyanopropyl/50% methyl silicone. Nitrogen has been used as the carrier gas at a flow rate of 25 mL per min, with split ratio of 1:100. Hydrogen and oxygen were used for ignition purpose.

Specification of the engine

- Type : Kirloskar AV-1 engine
- Cylinder : Single, vertical, water cooled
- Stroke : Four
- Fuel used : Diesel
- Speed : 1500 rpm
- Power : 3.7 kW
- Bore : 80 mm
- Stroke : 110 mm

Loading device: DC Electrical Swing Field Dynamometer

## Results and Discussion

### Analysis of oil and biodiesel blends

Referring Table 1 the properties of 20% blend are highly comparable with unblended petroleum diesel than that of other blends and 100% biodiesel. The nominal increase in specific gravity results in better Specific Fuel Consumption, as the resistance to flow of fuel through spray nozzle of engine increases considerably due to the higher specific gravity.

Flash and fire points increase with increase in methyl ester content, in the case of 20% blend this in turn assures better storage and handling properties of the fuel. Due to higher specific gravity, understandably the cloud and pour points fall on the higher side.

The diesel index is slightly higher for 20% blend than unblended petroleum diesel. This leads to low hydrocarbon emission, less noise and reduced ignition delay of the engine.

The kinematic viscosity of 20% blend is quite comparable with unblended petroleum diesel. This signifies the low degree of the injector coking and carbon deposition inside the engine.

### Optimization

From Fig. 1, the optimum values of variables for better biodiesel yield are,

Amount of catalyst (KOH) : 1.5 g
Volume of methanol : 45 mL
Temperature : 80°C
Time : 60 min

From Fig. 2, it is clear that the variable temperature exhibits lesser variations during the experiments at all levels. So, the "Control Parameter is - Temperature" that influences the product. Since this parameter has less variations in S/N ratios at all levels, controlling or varying this parameter results in desired output.

Figure 3 shows the percentage contribution of independent variables, and it is clear that the volume of methanol (% Contribution 59.50) heavily

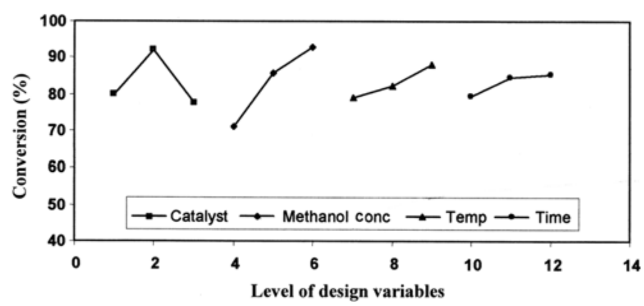


Fig. 1—Influence of design variables on product conversion

Table 1—Properties of petroleum diesel with biodiesel blends, biodiesel and Karanja oil

| Property | Unblended petroleum diesel | 20% Biodiesel blend | 40% Biodiesel blend | 100% Biodiesel | Karanja oil |
|---|---|---|---|---|---|
| Specific gravity | 0.83 | 0.84 | 0.85 | 0.9 | 0.94 |
| Flash point (°C) | 76 | 85 | 94 | 114 | 228 |
| Fire point (°C) | 78 | 88 | 97 | 122 | 235 |
| Cloud point (°C) | -10 | -2 | 1 | 5 | 9 |
| Pour point (°C) | -16 | -14 | -5 | -2 | 3 |
| Diesel index | 47.73 | 48.14 | 50.89 | 54.53 | 30.22 |
| Smoke point (mm) | 15 | 14 | 13 | 12 | 8 |
| Kinematic viscosity at 40°C $m^2/s$ | $3.06 \times 10^{-6}$ | $3.17 \times 10^{-6}$ | $3.87 \times 10^{-6}$ | $4.2 \times 10^{-6}$ | $7.3 \times 10^{-6}$ |

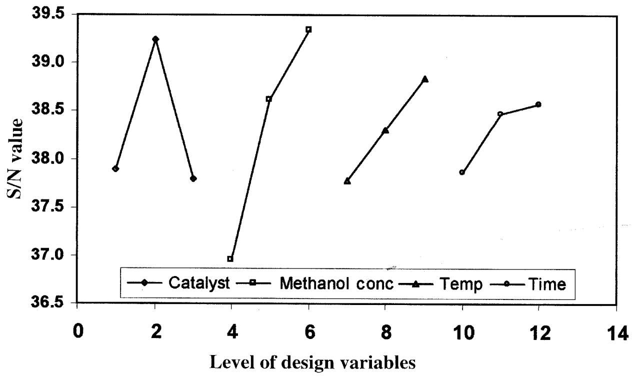


Fig. 2—S/N values for various levels of design variables

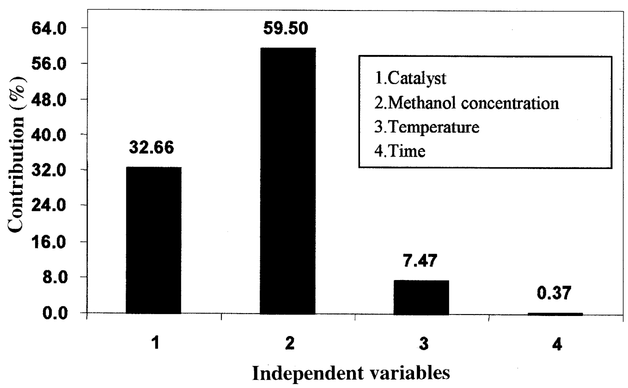


Fig. 3—Contribution of independent process variables on the product yield

influences the yield ahead of amount of catalyst (% Contribution 32.7). Other parameters affect the process very little towards the product yield. So, the "significant parameter is - volume of methanol". Controlling or varying this parameter during testing, will not result in the desired output.

#### Gas chromatograph

The biodiesel obtained using KOH as catalyst had the following composition of fatty acids: oleic, 50.74; linoleic, 18.72; palmitic, 9.83; stearic, 6.88; behanic: 5.62; linolenic: 3.67 and others, 4.53% (*w*/*w*).

#### Performance and emission characteristics

#### *Brake thermal efficiency*

From Fig. 4, it can be observed that the increase in brake power results in high fluctuation of BTE in the case of unblended petroleum diesel, this may due to the fluctuation in fuel power. Here the 20% blend shows better BTE than the others.

#### *Specific fuel consumption*

From Fig. 5, it is evident that the use of lesser biodiesel blends lowers Specific Fuel Consumption; this may be due to the higher viscosity of biodiesel than unblended diesel. Both 20% and 40% blends show better SFC than the 100% biodiesel. This suggests that only a nominal increase in viscosity helps to better SFC, and further increase leads to poorer SFC than unblended diesel.

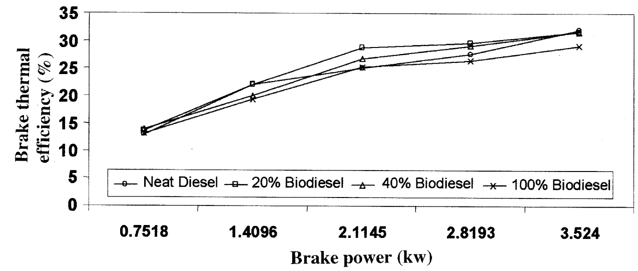


Fig. 4—Brake power versus Brake Thermal Efficiency

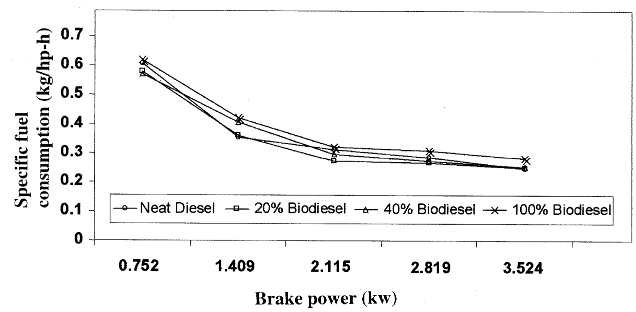


Fig. 5—Brake power versus Specific Fuel Consumption

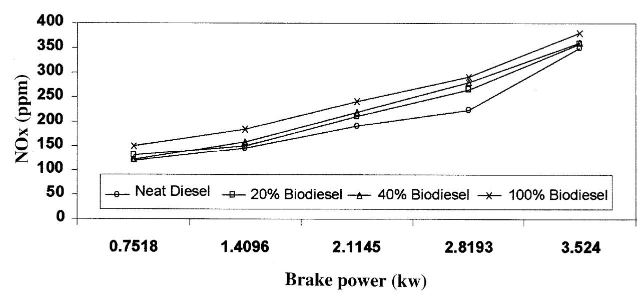


Fig. 6—Brake power versus NOx concentration

#### *Nitrogen oxides*

Figure 6 indicates that the biodiesel and its blends have higher NOx emission than unblended diesel. The increase in specific gravity leads to extended combustion time, which leads to high temperature, resulting in more NOx. Since the 20% blend has specific gravity value slightly higher than unblended diesel, it evolves less NOx than other blends.

#### *Particulate matter*

The exhaust gas contains solid carbon soot particles (particulate matter) that are generated in the

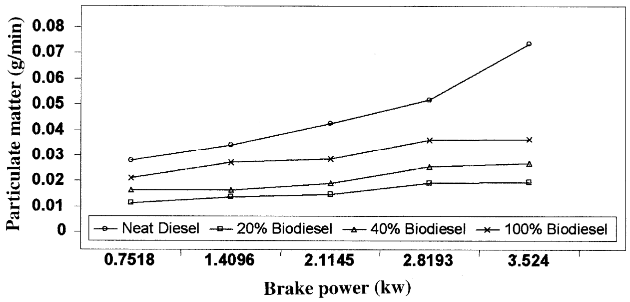


Fig. 7—Brake power versus particulate matter

fuel-rich zones leading to incomplete combustion within the cylinder. Figure 7, clearly distinguishes the progress in particulate matter emission between the blends. All the blends emit less when compared to unblended petroleum diesel. Again, the 20% blend exhibits the best results.

## Conclusion

Transesterification of Karanja oil has been carried out using KOH catalyst. The product and its blends were analyzed for their physical properties. Among them 20% Karanja oil methyl ester (KOME) was found highly comparable and even superior in many properties with un-blended petroleum diesel. The specific gravity, flash and fire points, cloud and pour points, kinematic viscosity were slightly higher than that of diesel, whereas the Diesel Index was much higher and the smoke point was slightly lower.

The process variables have been optimized using Taguchi's Technique. It was found that volume of methanol was the more significant parameter than that of amount of catalyst. The optimum parameters for using KOH as catalyst were; amount of catalyst 1.5 g, volume of methanol 45 mL, temperature 80°C and reaction time 60 min.

Among the blends 20% KOME showed better performance characteristics than others. It had better Brake Thermal Efficiency, Specific Fuel Consumption, and Indicated Thermal Efficiency. In the case of emission characteristics of 20% blend the oxides of nitrogen (NOx) were slightly more, understandably this was due to higher specific gravity of the fuel; particulate matter emission was least with lesser smoke density.

Finally, the experimental investigations revealed that,

- Diesel engines can perform satisfactorily on biodiesel derived from Karanja oil without any engine hardware modifications.
- Among the blends 20% Karanja oil transesterified biodiesel gave better engine performance and emission characteristics.
- Karanja oil should be considered seriously as an effective biodiesel source for the future.

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