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Studies on Transesterification of Non-Edible Vegetable Oils

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Abstract: *In present study, the production of fuel-quality bio-diesel from low-cost, high free fatty acid (FFA) feedstock's mainly Jatropha and Karanja oils was investigated. It was found that the feedstocks with high FFAs could not be transesterified with the commercially available alkali catalyst transesterification process. The reason is alkali catalysts react with the FFAs to form soap that prevents the separation of the glycerin and ester. A two-step transesterification process was observed to convert the high FFA oils to its esters. Influence of different process variables on the yield (%) of karanja and jatropha oil was studied under both the steps, i.e., effect of methanol to oil molar ratio and effect of acid catalyst on acid esterification and effect of different alkali catalysts (i.e., NaOH and KOH) on alkali transestefication. Temperature and reaction duration effects were also studied on both the steps. It was found that the yield (%) was strongly affected by molar ratio of alcohol to oil. Most of the fuel properties of karanja and jatropha methyl ester oil are quite comparable to those of ASTM bio-diesel standards and diesel. This two-step esterification method reduces the overall production cost of the bio-diesel, as it uses low cost unrefined non-edible oils. The results suggest that the two-step process combining acid esterification and alkali transesterification could be a feasible method for the production of high quality bio-diesel from high FFA non-edible vegetable oils.*

This paper discusses the various aspects of Transesterification of Karanja and Jatropha oil, Analysis for different fuel properties of Karanja and Jatropha methyl ester, Comparison of Karanja and Jatropha methyl esters with Diesel, Process parameter optimization of Karanja and Jatropha oil transesterification

Keywords: *Biodiesel, Transesterification, non-edible vegetable oil.*

1. INTRODUCTION

Today, the world is confronted with the twin crises of fossil fuel depletion and environmental degradation. In current scenario, Transport sector is the prime consumer of fossils fuels. Hence, the need for alternate energy for transport sector is becoming increasingly important due to diminishing petroleum reserves and the stringent environmental norms in recent years.

There is need for first marching step towards the journey for clean energy and sustainable fuel initiatives which are green, self-sustainable and environmental friendly. Also, it is necessary to draw up strategies for our country for the use of Biodiesel.

In India, attempts are being made for using non-edible and under-exploited oils for production of esters. The non-traditional seed oils available in the country, which can be exploited for this purpose, are Madhuca indica, Pongamia glabra, Mesua ferra (Linn), Garcinia indica, Jatropha curcas and Neem. Among these Jatropha curcas and Pongamia glabra (Karanja) are found to be suitable in our conditions [1-5]. The present work is concerned with the production of fuel-quality biodiesel from low-cost, high FFA feed stocks mainly Jatropha Curcas and Karanja oil.

1.1 DESCRIPTION OF BIODIESEL PRODUCTION

Transesterification (alcoholysis) is the chemical reaction between triglycerides (long and branched chain) and alcohol in the presence of catalyst to produce mono-esters and glycerin [6].

Brief of the process of transesterification in the laboratory

The unrefined oil was heated above 100°C. Its free fatty acid (FFA) content was determined by a standard titrimetry method [2]. FFAs were first converted to esters in a pretreatment process with methanol using an acid catalyst (i.e. H_2SO_4). The acid value of the product separated at the bottom was determined.The product having acid value less than 2 ± 0.25 mg

KOH/g was used for the main transesterification reaction.

Acid catalysis followed by alkali catalysis: The process consists of two steps namely, acid esterification and alkali transesterification [7,8]

(a) Acid esterification: Acid esterification reduces the FFA value of unrefined karanja oil to about 2% using acid catalyst.

$$\underset{\text{Ester}}{RCOOR^1} + \underset{\text{Alcohol}}{R^2OH} \xrightleftharpoons{\text{Catalyst}} \underset{\text{Ester}}{RCOOR^2} + \underset{\text{Alcohol}}{R^1OH}$$

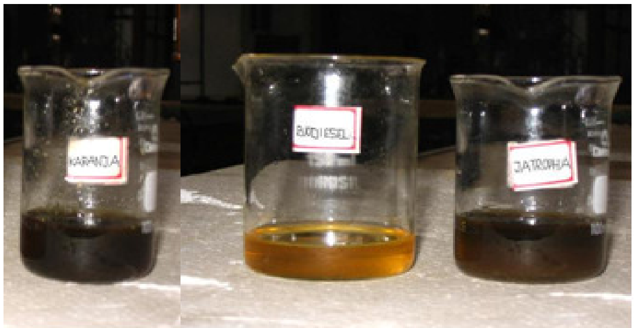
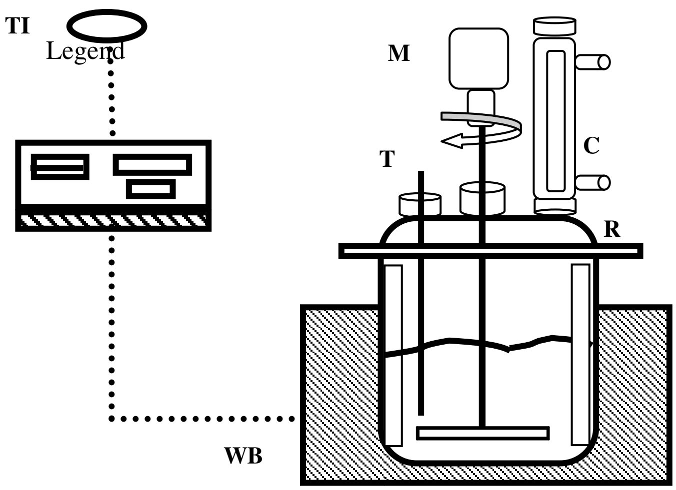


Fig. 1. Bio Diesel, Jatropha oil and Karanja oil

(b) Alkali transesterification: After removing the impurities of the product of first step, it is transesterified to monoesters of fatty acids using alkali catalyst. The parameters affecting the process are alcohol to oil molar ratio, catalyst amount, and reaction temperature and duration.

2. EXPERIMENTAL SET-UP

A round bottom flask and batch reactor set-up (Fig.3) is used to carry out transesterification reactions in the laboratory. A hot plate with magnetic stirrer arrangement is used for heating the mixture in the flask. The mixture is stirred at the same speed for all test runs.



TI: Temperature Indicator

WB: Water bath

R: Reactor with baffles

T: Thermometer

M: Motor

C: Reflux Condenser

Fig. 2. Schematic of experimental set up

3. RESULTS AND DISCUSSION

This include Analysis for acid esterification i.e., effect of Methanol to oil molar ratio, effect of acid catalyst concentration, then analysis for alkali transesterification ie., effect of methanol to oil molar ratio, effect of alkali catalyst concentration, effect of KOH and NaOH loading, effect of reaction duration and effect of reaction temperature.

The molar ratio of alcohol to vegetable oil affect the conversion as well as production cost of biodiesel. Effects of four different molar ratios were studied on the acid esterification. Theoretically, transesterification reaction requires three moles of alcohol for each mole of oil. However, in practice, the molar ratio should be higher than that of stoichiometric ratio in order to drive the reaction towards completion. That is, 96 g of methanol is required for 910 g of vegetable seed oil. Fig.4 and Fig.5 depict the effect of alcohol to oil molar ratio on the conversion of oil obtained in the first step (Acid Esterification).

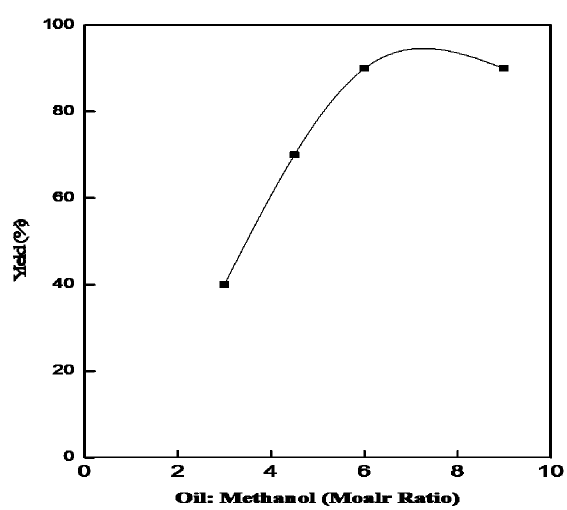


Fig. 3. Molar Ratio vs Yield for karanja oil-step1

Methanol to Oil molar ratio was varied for karanja and jatropha oil within the range of 3:1 to 9:1. The maximum ester conversions (%) for karanja and jatropha oils were found to be 80% and 90%, respectively at the molar ratio of 6:1(Methanol: Oil). With further increase in molar ratio there was only little improvement in the yield (%).

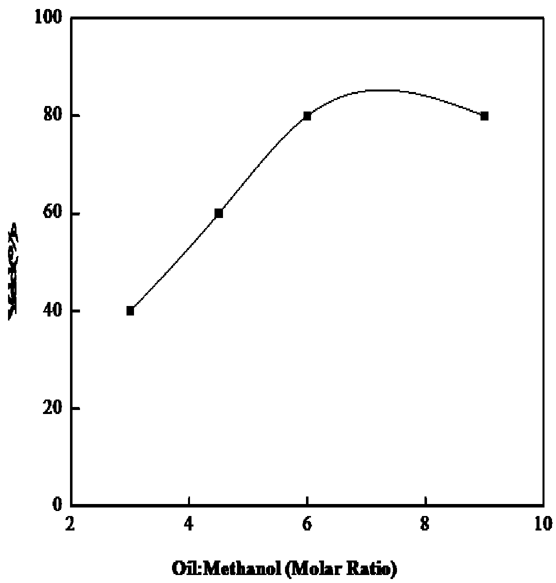


Fig. 4. Molar Ratio vs Yield for Jatropha Oil Step1

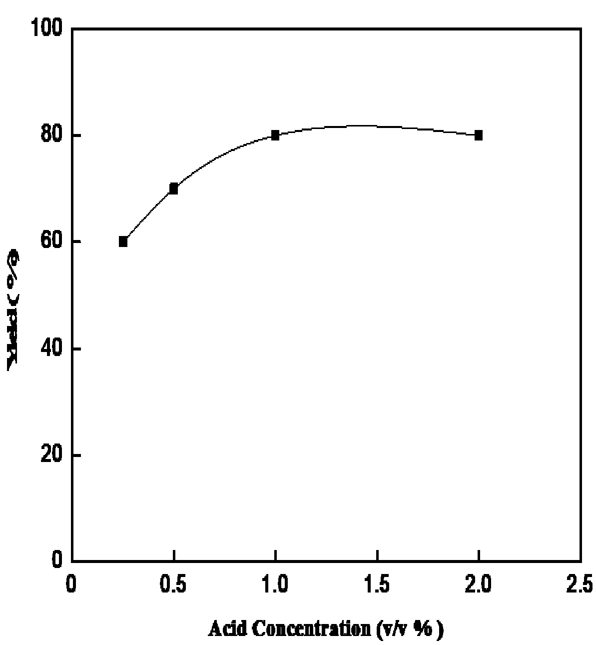


Fig. 5. Effect of catalyst (acid) concentration on yield (%) for karanja oil

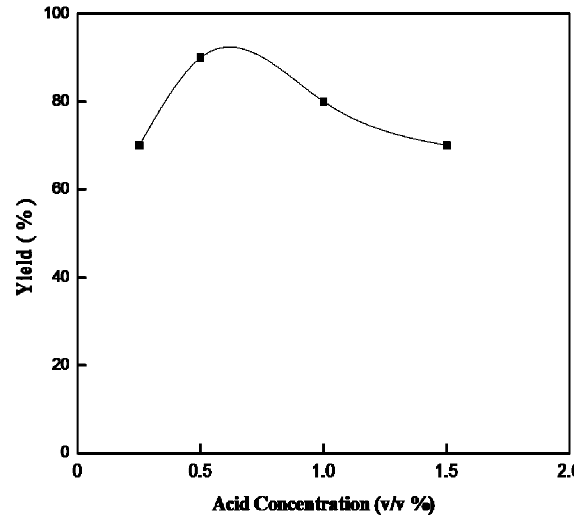


Fig. 6. Effect of catalyst (acid) concentration on Yield (%) for Jatropha Oil

The catalyst (i.e., sulphuric acid) amount was varied in the range of 0.25–2% (at four different values namely 0.25, 0.5, 1, and 2%) for karanja oil and for jatropha oil. It varied in range of 0.25-1.5%. The effect of catalyst amount on the yield (%) is shown in Fig.6 and Fig.7. It was observed during the present experiments that excess addition of sulphuric acid darkens the color of the product but yield (%) remains the same for karanja oil. However, smaller amount of sulphuric acid addition decreases the conversion (%) of the second step. For jatropha oil, it was observed that yield (%) was reduced after 0.5 %(v/v) catalyst concentration.

Stoichiometrically, the methanol: oil molar ratio required is 3:1. The effect of methanol to oil molar ratio on yield (%) is shown in Fig. 8 and in Fig 9. It has been seen that yield of the process increases with increase in methanol to oil molar ratio. The maximum yield for karanja and jatropha oil was obtained for the methanol to oil molar ratio of 9:1.

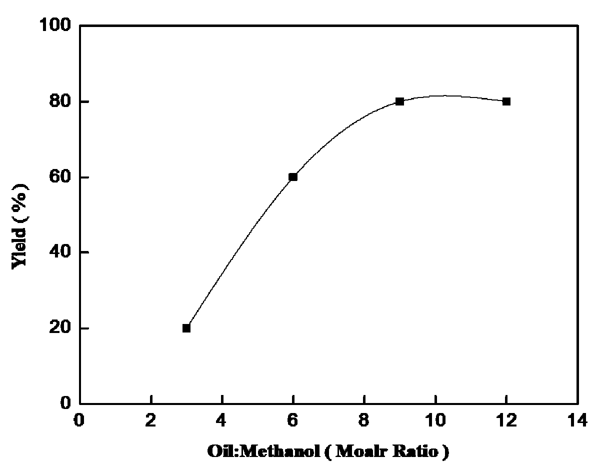


Fig. 7. Molar Ratio vs Yield for karanja oil-step2

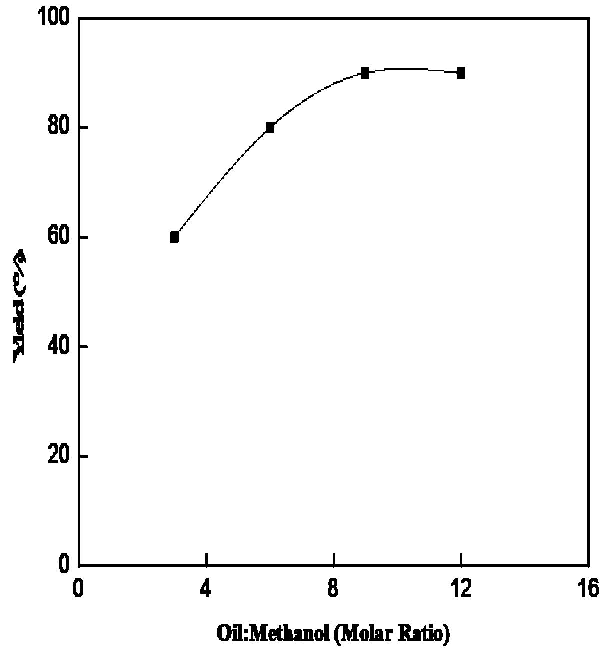


Fig. 8. Molar Ratio vs Yield for Jatropha Oil Step2

The effect of alkali catalyst was studied in the range of 0.3–1% (wt %) for karanja oil using NaOH as alkali catalyst and 0.5-2.5% (wt %) for jatropha oil using KOH as alkali catalyst. The effect of catalyst amount on yield (%) is shown in Fig. 10 and Fig 11. The maximum yield (%) was achieved for karanja and jatropha oil at 0.5% (wt %) and 2% (wt %) catalyst loading respectively.

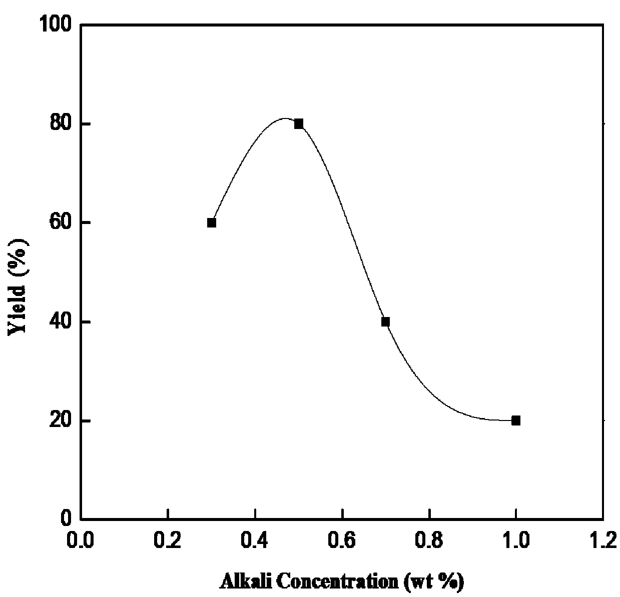


Fig. 9. Effect of alkali catalyst amount on yield (%) for karanja oil

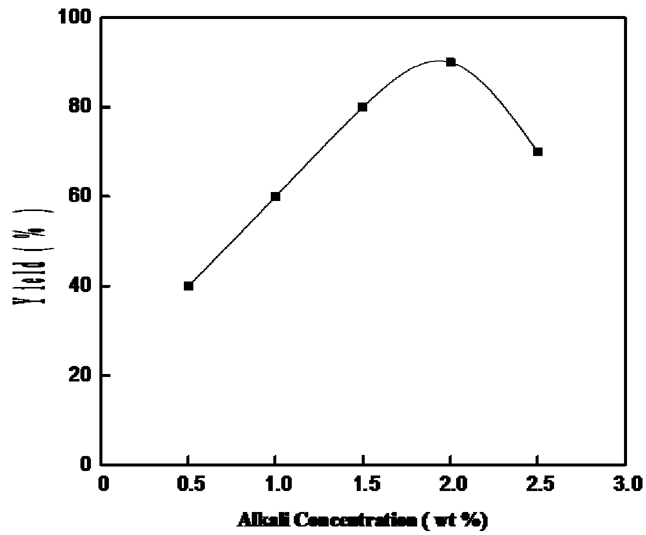


Fig. 10. Effect of alkali catalyst amount on yield (%) for jatropha oil

In order to achieve perfect contact between the reagents and the oil during transesterification, it must be stirred well at constant rate [9-11]. Observations showed 2 hours for acid esterification and 2 hours for alkali transesterification as sufficient for the completion of the reaction and for karanja oil, experiments revealed that, about 45 min for acid esterification and 30 min for alkali transesterification were enough for the completion of the reaction.

The reaction was conducted close to the boiling point of methanol. The maximum yield (%) was obtained at a temperature of 60°C for Karanja as well as for Jatropha oil as shown in Fig.12 and Fig.13. The decrease in yield (%) was observed when the reaction temperature went beyond 60°C because it tend to accelerate saponification of the glycerides by the alkali catalyst before completion of the alcoholysis and also, loss of methanol tend to lower the yield (%) at the end.

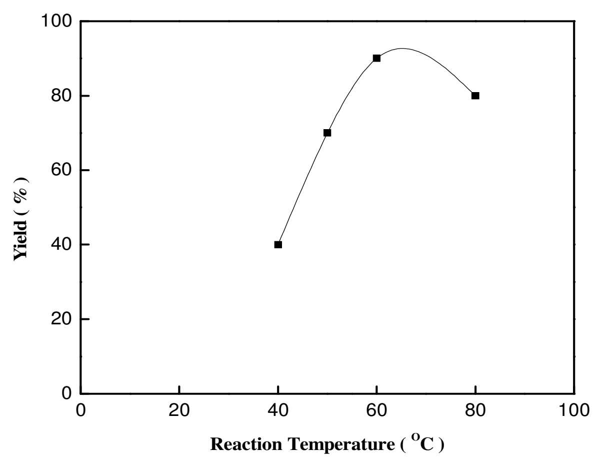


Fig. 11. Effect of temperature on yield (%) for Karanja oil

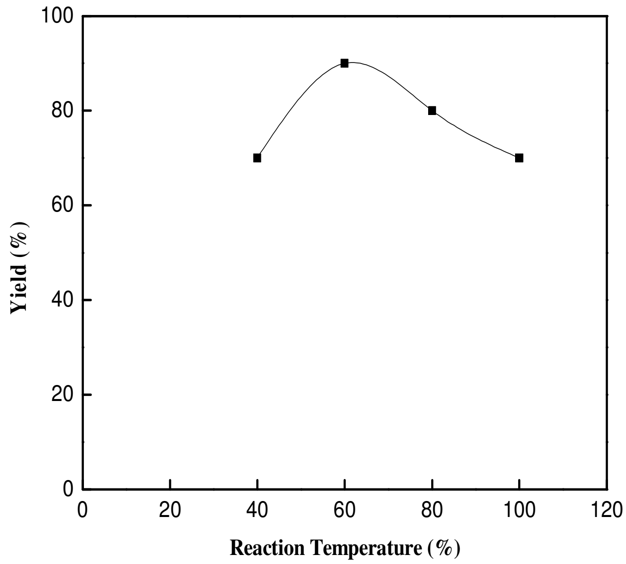


Fig. 12. Effect of temperature on yield (%) for Jatropha oil

3.1 CHARACTERIZATION OF PRODUCT BIODIESELS

3.1.1 PROPERTIES OF METHYL ESTERS OF KARANJA OIL

Large amount of methanol was observed to be required during both pretreatment steps to bring down the FFA content below 2%. However, this high consumption of methanol could be reduced in a commercial application by recovering part of it by fractional distillation of the water-mix that was separated from the top after each step. Also it is possible to further reduce the methanol consumption by continuous removal of water from the mixture during the reaction. As shown in Table 7, most of the fuel properties of karanja oil methyl ester are quite comparable to those of ASTM biodiesel standards and diesel [12]. The present results show that the transesterification process improved the fuel properties of the oil with respect to specific gravity, viscosity, flash point and acid value. The comparison of these properties with diesel shows that the methyl ester has a relatively closer fuel property values to that of diesel (than that of oil). The viscosity of biodiesel is closer to that of diesel. Hence, no hardware modifications are required for handling this fuel (biodiesel) in the existing engine. The calorific values of methyl esters are lower than that of diesel because of their oxygen content. The presence of oxygen in the biodiesel helps for complete combustion of fuel in the engine. The flash point of karanja oil is lowered by transesterification but it is still higher than that of diesel. A small percentage addition of biodiesel with diesel increases the flash point of diesel. Hence, it is safer to store biodiesel–diesel blends as compared to diesel alone. The properties of biodiesel are compared with ASTM biodiesel standards.

TABLE 1: Properties of methyl ester of karanja oil [13]

Properties	**Karanja oil**	**Karanja /NaOH**	**Karanja /KOH**	**ASTM (6751-02) Biodiesel standards**	**Diesel**
Specific Gravity	0.923	0.877-0.896	0.882-0.898	0.87-0.90	0.846
Kinematic Viscosity (mm^2/sec)	21.75	3.631-3.812	5.52-5.79	1.9-6.0	2.6
Cal Calorific Value (MJ/kg)	37.18	37.92-39.81	37.8-39.69	-----	42.21
Acid Value (mg KOH/g)	35.92	0.572-0.606	0.725-0.761	< 0.8	0.35
Flash Point (°C)	190	160-172	150-162	≥ 130	52
Aniline Point (°C)	48	80-87	70-76	-----	59.9
Cetane No.	28.58	45.88-47.82	41.68-42.91	47 min.	46
Diesel Index	25.81	49.83-52.52	44.01-45.71	-----	50
Pour Point (°C)	3.5	1 to 3	-1 to -3	-15 to 10	-20
Carbon Residue (%)	2	0.6	-----	-----	-----

NOTE: CONVERSION USING NAOH CATALYST: 80%, CONVERSION USING KOH CATALYST: 50%

3.1.2 PROPERTIES OF METHYL ESTERS OF JATROPHA OIL

The properties of product biodiesel from jatropha oil were determined at room temperature. A comparison of these properties with diesel is presented in Table 8. The methyl ester has a relatively closer fuel property values to that of diesel (than that of oil). The viscosity of biodiesel is closer to that of diesel. Hence, no hardware modifications are required for handling this fuel (biodiesel) in the existing engine. The calorific values of methyl esters are lower than that of diesel because of their oxygen content. The presence of oxygen in the biodiesel helps for complete combustion of fuel in the engine. The flash point of karanja oil is lowered by transesterification but it is still higher than that of diesel. Hence, it is safer to store biodiesel–diesel blends as compared to diesel alone. Pour point was found to vary between -6 to 2 ºC, which are found to be satisfactory but may create problem during winter season. Carbon residue in biodiesel is much lower which gives better engine performance and increased engine life. The properties of biodiesel are compared with ASTM biodiesel standards. Major difference lies between two methyl ester oil in their acid value, carbon residue and pour point. Comparison between Jatropha methyl ester and Karanja methyl ester shows that Jatropha methyl ester have good fuel properties which would give better engine performance and reduce engine exhaust emissions. Therefore, Jatropha Curcas oil has shown better potential as biodiesel production in India as well as worldwide.

TABLE 2: Summary of Properties

Properties	**Jatropha oil**	**Jatropha Methyl ester (KOH)**	**ASTM (6751-02) Biodiesel standards**	**Diesel**
Specific Gravity	0.912	0.868-0.884	0.87-0.90	0.846
Kinematic Viscosity (mm^2/sec)	20.5	2.355-2.472	1.9-6.0	2.6
Cal Calorific Value (MJ/kg)	37.07	39.65-41.63	-----	42.21
Acid Value (mg KOH/g)	28.15	0.6145-0.6652	< 0.8	0.35
Flash Point (°C)	225	175-189	≥ 130	52
Aniline Point (°C)	65	82-88	-----	59.9
Cetane No.	35.37	50.74-53.27	47 min.	46
Diesel Index	35.24	56.59-59.41	-----	50
Pour Point (°C)	1	-6 to 2	-15 to 10	-20
Carbon Residue (%)	0.4	0.2-0.22	-----	-----

Following are the main areas of concern for commercialization of biodiesel production -

1. Production cost of biodiesel due to non-availability of raw material, i.e., non-edible vegetable oil plants.
2. Viscosity of biodiesel - still it is higher than that of diesel, makes problem during blending.
3. Increase in percentage of NOx emission by 2 to 5 %.
4. Pour point is still higher than diesel, makes problem during winter, and lowers the engine life.
5. Biodiesel degrades the rubber.

4. CONCLUSIONS

A two-step transesterification process was developed to convert the high FFA oils to its esters. The first step (acid catalyzed esterification) reduced the FFA content of the oil to less than 2%. The alkali catalyzed transesterification process converted the products of the first step to its monoesters and glycerol. The properties of biodiesel produced from Karanja and Jatropha oil were compared with ASTM biodiesel standards and with diesel also. The viscosity of biodiesel was determined to be nearer to that of diesel. The flash point of biodiesel was greater than that of diesel and the calorific value was slightly lower than that of diesel. The two-step esterification method reduces the overall production cost of the biodiesel, as it uses low cost unrefined non-edible vegetable oils. Carbon residue content in biodiesel was much lower which gives better engine performance and increased engine life. Major differences lie between two methyl esters (of Karanja and Jatropha oils) in their acid values, carbon residues and pour points. The results of Karanja and Jatropha methyl esters suggested that the two step process, which combined acid esterification and alkali transesterification, could be feasible method for the production of high quality biodiesel from high FFA non-edible vegetable oils. Comparison between Jatropha methyl ester and Karanja methyl ester showed that Jatropha methyl ester has good fuel properties which would give better engine performance, better engine life and ultimately reduce engine exhaust emissions which are necessary to reduce pollution and to save environment. Thus Jatropha Curcas oil and Karanja oil has shown better potential as biodiesel production and as blend with conventional diesel and could be an environmentally benign solution for energy security and rural economy of India.

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5. FUTURE SCOPE OF WORK

It includes Kinetic study of jatropha and karanja oil transesterification to study and develop suitable catalyst which gives better yield with optimal performance. To study cost estimation of biodiesel production and To study the engine emmision characteristics for methyl esters of karanja and jatropha oils.

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