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# Production of Biodiesel from a mixture of Karanja and Linseed oils: Optimization of process parameters

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*A B S T R A C T*

Karanja and linseed are the potential non-edible oil crops which can be used for the biodiesel production. The main objective of this study is to find out the feasibility of using a mixture of karanja oil and linseed oil to produce biodiesel. Karanja oil has high amount of free fatty acid in it and linseed oil has low amount of free fatty acid content. Karanja biodiesel is produced by two step esterification/transesterification process which is costly, health hazardous & corrosive due to use of concentrated acids. Linseed biodiesel can be produced by alkali-base transesterfication which is much faster and gives higher yield than acid-base transesterification. A production method is developed to produce biodiesel from the mixture of karanja and linseed oil which is faster, safer and non-corrosive. The yields in the range of 68.2 to 78.9% have been achieved with varying different parameters like molar ratio, stirring time, mixture ratio and amount of catalyst. Optimum parameters are also established to achieve maximum biodiesel yield from the transesterification of a mixture of linseed and karanja oils.

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## INTRODUCTION

Biodiesel is considered as a carbon neutral fuel because all the carbon dioxide released during its combustion segregate from the atmosphere for the growth of biodiesel plants [1]. In developing countries, edible vegetable oils can not be used as fuel because it may cause starvation and other environmental problems by utilizing much of the arable land. Therefore, non-edible vegetable oils become more attractive for biodiesel production. Feedstock which contains free fatty acids and triglyceride such as vegetable oils, waste oils, animal fats and waste greases can be converted into biodiesel by transesterification process [2, 3]. Depending upon the various properties of feedstocks, the production processes may have their own advantages and disadvantages. Biodiesel is produced as fatty acid methyl esters from the transesterification process in vegetable oils and animal fats with methanol [4]

Karanja seeds contain 30-40% oil [5]. It belongs to nitrogen fixing trees [6]. Karanja tree is widely available because it can grow in humid as well as subtropical regions with annual rainfall ranging from 500 to 2500mm [7, 8]. Oleic (C18:1) and linoleic (C18:2) acids are the major fatty acids of karanja oil with oil content varies from 9 to 46% [9]. Karanja biodiesel has lower emissions, higher the cetane number, higher flash point temperature, lower sulfur content and lower calorific value as compared to diesel. It has good lubrication property, anti-knocking property, biodegradable, renewable and non-toxic [10].

It was also reported that the alkali catalyzed transesterification process cannot be used effectively for biodiesel production for high free Faty acid (FFA) feedstock like karanja oil [11]. Canakci and Gerpan informed that the oils having high FFA value like Karanja oil cannot be converted into biodiesel by the direct trasesterification process as it results in the formation of soaps causing reduction in conversion efficiency to a

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large extent. In this case, two step process, i.e esterification followed by transesterification is required [12].

Linseed seeds can yield from 33- 44% oil content under optimum conditions. Linseed oil has the disadvantage of low volatility and high viscosity due to the long chain structure [13]. It is available world wide. It is less water consuming crop for its growth as it is naturally grown [14]. Demirbas observed that Linseed oil has higher linolenic acid content in fatty acid compositions [15]. Linseed oil contains three double bonds linolenic (47.4%), two bonds Linoleic (24.1%) and one double bond oleic (19%) fatty acids [16]. Linseed oil contains 60% linolenic acid, which is the most unsaturated acids. This linolenic acid affects the drying property of oil to make it suitable for drying in alkyd paints [17]. The comparison of fatty acid composition of linseed oil and karanja oil are given in Table 1 [18]. Iyer informed the possibility of polymerization and oxidation for linseed biodiesel due to two double bonds between the reactive methylene groups in diesel engine when its temperature is $900^0$C in running condition [16].

Biodiesel can be produced from Linseed oil from the transesterification process by using methanol and potassium hydroxide as an alkali catalyst. After transesterification process, the viscosity of Linseed oil biodiesel decreases to a large extent. 88% yield of biodiesel was obtained using 20% methanol, 0.5% NaOH and $55^0$C reaction temperature [14].

**TABLE 1**: Comparison of fatty acid composition of karanja and linseed oil [18]

| S.N | Fatty acid | Linseed Oil (% wt) | Karanja Oil (% wt) |
|---|---|---|---|
| 1 | Myristic | 0.045 | 3.7-7.7 |
| 2 | Palmitic | 6.21 | 44.5-71.3 |
| 3 | Oleic | 20.17 | 2.4-8.9 |
| 4 | Stearic | 5.63 | 2.4-8.9 |
| 5 | Linoleic | 14.93 | 10.8-18.3 |
| 6 | Linolenic | 51.12 | 00 |

## General concept of mixing oils for biodiesel production

Mahua oil and Simarouba oil with FFA levels of 13 and 1.43%, respectively were mixed in equal proportions to reduce the consumption of methanol in the production of biodiesel. The FFA of mixed oil was observed at 7.19%. A two step process, an acid pretreatment followed by base transesterification was followed to bring down the FFA level at around 1% to produce biodiesel [19]. It was reported that dual biodiesel blends of Pongamia pinnata oil and mustard oil with diesel can be used in a single cylinder diesel engine. It was also found that calorific values of dual biodiesel blends with diesel were found to be close to diesel, which was more than single biodiesel blend with diesel [20].

It was mentioned that the use of blends of biodiesel could be an alternative to improve the oxidation stability of biodiesel instead of using antioxidants. It was stated that the composition of unsaturated fatty acids in oil was proportional to the oxidation instability of biodiesel and therefore, biodiesel blends of opposite properties (low and high content of unsaturated fatty acids) can be used to get a final biodiesel with improved oxidation stability [21]. Studies of blends of palm biodiesel with jatropha biodiesel had been carried out to cut the cost of antioxidants. It was also stated that palm biodiesel had good oxidation stability because of presence of saturated fatty acids causing resistance to autoxidation. It was concluded that when jatropha biodiesel blended with palm biodiesel, it gave a final biodiesel, which was having good oxidation stability and improved low temperature property. It was also stated that jatropha biodiesel had good low temperature properties as compared to palm biodiesel, which was having poor low temperature properties [22].

The yield of biodiesel obtained from the base catalyzed transesterification of mixtures of castor oil and soybean oil in the presence of ethanol increased as the proportion of castor oil decreased, but no significant substrate preference was observed. Ethanolysis of vegetable oil mixtures containing up to 25 wt% of castor oil yielded biodiesels that were more easily purified than those obtained from neat castor oil and hence, relatively high process yields could be obtained [23]. The major hurdles in the successful commercialization of biodiesel are high feedstock cost and conversion technology to reduce viscosity. The choice of raw material and biodiesel production method must depend upon techno-economical view. It is investigated that hybrid biofuels could be prepared from local crude vegetable oils i.e. Gmelina arborea Roxb (GAO), Mimusops elengi Linn (MEO), Acer laurinum Hasskarl (ALO), Thevetia peruviana Schum (TPO) and Mesua Ferrea Linn (MFO) which does not involve any chemical reaction thus reducing the production cost of biofuels [24]. It is also investigated that soapnut oil methyl esters (SNME) and jatropha oil methyl esters (JME) showed complimentary fuel properties and hence a blending ratio of 35:65 by weight of SNME-JME can improve high cold filter plugging point (CFPP) of SNME and poor oxidation stability of JME to satisfy all specifications of biodiesel[25]. Mixture of biodiesel blends of soybean (25%), canola (25%), palm (25%) with diesel (25%) were found to give acceptable fuel properties like kinematic viscosity 4.3mm$^2$/s, cetane number 53 and pour point -$4^0$C[26]. It was informed that biodiesel produced by two step acid transesterification from a mixture of karanja oils and jatropha oils can meet the requirements of diesel fuels in near future[27].

## MATERIAL AND METHODS

### Materials

The biodiesel was prepared from the mixture of oils of Karanja and linseed by alkali based transesterification. Different proportions of oils (50-50, 75-25 and 25-75%) have been taken to mix for biodiesel production. The biodiesels were produced by different molar ratio of 4.5:1 and 6:1 with change in the amount of KOH catalyst as 1, 1.5 and 2 g for every sample. The stirring time was also changed for these samples from 30 to 60 minutes and the yields of biodiesel were observed.

### Experimental Set Up & Alkali based Transesterification

Experiments were conducted in a 250ml glass vessel. Mixtures of karanja oil and linseed oil were taken and preheated to $110^0$C to remove any moisture content and then cool down to room temperature. Methanols were taken as per the molar ratio and mix with required amount of KOH catalyst and allow stirring at $50^0$C temperature till KOH dissolve completely. Now this methanol containing dissolved KOH mixed with 100ml mixed karanja and linseed oils and allow to stir for 30, 45 and 60 minutes at $60^0$C. After completion of reaction, it was cool and then allowed to settle down overnight. Next day, the upper layer of biodiesel was separated from lower layer of glycerol in a separating funnel. The biodiesel was water washed by hot water and then again, pure biodiesel were separated by physical separation method and the biodiesel was heated to $110^0$C to remove any moisture content. The biodiesel was weighed and the yields were estimated.

## RESULTS AND DISCUSSION

The various physico-chemical properties like specific gravity, density, kinematic viscosity and calorific value of raw oils and biodiesel produced from mixture of oils were determined by using ASTM methods and compared with diesel properties as shown in Table 2.

### Calorific value of fuels

The digital bomb calorimeter is used to determine the calorific value of fuels. The karanja oil and linseed oil have very low calorific value as compared to diesel. But, after transesterification, calorific values of biodiesel of mixture of these oils are found to be nearer to that of diesel. It varies in the range of 37.89 to 39.06 MJ/kg for biodiesel in the different mixing ratio of oils whereas it is 42.47 MJ/kg for diesel.

### Specific Gravity of fuels

Specific gravity of biodiesel is measured by precision hydrometer. The specific gravity of biodiesel of mixture of oils in different mixing ratio varies from 0.89 to 0.90 whereas for diesel it is 0.822.

### Viscosity of fuels

Redwood Viscometer is used to determine the kinematic viscosity. ASTM D0445 procedure is followed. The viscosity of karanja and linseed oil are very high as compared to diesel. Viscosity of Karanja oil and Linseed oil are found to be 27.32 and 29.2 cSt, respectively. The viscosities of mix oil biodiesel are reduced to a great extent by a transesterification reaction which varies in the range of 5.61 to 6.76 cSt whereas it is found to be 2.54 cSt for diesel.

### Effect of parameters for biodiesel production

The important factors which affect the quantity of biodiesel yield are oil to methanol molar ratio, quantity of catalyst used, time of reaction, and proportions of mixed oils.

### Effect of molar ratio (Methanol to oil ratio)

The molar ratio is one of the important factors which affect the yield of biodiesel. Effect of two different molar ratio of 4.5:1 and 6:1 are investigated in transesterification reaction. It is observed that maximum yields are obtained when molar ratio was 6:1 as compared to 4.5:1. The obtained data are shown in Figures 1 to 6.

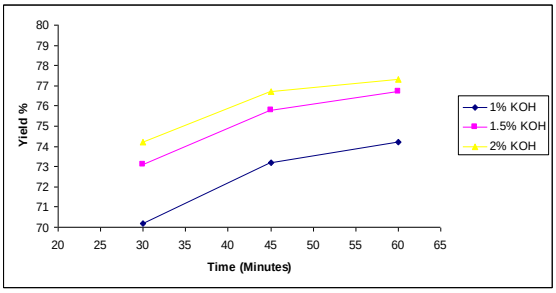


**Figure 1.** Effect of molar ratio 4.5:1 for biodiesel from mixture of 50% karanja and 50% linseed oil

### Effect of alkali catalyst concentration

The effect of alkali catalyst is investigated for 1, 1.5 and 2 wt% KOH with methanol to oil molar ratio of 4.5:1 and 6:1 at $60^0$C with different reaction time of 30, 45 and 60 minutes. It is observed that the biodiesel yields are found to be higher when 2% catalyst amount is used. Insufficient amount of catalyst does not give proper results during the transesterification reaction and higher amount of catalyst (more than 2 wt%) results in the saponification leading to decrease in yield. Obtained data are shown in Figures 1 to 6.

### Effect of reaction time

The effect of reaction time influences the quantity of biodiesel yield. It is observed that 60 minutes duration gives an optimum yield of biodiesel as compared to 30 and 45 minutes. Results are shown in Figures 1 to 6.

### Effect of proportions of oils for biodiesel production

It is also observed that a mixture of 75% linseed oil with 25% karanja oil give higher yield of biodiesel as compared to 50% each of linseed oil and karanja oil mixture and 25% linseed oil and 75% karanja oil mixture. It is shown in Figures 1 to 6.

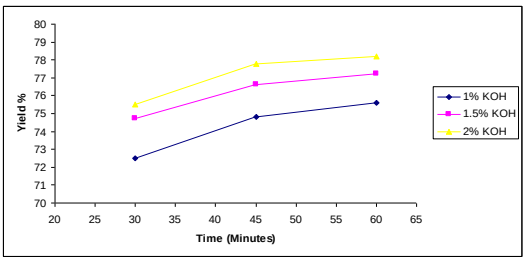


**Figure 2** Effect of molar ratio 6:1 for biodiesel from mixture of 50% karanja and 50% Linseed oil

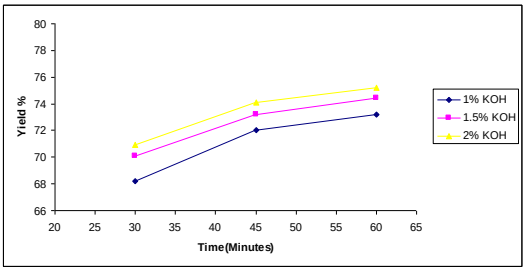


**Figure 3.** Effect of molar ratio 4.5:1 for biodiesel from mixture of 75% karanja and 25% linseed oil

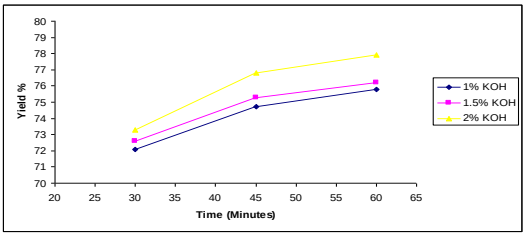


**Figure 4.** Effect of molar ratio 6:1 for biodiesel from mixture of 75% karanja and 25% linseed oil

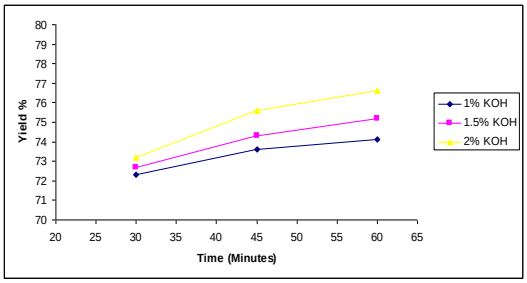


**Figure 5** Effect of molar ratio 4.5:1 for biodiesel from mixture of 25% karanja and 75% linseed oil

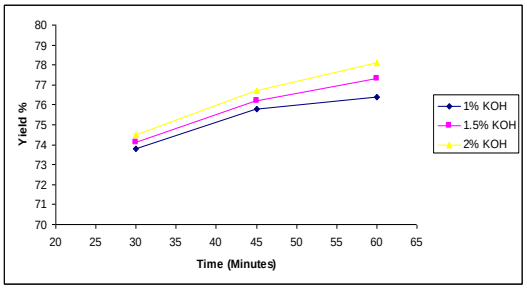


**Figure 6.** Effect of molar ratio 6:1 for biodiesel from mixture of 25% karanja and 75% linseed oil

## CONCLUSION

Karanja oil has high FFA content and, therefore, it requires two steps, acid esterification followed by an alkali catalyzed transesterification reaction which is costly and corrosive production method. Linseed oil has low FFA content and it can be converted into biodiesel by the alkali catalyzed transesterification reaction. An efficient biodiesel production method is developed by mixing proper proportion of karanja and linseed oils using the alkali catalyzed transesterification process.

This process is single step, simpler, safer, faster, non-corrosive and economically and therefore, it is very useful for biodiesel production from a mixture of non-

**TABLE 2**: Comparison of Physico-Chemical Properties

| S.N | Properties | KO | LO | D | A BD | B BD | C BD |
|---|---|---|---|---|---|---|---|
| 1 | Kinematic Viscosity cSt | 27.32 | 29.2 | 2.54 | 5.61 | 6.76 | 6.35 |
| 2 | Calorific Value MJ/kg | 34.12 | 30.6 | 42.47 | 37.89 | 38.53 | 39.06 |
| 7 | Specific Gravity | 0.913 | 0.9 | 0.822 | 0.8934 | 0.9001 | 0.8974 |
| 8 | Density kg/m$^3$ | 912.4 | 926.3 | 840 | 892.59 | 899.33 | 896.6 |

Abbreviations: KO: Karanja Oil, LO: Linseed Oil, D: Diesel, A BD: Biodiesel obtained from a mixture of 50%KO:50% LO, B BD: Biodiesel obtained from a mixture of 25%KO:75% LO, C BD: Biodiesel obtained from a mixture of 75%KO:25% LO

edible oils like karanja and linseed oils. The biodiesel yields are obtained in the range of 68.2 to 78.9%, which is satisfactory from the point of view of single step transesterification process. The following points may be concluded:-

1. Higher yield has been achieved with molar ratio of 6:1 in comparison to 4.5:1 molar ratio.
2. Higher yield has been achieved with 2 wt% KOH catalytic concentration in comparison to 1 wt% KOH and 1.5 wt% KOH catalytic concentration.
3. Higher yield has been achieved with 60 minutes reaction time in comparison to 30 and 45 minutes reaction time.
4. Higher yield has been achieved from mixing ratio of 75% linseed oil and 25% karanja oil in comparison to mixing ratio of 50% linseed oil and 50% karanja oil and 25% linseed oil and 75% karanja oil
5. Maximum yield of 78.9% has been achieved with a mixing ratio of 75% linseed oil and 25% karanja oil, 60 minutes reaction time, 6:1 molar ratio and 2 wt% catalytic concentration.

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**Persian Abstract**

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**چکیده**

کارانجا و بذر کتان محصولات روغن غیر خوراکی بالقوه هستند که می‌توانند برای تولید بیودیزل استفاده شوند. هدف اصلی این تحقیق یافتن امکان استفاده از مخلوط روغن کارانجا و روغن بذر کتان برای تولید بیودیزل است. روغن کارانجا مقادیر زیادی اسیدهای چرب آزاد دارد و روغن بذر کتان مقادیر کمی اسیدهای چرب آزاد دارد. بیودیزل کارانجا توسط دو مرحله استریفیکاسیون و ترنس استریفیکاسیون تولید می شود که بسیار هزینه بر، مضر برای سلامت و خورنده به علت استفاده از اسیدهای غلیظ است. بیودیزل بذر کتان می‌تواند با ترانس استریفیکاسیون قلیایی تولید شود که بسیار سریع‌تر و پربازده تر از ترانس استریفیکاسیون اسیدی است. یک روش تولید برای تولید بیودیزل از مخلوط روغن‌های کارانجا و بذر کتان که بسیار سریع‌تر، ایمن‌تر و غیر خورده است، گسترش یافته است. بازده‌ها در بازه‌ی ۶۸/۲ تا ۷۸/۹ ٪ با تغییر پارامترهای مختلف نظیر نسبت مولی، زمان چرخش، نسبت مخلوط و مقدار کاتالیست متغیر بود. شرایط بهینه برای رسیدن به بازده بالای بیودیزل از ترانس استریفیکاسیون مخلوط روغن‌های بذر کتان و کارانجا به دست آمد.