High Yield and Conversion of Biodiesel from a Nonedible Feedstock (*Pongamia pinnata*)

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An efficient approach has been adopted for the synthesis of biodiesel developed from karanja, a nonedible oil feedstock. A two-step reaction was followed for synthesis of biodiesel. Karanja oil possessing a high free fatty acid content was esterified with sulfuric acid, and the product obtained was further converted to fatty acid alkyl esters (biodiesel) by transesterification reactions. A moderate molar ratio of 6:1 (methanol/oil) was efficient for acid esterification with 1.5% v/v H_2SO_4 and 1 h of reaction time at 60 ± 0.5 °C, which resulted in reduction of FFA from 19.88 to 1.86 mg of KOH/g. During alkaline transesterification, 8:1 molar ratio (methanol/oil), 0.8 wt % sodium hydroxide (NaOH), 1.0 wt % sodium methoxide (CH_3ONa), or 1.0 wt % potassium hydroxide (KOH) as catalyst at 60 ± 0.5 °C gave optimized yield (90−95%) and high conversion (96−100%). Optimum times for alkaline transesterification were 45 min for CH_3ONa and 1 h for NaOH and KOH. Conversion of karanja oil feedstock to its respective fatty acid methyl esters was identified on a gas chromatograph−mass spectrometer and determined by ^{1}H nuclear magnetic resonance and gas chromatography. The fuel properties, such as cetane number of the methyl ester synthesized, were studied and found to be within the limits and specification of ASTM D 6751 and EN 14112 except for oxidation stability.

KEYWORDS: Biodiesel; transesterification; catalyst; methanol; nonedible feedstock

INTRODUCTION

Stringent environmental rules and legislation governing worldwide and recent awakening to the realization of dismal scenario of fossil fuel availability have led to the emergence of renewable fuels. Biodiesel, derived from locally available feedstock, has shown promise as an alternative to the depleting fossil reserves. In addition, being renewable, it also helps in curbing the now so-called notorious "carbon" and other harmful emissions in the form of hydrocarbons; particulate matter; benzene, toluene, ethylbenzene, xylene (BTEX); and other undesirable elements. Biodiesel has been developed from feedstocks ranging from a variety of edible and nonedible oils. Prominent edible oils that are being developed for biodiesel preparation are rapeseed, soybean, sunflower, canola, palm, and coconut oils (*1−9*). Those falling into the category of nonedible oils are mainly jatropha, karanja, mahua, polanga, sea mango, and others (*10−15*). The fruit of the trees (i.e., in form of seeds) is used to extract oil. As the oil extracted from karanja seeds is nonedible, its application becomes limited and is used in industries that pertain mainly to soap manufacture. The karanja tree grows naturally in many parts of the world including India, and the oil extracted from their seeds is economical, comparable to edible vegetable oils. Also, cultivation of these plants is easy as they can be grown even on wastelands. Karanja is a medium-sized tree found in all parts of India. The

plant has striking features: it is resistant to drought and has a high tolerance to salinity. The tree takes 4−7 years to mature. In a hectare, 1111 karanja trees can be planted with a spacing of 3 × 3 m. The yield of kernels per tree is reported between 8 and 24 kg. Each kernel contains one seed of karanja. Thirty-three percent of oil can be extracted from the seeds of karanja (*16*, *17*), so the amount of oil that can be harvested from a hectare of land will range between 2933 and 8799 kg. In Indian context, those plants that have been explored for biodiesel development are the ones whose oil extract is nonedible. The reason for this is that India is a developing nation and a net importer of edible oils and, hence, cannot afford any edible oil for biodiesel production. The commonly employed feedstocks for biodiesel synthesis at the research level in India are jatropha (*Jatropha curcas*), karanja (*Pongamia pinnata*), mahua (*Madhuca indica*), rubber (*Ficus elastica*), polanga (*Calophyllum inophyllum*), and others. Jatropha and karanja are particularly emphasized for biodiesel synthesis mainly because they contain toxicants and hence have limited applications. In Indian context, the National Policy on Biofuel has been prepared by the Ministry of New and Renewable Energy (MNRE), which is the body governing the usage of renewable energy resources. MNRE targets a 20% blending of biofuels such as bioethanol and biodiesel with the fossil-derived mineral fuel by 2017 (*18*). It thus becomes imperative to search for potential nonedible feedstocks and their suitability for biodiesel synthesis. The government of India has taken an initiative and has chosen jatropha and karanja for growth along railway tracks, which can

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Table 1. Fatty Acid Composition of *Pongamia pinnata*

fatty acid	systematic name	formula	structure	wt%
palmitic	hexadecanoic	$C_{16}H_{32}O_2$	16:0	8.9
stearic	octadecanoic	$C_{18}H_{36}O_2$	18:0	8.2
oleic	*cis*-9-octadecenoic	$C_{18}H_{34}O_2$	18:1	65.8
linoleic	*cis*-9,*cis*-12-octadecadienoic	$C_{18}H_{32}O_2$	18:2	12.1
arachidic	eicosanoic	$C_{20}H_{40}O_2$	20:0	0.9
gadoleic	11-eicosenoic	$C_{20}H_{38}O_2$	20:1	0.9
behenic	docosanoic	$C_{22}H_{44}O_2$	22:0	2.8
lignoceric	tetracosanoic	$C_{24}H_{48}O_2$	24:0	0.4

Table 2. Variation of Parameters before and after Reaction

	viscosity (cSt) at 40 °C	acid value (mg of KOH/g)	specific gravity
initial	26.88	19.88	0.911
after acid esterification	14.64	1.86	
after alkaline transesterification	5.44	0.44	0.886
ASTM Standard D6751	1.9−6.0	0.50	

be considered utilization of the land, and in the long run, these two plants can serve as potential sources for feedstock for biodiesel production.

Thus, these oils have drawn the attention of researchers for a possible biodiesel feedstock. Among them, karanja is also sought after owing to its limited usage and the presence of toxicants (*12*). The toxicants that make the karanja oil nonedible are furano-flavones, furanoflavonols, chremenoflavones, flavones, and fur-anodiketones. Its limited applicability is quite obvious. Its usage is reported to be just 6% of its potential, which amounts to 8000 million tones of 135,000 million tones (*19*). Initial work done by us has also been reported on the possible application of karanja oil as potential feedstock for the preparation of biodiesel (*12*). In continuation of the above work, further work has been carried out for high yield of biodiesel and optimization of parameters to obtain high yield and conversion to methyl esters. Further study will strengthen its applicability as a popular feedstock for biodiesel synthesis in the Indian scenario. Transesterification reaction was adopted for conversion of triglycerides to their respective esters and glycerol as a coproduct.

MATERIALS AND METHODS

Materials. *P. pinnata* seeds were procured from a rural area of Jharkhand state of India. Oil from the seeds was expelled in a mechanical expeller and thereafter in a Soxhlet extraction apparatus using cyclohexane as solvent. The method adopted was as given by Manirakiza et al. (*20*). Sodium methoxide (CH_3ONa) was purchased from Lobachemie, Mumbai, India. Sodium hydroxide (NaOH) and potassium hydroxide (KOH) were purchased from Qualigens Fine Chemicals, Mumbai, India. Synthesis grade methanol of ≥99% assay and ≤0.2% water content, orthophosphoric acid (85% pure), sodium sulfate dry purified, and sulfuric acid (H_2SO_4) 98% GR were procured from Merck Limited, Mumbai, India. Doubly distilled water was prepared in the laboratory.

Transesterification Reaction. Transesterification has been known to be the best available technology for conversion of oils to their respective esters (*21*). For alkaline transesterification to take place, the acid value of the feedstock should be lowered to a safe limit to avoid saponification reaction. The desired acid value of the feedstock is <2% for alkaline transesterification to take place (*22*). As karanja oil possesses a high amount of free fatty acids (FFA), a two-step reaction was carried out. The first step, called esterification reaction, was performed to lower the FFA to the desired limit (i.e., <2%). In the process, the FFA is converted to fatty acid methyl esters. Thereafter, alkaline transesterification was performed for conversion of oil with lowered acid value to fatty acid methyl esters. The reaction was carried out in a three-neck round-bottom flask fitted over a condenser with a thermometer in the side neck. A mechanical stirrer was inserted through the middle neck for thorough stirring. Two hundred grams of oil was taken for experimentation purpose. The oil was previously dried in a hot-air oven. Drying of oil was done until a constant weight was obtained. No change in the weight of oil was observed after 2 h at 105 °C and thus is considered optimum to remove the moisture content from karanja oil. One milliliter of H_2SO_4 was added to methanol (6 mol of that of oil) and then kept in the glass reactor over a heating mantle for reaction. The reactants were stirred continuously for 1 h duration at 600 rpm at 50 ± 0.5 °C. The temperature and rate of stirring were monitored continuously to maintain uniformity. After completion of the

acid esterification reaction, the products were kept over a separating funnel until separation of the oil, water, and unreacted methanol phase. The top layer comprised unreacted methanol, whereas the middle layer was oil and FAME (small amount obtained by conversion of free fatty acids to esters), and water at the bottom layer. Alkaline transesterification is feasible with low free fatty acid (i.e., <2%) content in the oil. Thus, after observation of the desired low acid value, alkaline transesterification was carried out with 1 wt % of the catalyst (either CH_3ONa, NaOH, or KOH) with methanol (6 mol of that of oil). Reactants were then stirred for 1 h in a mechanical stirrer over a heating mantle at 600 rpm at 50 ± 0.5 °C. After completion of transesterification reaction, the product was again kept in a separating funnel for separation. A distinct layer was formed separating glycerol with fatty acid methyl esters. Whereas glycerol settled at the bottom due to gravity, the fatty acid methyl esters formed by conversion of fatty acids to their respective esters occupied the topmost layer. Methanol that was left over after reaction emulsified in both the glycerol phase and ester phase. As methanol is soluble in water, it was removed from the ester phase by washing with water. Methanol dissolved in water was drained. Water left over in the biodiesel product was then removed by passage over anhydrous sodium sulfate.

Purification of Biodiesel. After completion of the reaction, the product obtained was kept in a separating funnel until separation of distinct layers of esters and glycerol. Glycerol, being dense compared to esters, settled at the bottom of the separating funnel. After removal of glycerol, the reaction was quenched with orthophosphoric acid. Temperature was brought to room temperature by applying ice to the outer surface of the separating funnel. The product was washed with doubly distilled water and dried over anhydrous sodium sulfate. Methanol was used as alcohol for esterification and transesterification because of its lower cost and shorter reaction time taken for completion of reaction as compared to ethanol (*23*).

Characterization of Biodiesel and Instrumentation Involved. Gas chromatography (GC) has been used for the determination of the fatty acid profile of the oil. The composition and constituents of fatty acids present in *P. pinnata* oil are shown in **Table 1**. The instrument GC (Perkin-Elmer XL Autosystem GC) was equipped with a FID detector with a 14 mL carrier packed column. The temperature was raised from 60 to 240 °C at 4 °C/min and held for 5 min.

The fatty acid methyl ester (biodiesel) identification was confirmed by gas chromatography−mass spectrometry (GC-MS) on a Shimadzu QP-2000 instrument at 70 eV and 250 °C. GC column configurations were as follows: ULBON HR-1 equivalent to OV-1, fused silica capillary (0.25 mm × 50 M) with film thickness of 0.25 μm. The initial temperature was 60 °C for 5 min and then raised at the rate of 5 °C/min to 250 °C. ^{1}H NMR performed on the instrument JEOL AL300 FTNMR has been used in the estimation of conversion of oil to fatty acid methyl esters using $CDCl_3$ as solvent at 300.40 MHz. Elemental analysis of the product was performed on a Universal CHNOS Elemental Analyzer Vario EL III.

Optimal conditions of parameters such as molar ratio, catalyst amount, and temperature were optimized to achieve maximum biodiesel yield. Important parameters such as viscosity, acid value (AV), and cetane number were determined as per ASTM D6751 standards.

RESULTS AND DISCUSSION

Parameters that influence the esterification and transesterification reaction are molar ratio, catalyst amount, temperature, and rate of stirring. These parameters were studied separately for acid esterification and alkaline transesterification reaction.
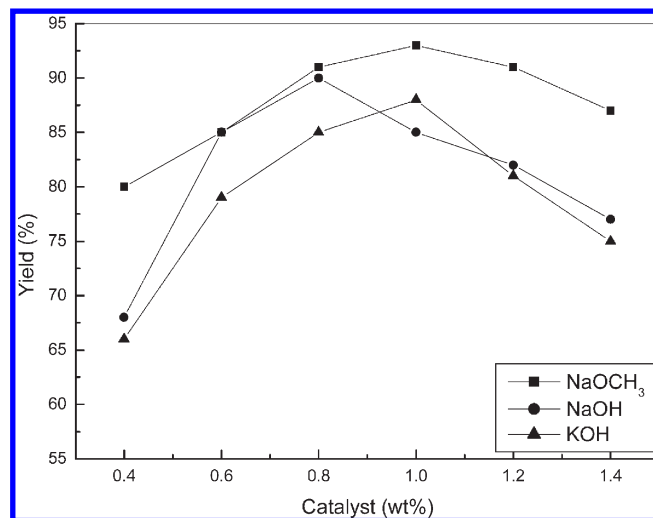
Optimization during Acid Esterification. The sole aim of esterification is to lower the acid value of the oil to a value within the

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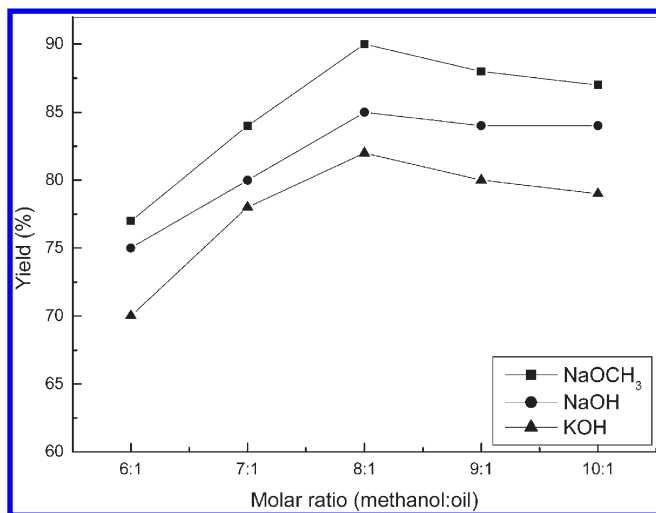
Figure 1. Effect of molar ratio during alkaline transesterification on yield (%) of karanja oil methyl esters. Catalyst amount, 1 wt %; temperature, 50 ± 0.5 °C; agitation speed, 600 rpm; reaction time, 1 h.

Figure 2. Effect of catalyst during alkaline transesterification on yield (%) of karanja oil methyl esters. Molar ratio, 8:1; temperature, 50 ± 0.5 °C; agitation speed, 600 rpm; reaction time, 1 h.

desired limit for alkaline transesterification. The stoichiometric ratio for esterification and transesterification reaction is just 3:1. However, as the reaction is reversible, a higher molar ratio is employed to move the reaction toward the formation of products. A minimum molar ratio of 6:1 is necessary for the reaction to achieve completion (*22*). Hence, various molar ratios of methanol to oil beginning with 6:1 and above (7:1, 8:1, 9:1, and 10:1) were tested. It was found that a 6:1 molar ratio was sufficient to lower the acid value. Further increase in molar ratio resulted only in generation of unreacted methanol, which is a well-known toxicant (although it is biodegradable in aerobic and anaerobic conditions) and should not be used beyond the required amount (*22–24*). This will also reduce the cost of biodiesel. Catalyst amount is another important parameter as it is responsible for esterification of FFA. The concentration of H_2SO_4 was varied from 0.5 to 2% (v/v ratio with oil). It was observed that the acid value reduced to just 10.88 mg of KOH/g with 0.5% of H_2SO_4, which further reduced to 5.80 with 1.3% of H_2SO_4; 1.5% H_2SO_4 lowered the FFA value from 19.88 to 1.86 mg of KOH/g, which later gave good conversion and yield of biodiesel on alkaline transesterification (**Table 2**). A temperature variation study was performed from 45 to 65 °C at intervals of 5 °C. It was found that 60 ± 0.5 °C, which is near the reflux of methanol, was an optimum temperature for maximum reduction of acid value. At 45 ± 0.5 °C, reduction in acid value was found to be 7.06 mg of KOH/g. The reduction was found to reduce further with increase in temperature. At 55 ± 0.5 °C, the value of FFA was 4.50 mg of KOH/g, which is still above the safe limit for transesterification reaction (i.e., 4 mg of KOH/g). Lower temperatures could not reduce the FFA to < 2%, and temperatures higher than 60 ± 0.5 °C showed no further reduction in FFA. Temperatures higher than 65 °C were not tried as the reflux of methanol is 64.7 °C. Rate of stirring was varied from 150 to 1200 rpm at intervals of 150 rpm; 600 rpm was found to be sufficient for thorough mixing of alcohol and oil. The same reduction of free fatty acid value (i.e., 1.86 mg of KOH/g) was observed with rpm in the range from 600 to 1200. Stirring at < 600 rpm could not reduce the FFA value to the desired limit. The 1 h of reaction time adopted was found to be adequate for reduction of acid value to the desired limit.
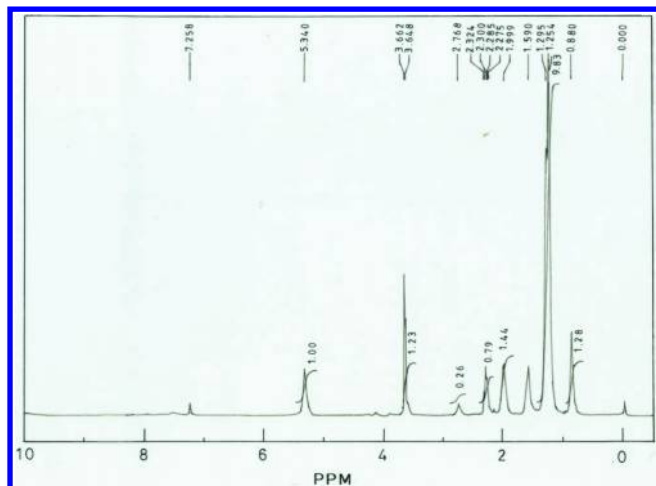
Optimization during Alkaline Transesterification. The aim of alkaline transesterification is conversion of triglycerides in the oil to their respective methyl esters and to obtain high yield of the product. Parameters to be optimized for alkaline transesterifica-
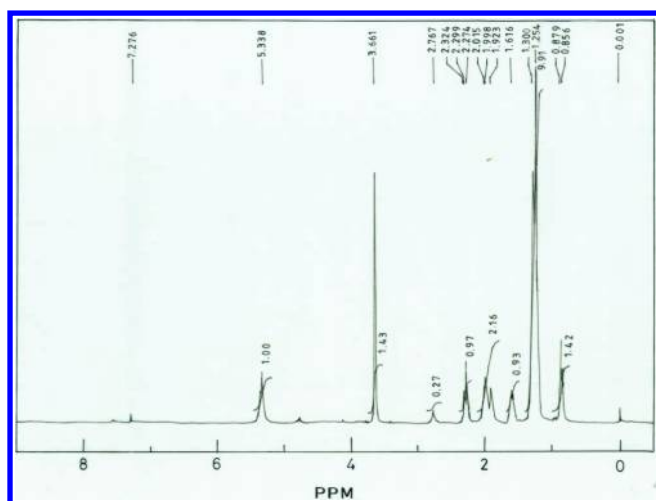
tion are the same as those of acid esterification. Optimization was followed in the sequence molar ratio, catalyst amount, temperature, and then rate of stirring (i.e., agitation speed). The three catalysts that were used for alkaline transesterification were CH_3ONa, NaOH, and KOH. Molar ratios employed during alkaline transesterification were 6:1, 7:1, 8:1, 9:1, 10:1, and 12:1. Of the different molar ratios tried, 8:1 molar ratio was observed to be optimum for high yield of biodiesel (**Figure 1**). The amount of catalyst was varied from 0.4 to 1.4 wt %. The amount of NaOH optimum for maximum yield was found to be 0.8 wt %. $NaOCH_3$ and KOH gave optimized yield with 1.0 wt % (**Figure 2**). The lower amount of NaOH than of KOH and $NaOCH_3$ for optimized conversion and yield is attributed to the lower molar mass of NaOH (40 g/mol) as compared to $NaOCH_3$ (54 g/mol) and KOH (56 g/mol) (*25*). $NaOCH_3$ has molar mass very near that of KOH and could be the reason the same quantity of catalyst was required for optimum yield. Although a lesser amount of NaOH was needed for the same yield and conversion of biodiesel, KOH was easily separable from the mixture owing to the soft nature of potassium soaps compared to sodium soaps. Also, KOH was found to be more easily soluble in methanol than NaOH. This finding is in accordance with Tremblay et al. (*26*). It is also suggested that the waste stream occurring from biodiesel purification while using KOH as catalyst may act as a fertilizer for soil due to potassium content (*26*). Similarly, $NaOCH_3$ was also easily soluble in methanol and separable from the fatty acid methyl ester synthesized. Less catalyst resulted in lower yield, whereas more catalyst could not increase the yield further but rather reduced the yield substantially (**Figure 2**). High catalyst amounts have caused side reaction "saponification" and might have rendered lowered yield. Temperature was varied from 45 ± 5 to 65 ± 5 °C at intervals of 5 °C. Yield gradually increased from increasing the temperature from 45 ± 5 to 60 ± 5 °C. Thereafter, a decrease in yield was observed when the temperature was increased to 65 ± 5 °C. Methanol has a boiling point near this temperature, and its loss may have resulted in lowered yield at this temperature. A temperature of 60 ± 0.5 °C was optimum for the best conversion and yield of biodiesel (**Figure 3**). Stirring rate was varied from 150 to 1200 rpm. A much lower yield at 150 rpm was observed, which increased on increase in agitation. The optimum yield was found to be at 600 rpm. Beyond this, no further increase in the yield was observed. As the oil and methanol are not miscible, they have to be brought in contact via agitation for

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Figure 3. Effect of temperature during alkaline transesterification on yield (%) of karanja oil methyl esters. Molar ratio, 8:1; catalyst amount, 0.8% for NaOH, 1.0% for NaOCH$_3$ and KOH; agitation speed, 600 rpm; reaction time, 1 h.

Figure 5. Effect of time during alkaline transesterification on yield (%) of karanja oil methyl esters. Molar ratio, 8:1; catalyst amount, 0.8% for NaOH, 1.0% for NaOCH$_3$ and KOH; reaction time, 1 h; temperature, 60 ± 0.5 °C; agitation speed, 600 rpm.

Figure 4. Effect of agitation intensity during alkaline transesterification on yield (%) of karanja oil methyl esters. Molar ratio, 8:1; catalyst amount, 0.8% for NaOH, 1.0% for NaOCH$_3$ and KOH; temperature, 60 ± 0.5 °C; agitation speed, 600 rpm; reaction time, 1 h.

the forward reaction to take place. At an agitation speed lower than 600 rpm, sufficient contact could not be established, resulting in a much lowered yield (**Figure 4**). Reaction time was varied from 30 to 90 min to optimize the reaction time for reaction. With NaOCH$_3$ as catalyst, optimum yield was achieved in 45 min, whereas 1 h of reaction time resulted in optimum yield of fatty acid methyl esters from karanja oil with NaOH and KOH as catalyst. Beyond this value, no significant increase in yield or conversion was observed (**Figure 5**). **Figure 5** thus depicts the maximum yield with the three catalysts after optimization of all parameters. Reduction in values of viscosity, acid value, and specific gravity after acid esterification and alkaline transesterification has been listed in **Table 2**.

Calculation of Conversion and Yield. The extent of the transesterification of karanja oil was determined by ^{1}H NMR spectroscopy. **Figure 6** depicts ^{1}H NMR spectroscopy of raw oil, whereas **Figures 7−9** depict the biodiesel developed from the raw oil with the catalysts KOH, NaOH, and NaOCH$_3$. Leadbeater and Stencel (*27*) reported the relevant signals chosen for integration

Figure 6. ^{1}H NMR of karanja oil.

Figure 7. ^{1}H NMR of fatty acid methyl ester derived from karanja oil with KOH as catalyst after transesterification.

were those of methoxy groups in the FAME (3.66 ppm, singlet) and those of the *R*-methylene protons present in all triglyceride

Figure 8. ^{1}H NMR of fatty acid methyl ester derived from karanja oil after transesterification with NaOH catalyst.

Figure 9. ^{1}H NMR of fatty acid methyl ester derived from karanja oil after transesterification with NaOCH$_3$ catalyst.

Table 3. Properties of Karanja Oil Methyl Esters

parameter	method	value	ASTM D 6751-08 limits
cetane no.	ASTM D613	57	min 47
cloud point (°C)	ASTM D2500	5	report
flash point (°C)	ASTM D93	158	min 130
ester content	EN14103	96–100	96.5
methanol (% vol)	EN14100	0.12	max 0.2
free glycerin (% mass)	ASTM D6584	0.01	max 0.02
total glycerin (% mass)	ASTM D6584	0.15	max 0.24
water and sediment (% vol)	ASTM D2709	0.035	max 0.050
oxidation stability (h)	EN 14112	2.33	min 3 h

Table 4. Elemental Analysis of Biodiesel

component	carbon	hydrogen	nitrogen	oxygen	sulfur
content (wt %)	75.44	12.62	0.10	11.94	<0.05

derivatives (2.3 ppm, triplet) of the soybean oil. Similarly, Knothe (28) also reported methyl ester protons to peak at 3.6 ppm and the protons on the carbons next to the glyceryl moiety (α-CH$_2$) to peak at 2.3 ppm. An equation given by Knothe (29) for calculation of methyl ester conversion is shown below.

$$\text{conversion } (\%) = 100 \times (2A_{ME}/3A_{\alpha\text{-CH2}}) \qquad (1)$$

C is the conversion percentage of triglycerides present in the feedstock to their respective methyl esters. $A_{ME}A_1$ is the integration value of the protons of the methyl esters, and $A_{\alpha\text{-CH2}}$ is the integration value of the methylene protons. A_{ME} appears at 3.7 ppm, whereas $A_{\alpha\text{-CH2}}$ appears at 2.3 ppm. Integration of the areas under these signals in the mentioned equation gives the methyl ester (biodiesel) conversion. Samios et al. (30) also discussed ^{1}H NMR results in their study with sunflower oil. Disappearance of the resonance signal between 4.22 and 4.42 ppm in the emergence of new signal is an indication of biodiesel formation. A similar result has been observed with our study (**Figures 7−9**). The peak obtained, which is indicative of ME (methyl ester), is obtained at 3.661, 3.648 and 3.662, and 3.661 with the catalysts KOH, NaOH, and NaOCH$_3$, respectively. The conversions as calculated by the above equation were found to be 96.8, 98.28, and 100% with KOH, NaOCH$_3$, and NaOH,

respectively. GC studies also revealed high conversion of fatty acids to their respective esters after identification with GC-MS. A high yield of 95% was obtained with NaOCH$_3$ as catalyst followed by NaOH (92%) and KOH (90%). The high yield obtained with NaOCH$_3$ has been attributed to its dissociation to Na$^+$ and CH$_3$O$^-$, whereas, in the case of NaOH and KOH as catalyst, water is formed when dissolved in methanol, resulting in the formation of water, which causes saponification in the transesterification reaction. This results in lowered yield with sodium and potassium hydroxide as compared to sodium methoxide (25).

Study of Properties of Karanja Oil Methyl Esters as Fuel. Various physical and chemical parameters of the biodiesel (karanja oil methyl esters) were characterized with methods ASTM D 6751 and EN 14112 and are listed in **Table 3**. Cetane number, which is an indicative of ignition delay time of the fuel upon injection into combustion chamber, was found to be 57, which is quite above the minimum value of 47 specified by ASTM standards. The cloud formation was observed at 5 °C, and flash point was 158 °C. A high flash point of biodiesel is an advantage as it becomes less dangerous during storage and transport. The ester content was observed to be between 96 and 100%, which is indicative of high conversion of the karanja oil feedstock to biodiesel. The EN standard reports the conversion to be, minimum, 96.5%. Methanol, free glycerine, total glycerine, water, and sediment were within the specified limit, and this confirms the suitability of the methyl esters synthesized to be used as fuel. The methyl esters developed could not fulfill the oxidation stability criteria, and was found to be 2.33 h. The EN 14112 specification warrants the oxidation stability to be, minimum, 3 h. This could be overcome by the addition of antioxidants. However, this might result in some additional cost of the biodiesel. Elemental analysis indicated the presence of carbon as a major constituent (75.44 wt %), with hydrogen and oxygen contents of 12.62 and 11.94%, respectively (**Table 4**). Nitrogen was present in a negligible amount of 0.10%, and sulfur content was observed to be < 0.05%.

In conclusion, biodiesel, a renewable source of energy, has been synthesized from an underutilized feedstock, that is, karanja. A high yield has been achieved on optimization of parameters such as molar ratio (oil to alcohol), amount of catalyst, temperature, and rate of agitation of reactants by mechanical stirrer. Karanja possessing high free fatty acid of 19.88 mg of KOH/g was esterified with H$_2$SO$_4$ to lower its acid value to 1.86 mg of KOH/g and was followed by alkaline transesterification. Parameters optimized during acid esterification were molar ratio 6:1 (methanol to oil) and H$_2$SO$_4$ (1.5% v/v) at 60 ± 0.5 °C for 1 h.

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Similarly, the same parameters were optimized for alkaline transesterification. The optimized values obtained were 8:1 (methanol to oil) molar ratio and 0.8 wt % NaOH, 1.0 wt % NaOCH$_3$, or 1.2 wt % KOH to obtain optimum conversions of 100, 98.28, and 96.8%, respectively (calculated from a ^{1}H NMR instrument) at 60 ± 0.5 °C at 600 rpm. The reaction time was optimized to be 45 min for NaOCH$_3$ and 1 h for NaOH and KOH. A high yield of 95% was obtained with NaOCH$_3$ as catalyst followed by NaOH (92%) and KOH (90%). The fuel properties of the fatty acid methyl esters derived from karanja oil fulfilled the fuel properties such as cetane number and flash point. Also, other important parameters such as methanol content, free glycerin, total glycerin, water, and sediment were within the limits specified. However, the oxidation stability of the methyl esters was lower than the minimum specification and will warrant addition of antioxidants so that it does not deteriorate with time. The total molar ratio of methanol to oil becomes (6 + 8) = 14:1, which comes by adding the molar ratio (alcohol to oil) taken during acid esterification (6:1) and alkaline transesterification (8:1) reaction. This value of molar ratio will escalate the cost of biodiesel. This can be managed by utilizing the unreacted methanol that is formed during acid esterification as well as alkaline transesterification. By fractional distillation, the unreacted methanol can be recovered from the biodiesel product and can be further reutilized to make biodiesel development cost-effective. Spillage of methanol in the environment will be also be reduced in this way.

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