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Studies on Thermal, Oxidative and Cold Flow Properties of Ethyl Esters prepared from High FFA Karanja Oil

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Abstract – *Transesterification of high FFAs karanja oil was carried out with ethanol in presence of KOH as a catalyst. Two-step process was used to produce biodiesel from karanja oil. Initially pre-treatment i.e. acid –catalyzed esterification process was carried out to reduce FFAs content. The maximum decrease in the FFAs of karanja oil was found to be 2% at 55°C, ethanol to oil molar ratio, 6:1; catalyst loading, 1 wt% (H_2SO_4) and reaction time, 75 min. In the second step, pretreated oil was transesterified using alkali (KOH) catalysts. Effect of different process parameters such as temperature, KOH loading, ethanol to molar oil ratio on the yield of ethyl esters was investigated. The maximum yield of ethyl esters was found to be 96-97%. Important fuel properties of karanja ethyl ester were estimated and compared with ASTM standard specifications. The study showed that low viscosity of ethyl ester increases the susceptibility of esters to oxidation and hence enhances the auto oxidation process and gives lower thermal and oxidative stability than the original oil. The cold flow property i.e. pour point of the prepared ethyl esters estimated using differential scanning calorimetry (DSC) technique was found to be -2°C.*

Keywords – Biodiesel, cold flow properties, ethyl esters, karanja oil, thermo gravimetric analysis.

1. INTRODUCTION

Biodiesel as an alternative fuels are attracting considerable attention in recent years worldwide as a blending component or direct replacement for diesel fuel in vehicle engines [1]. Biodiesel is a nontoxic, biodegradable and renewable fuel which can be prepared from range of organic feedstocks, including new or waste vegetable oils, animal fats, and oilseed plants [2]-[4]. In India, the prohibitive cost of edible oils prevents their use in biodiesel preparation, but non-edible oils are affordable for this purpose [5]. There are several non edible oil seeds such as Mahua (*Madhuca indica*), Simarouba (*Simarouba indica*), Karanja (*Pongamia pinnata*), Jatropha (*Jatropha curcas*) etc. among these *Jatropha curcas* and *Pongamia pinnata* (karanja) are found to be suitable in Indian climatic conditions [6]-[8]. The potential of total non-edible oils in India is around 100,000 tons/annum. Among these karanja (*Pongamia pinnata*) is one such forest-based tree-borne oil, which is non edible, having oil content of the kernel about 30–40% [9]. The oil obtained from karanja seeds contains number of unique non-lipid chemical compounds *viz.* flavonoids, furanoavonoids and furano derivatives. The karanja oil does not bear any suitable application with the exception of only 6% out of 200 million tons per annum production is utilized in soap manufacture and in the leather industry [10], [11].

The chemical structure of non edible oil generally consist of triglyceride molecules which have three long chain fatty acids, that are ester bounded to single glycerol molecule. These fatty acids differ by length of carbon chain, orientation and position of double bonds in these chains. Thus bio-diesel refers to lower alkyl esters of long chain fatty acids, which are synthesized either by transesterification or esterification of fatty acids [12].

This study aims to elucidate the production of fatty acid ethyl esters (FAEE) from karanja oil, and it has been found that the production of FAEE is as good as the production of fatty acids methyl esters, (FAME) both technically and chemically. But based on the limited information, it is accepted that FAME and FAEE have similar properties. FAEE prepared using sugar cane ethanol and with operation of larger fraction of vegetable oil could perform much better on the greenhouse gas balance than FAME.

As the production of ethanol is increasing and at the same time there is increase in demand for alternative fuels, biodiesel production with ethanol may be in great demand for future. In the coming years, if methanol prices continue to increase faster than ethanol prices, FAEE production can become another option from the economic point of view [13],[14]. The advantage of using FAEE over FAME is that FAEE gives little less negative effect on environment regarding emission of nitrogen oxides (NO_X), carbon monoxide (CO) and smoke density. Compare to diesel, pure FAEE gives less exhaust emission, high calorific value and smooth running of engine. Patil *et al.* [15] in their study reported that biodiesel production from high free fatty acid oil needs two-step transesterification processes *viz.* acid esterification followed by alkali transesterification to achieve high yield of biodiesel. Karanja oil consist of high free fatty acids (FFAs) much greater than 3%, therefore it has to undergo esterification process to reduce its FFAs value less than 3% above which transesterification reaction is not possible.

Hence in this study two step transesterification process was used, in the first step acid esterification was carried out followed by transesterification to produce biodiesel. Fuel properties of the prepared biodiesel were

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estimated using ASTM standards. Further thermal and oxidative stability of ethyl esters sample was determined by thermo gravimetric analysis (TGA) and differential thermo gravimetric analysis (DTG). The cold flow property, pour point was estimated using differential scanning calorimetry (DSC).

2. MATERIALS AND METHODS

2.1 Materials

Karanja oil used in this study was obtained from Andhra Pradesh and oil after filtration was used for experiment without further pre-treatment. The physico-chemical properties of oil were determined as per ASTM standard methods (Table 1). The fatty acid composition of oil estimated by gas chromatography is shown in Table 2. Potassium hydroxide pellets was purchased from Ranbaxy. Sulphuric acid (97% pure) and ethanol were procured from Merck, India Ltd. Other reagents such as standards were purchased from Sigma Aldrich.

2.2 Experimental Set-up

The apparatus used for transesterication consists of oil bath, reaction kettle with condenser and digital rpm controlled mechanical stirrer. Biodiesel was prepared in 500 ml glass kettle with quick –fit style three necks. One neck was attached with a condenser to avoid the vapor loss. The mechanical agitator with digital rpm controller and thermometer were inserted through other two necks. A silicon oil bath incorporated with digital temperature controller was employed to maintain the required reaction temperature. Karanja oil was preheated to desired temperature before starting the reaction. The potassium hydroxide–ethanol solution was pre-pared freshly in order to maintain the catalytic activity and to prevent moisture absorbance. The ethanolic solution was added to karanja oil in the reaction kettle and was considered as the zero time.

Table 1. Physico-chemical properties of karanja oil.

Properties	Karanja oil
Acid value (mg KOH/g)	28
Moisture (%)	0.47
Density (g/cc)	0.93
Saponification value (mg KOH/g)	182
Unsaponifiable matter (wt%)	2.5
Iodine value (gI_2/100g oil)	79.87
Viscosity @24^{o}C (cSt)	63.2
Viscosity@40^{o}C (cSt)	49.2
Refractive index @ 27^{o}C	1.47

Table 2. The fatty acid composition of karanja oil.

Fatty acid (wt%)	Karanja oil
Palmitic acid $C_{16:0}$	12.30
Stearic acid $C_{18:0}$	07.00
Oleic acid $C_{18:1}$	50.00
Linoleic acid $C_{18:2}$	15.21
Linolenic acid $C_{18:3}$	1.98

2.3 Procedure

Production of biodiesel using ethanol consists of two steps, namely acid esterification and alkali transesterification. Initially oil was pre-heated for 1h to remove the water and other impurities. After reaction, the mixture was allowed to settle for 8h in a separating funnel. The acid value of pretreated oil from step 1 was determined using a standard method. Then after the pretreated oil sample was used for transesterification reaction. The parameters optimized for reaction were ethanol to oil molar ratio, catalyst concentration, reaction temperature and time.

For esterification, 30 g high FFA (14%) karanja oil was charged into the reactor and heated to about 55^{o}C. Then 9.5 g ethanol (alcohol to oil molar ratio 6:1) and 0.39 g (1 wt %) sulphuric acid were added and mixed with the help of mechanical agitator at 400 rpm. After 75 mins, reaction mixture was poured into a separating funnel to remove excess alcohol, sulfuric acid, and impurities. The oil was separated and washed with hot Millipore water to remove ethanol and acid catalyst, which was then dried in rotavapor to remove moisture and ethanol. The reduced acid value after the reaction was 4.0 mg KOH/g. It has been reported that transesterification reaction would not occur if FFA in the oil is above 3% [6], [7].

For transesterification, acid pretreated oil was used and experiments were carried out in a same set up which was used for acid esterification. The reaction was conducted with different ethanol to oil molar ratios *viz.* 3:1, 6:1, 9:1 and 12:1, catalyst loading 0.5-1.5 (wt%, KOH) under the heating condition (55-85°C), reaction time 120 min, and constant stirring speed of 400 rpm. After transesterification, reaction mixture was charged into a separating funnel and allowed to settle. The transesterified product after separation was washed with hot water (60°C) for three-four times to remove catalysts and glycerol present. The moisture from washed biodiesel was removed using anhydrous sodium sulphate.

2.4 ^{1}H NMR Analysis

^{1}H NMR spectrum of sample was recorded using 400 MHz NMR spectrometer (Oxford, AS400, China) using a 5 mm broad band inverse probe head equipped with shielded z-gradient accessories. The sample (5-6 mg) was dissolved in 400 µl of deuterated chloroform ($CDCl_3$) and tetramethylsilane (TMS) was used as internal standard. The thermo gravimetric analysis was performed to measure thermal and oxidative degradation using (TGA) model TG/SDTA851e, METTLER TOLEDO at constant heating rate, 10°C/min from room temperature to 800°C. Nitrogen and oxygen was used as a purge gas at constant flow rate of 40 ml/min for thermal and oxidative stability study respectively. The samples were charged in an open silica crucible and % weight loss against temperature was plotted to obtain onset thermal and onset oxidative temperature.

Pour point of bio-diesel was evaluated using differential scanning calorimetry (DSC) (model DSC1, star^e system, Mettler Toledo). Dynamic DSC measurements were carried out in aluminum crucible with a small variation in sample mass of approximately 3-5 mg of oil and placed in DSC module with a similar empty pan as reference. The analysis involved rapid heating of sample to 50°C from room temperature. The system was then cooled to -30°C at steady rate of 5°C/min using air-cooled refrigeration machine and R290 refrigerant (Huber, TC-45, USA). Similarly the same sample was heated from -30°C to 50 °C using same heating rate. The plots of heat flow (mw) versus temperature (°C) for each experiment were used to estimate the pour point of sample.

3. RESULTS AND DISCUSSION

3.1 Influence of Ethanol to Oil Molar Ratio

The alcohol to oil molar ratio is one of the important factors that affects reaction. In the present work ethanol to oil molar ratio was varied in the range of 3:1 to 12:1. The maximum decrease in FFA content of karanja oil was found to be 2% at 55°C, 6:1 ethanol to oil molar ratio, 1 wt% catalyst loading (H_2SO_4) and reaction time 75 min. Further increased in ethanol : oil molar ratio shows little improvement in the conversion efficiency, this could have been the result of water produced during esterificaton of FFA which prevents further reaction [16]. Similarly, first step also reduces the viscosity of oil and it was observed that reduction in viscosity increases with an increased molar ratio.

In alkali transesterification reaction, ethanol to oil molar ratio was varied from 3:1 to 12:1. The maximum ethyl ester yield of 96.5% was obtained at 9:1 molar ratio and reaction time of 120 min. Further increase in the ratio to 12:1 yield was found to be decreased, that is because high molar ratio of alcohol to oil interferes with separation of glycerin due to the solubility of glycerol in the biodiesel (Figure 1).

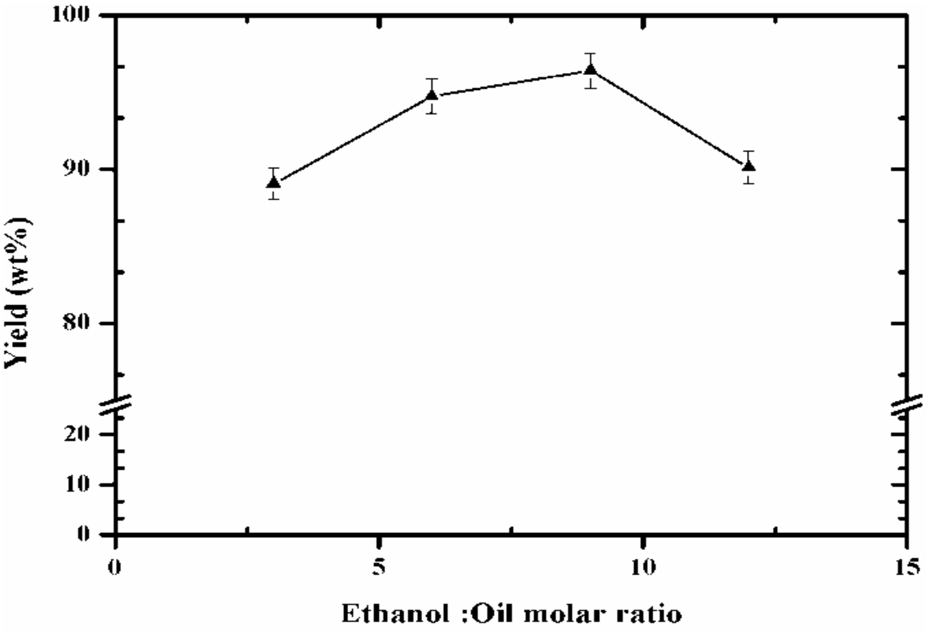

Fig. 1. Effect of ethanol to oil molar ratio on ethyl esters yield.

3.2 Influence of Temperature

In this study the effect of reaction temperature on alkali catalysed trasesterification was conducted, efforts were made to maintain the reaction temperature close to the boiling point of ethanol. Transesterification reactions was carried out at different temperature ranging from 55^{o}C to 85^{o}C with 1wt% KOH as catalyst and 9:1 ethanol to oil molar ratio at stirring speed 400 rpm and reaction time 120 min. The yield versus temperature plot is shown in Figure 2. The maximum conversion was recorded at 75^{o}C with optimum catalyst loading of 1 wt% KOH.

The effect of reaction temperature on yield at different alkali concentration is shown in Figure 3. As the temperature increases viscosity of oil decreases which helps to enhance the reaction rate and reduces reaction time. In this study reaction temperature above boiling point of alcohol was avoided since at high temperature it tends to accelerate the saponification of triglycerides by alkaline catalyst before completion of the alcoholysis [17]. Hence, reaction temperature must be lower than the boiling point of alcohol in order to avoid the escape of alcohol through vaporization.

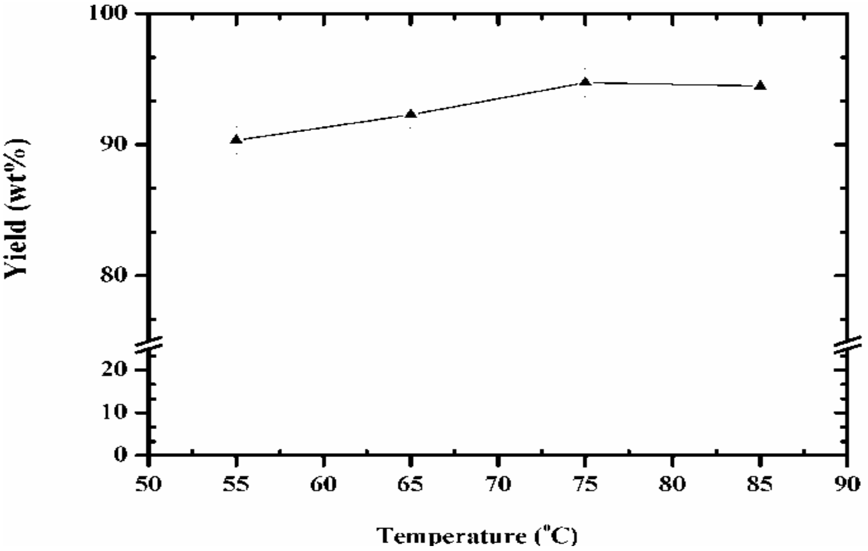

Fig. 2. Effect of reaction temperature on ethyl esters yield.

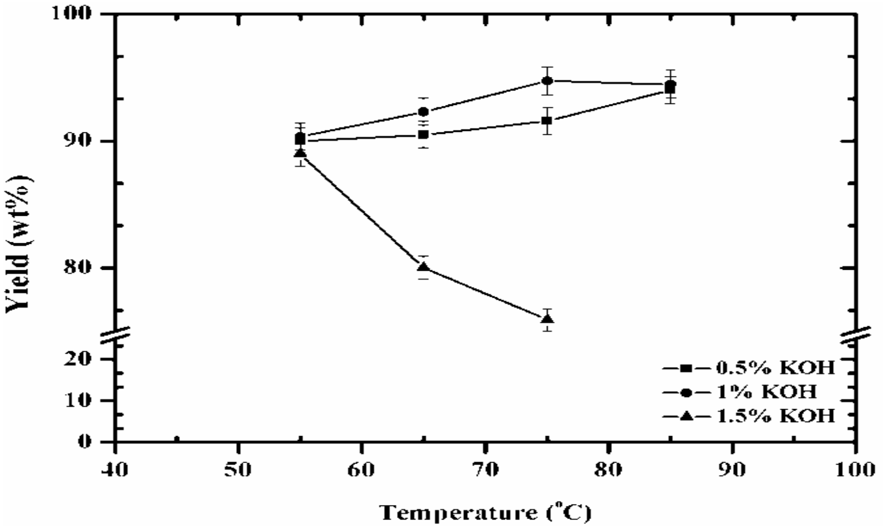

Fig. 1. Effect of reaction temperature on ethyl esters yield at different alkali concentration.

3.4 Quantification of Ethyl Esters

The conformation of ethyl ester conversion was quantified through ^{1}HNMR spectroscopy. The ^{1}H NMR spectrum of pure karanja oil is shown in Figure 4. The eight signal groups as described earlier by Miyake *et al.* [19] may be observed in this study and are comparable to previously reported values.

The ^{1}H NMR spectrum of ethyl ester is shown in Figure 5. Using ^{1}H NMR technique, ethyl esters conversion was determined with three sets signals: 4 to 4.20 ppm peak signifies the presence of two hydrogen of group –O-CH$_{2}$- in the fatty acid ethyl ester product (A); 4.20-4.4 ppm signal area was characterized by two terminal CH$_{2}$ groups of glycerol molecule in the oil (B); 2.20-2.40 ppm signal range are related to two hydrogen from the groups R-CH$_{2}$-CO (acyl group) which may be found in both oil and fatty acid esters(C). The ethyl ester conversion from karanja oil was obtained from ^{1}H NMR technique using Equation 1 [20]. The calculated value of the conversion of karanja oil with ethanol was 79%, which was relatively less compared to previously reported values.

$$Ethyl\ ester\left(\%\right) = \frac{\mathrm{A}-\mathrm{B}}{C}\times 100 \qquad (1)$$

3.5 Thermal and Oxidative Stability

Thermo gravimetric analysis was performed in both nitrogen and oxygen atmospheres to estimate the thermal and oxidative stability of ethyl esters. Thermal and oxidative stabilities were determined from the onset temperature of decomposition under nitrogen and oxygen atmosphere respectively. Onset temperature is the temperature at which decomposition of sample starts and was estimated at two percent weight loss of mass, which allocate weight loss due to moisture content and more volatile core components [21]. Figure 6 and 7 shows TG, DTG curves of karanja oil and its ethyl esters in N_2 and O_2 atmospheres at constant heat rating 10^{o}C/min. The TG plot show percentage weight loss against temperature and DTG curve shows the number of steps required for thermal and oxidative decomposition of sample.

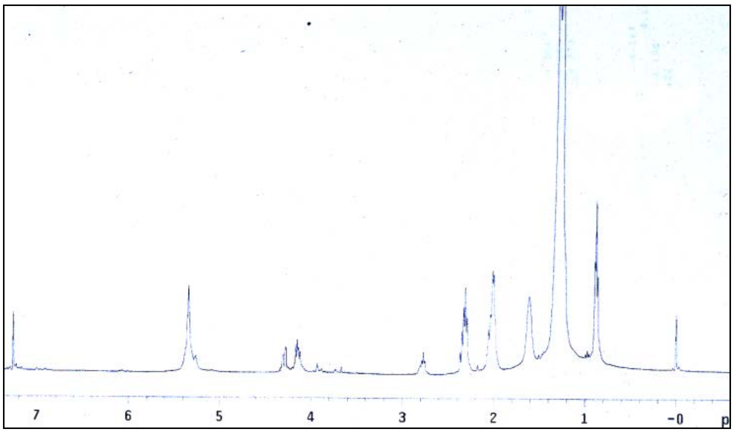

Fig. 4. ^{1}H NMR spectrum of pure karanja oil.

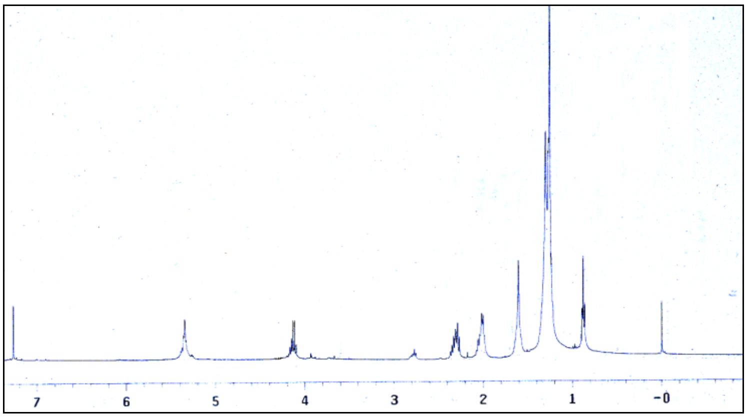

Fig. 5. ^{1}H NMR spectrum of karanja ethyl ester.

From DTG curve (Figure 6) it was observed that thermal decomposition of samples occurred in two distinct stages. It involves breaking of heavier oxygenated hydrocarbons into lower molecular hydrocarbons, carbon dioxide and carbon monoxide [22]. At the first stage both oil and ethyl esters were stable (weight loss remains constant) up to 192 ^{o}C and 178 ^{o}C and was considered as the onset temperature of oil and ester respectively (Table 4). In this temperature range weight loss was mainly due to moisture and evaporation of lower boiling point (highly volatile) compounds. The weight loss profile of oil and ethyl esters takes into account the decomposition behaviour and mass loss with respective temperature as shown in Table 3. From table it can be also seen that all the components of karanja oil and ethyl esters which accounted for almost 50% weight loss were decomposed at 357^{o}C and 341^{o}C respectively, which involves breakdown of unsaturated fatty acids. The remaining 10 % was pyrolysis products which were highly viscous liquids and experiences secondary decomposition up to 357- 700 ^{o}C for oil and 341-700 ^{o}C for ethyl esters, which includes breakdown of poly unsaturated fatty acids. This specifies that decomposition of ethyl esters completed within a temperature range inferior to oil which confirms that oil was thermally more stable compared to ethyl esters (Table 4). The study of thermal stability is highly significant factor to define the useful life time and storage stability of biofuels.

Different steps in the decomposition of oil and ethyl ester under oxygen atmosphere correspond to decomposition of unsaturated fatty acids, saturated fatty acids and oxidation of carbon residue [22]. Comparative TG and DTG plots of karanja oil and its ethyl esters in presence of oxygen are shown in Figure 8. The TG/DTG curves of karanja oil shows that oxidative decomposition takes place in three consecutive stages, while ethyl esters decomposition occurs in two steps. The percentage weight loss of oil and ethyl esters sample during oxidative stability study is shown in Table 3. The oxidative degradation of ethyl ester was relatively fast compared to oil. High viscosity and high molecular weight of oil could be one of the reasons for slow degradation of oil. The low viscosity of ethyl ester increases the susceptibility of esters to oxidation and enhances auto oxidation process and gave lower thermal and oxidative stability (Table 4). The oxidative stability of ester can be improved either by using synthetic antioxidants which are available in market or vegetable oil based antioxidant additives.

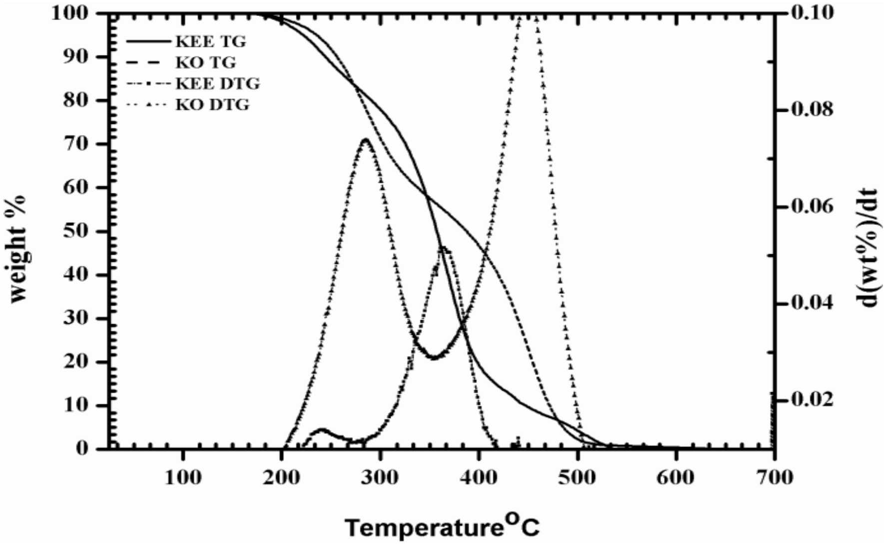

Fig. 6. TG and DTG curves of karanja oil, ethyl esters at heating rate of 10 °C/min in N_2 atmosphere.

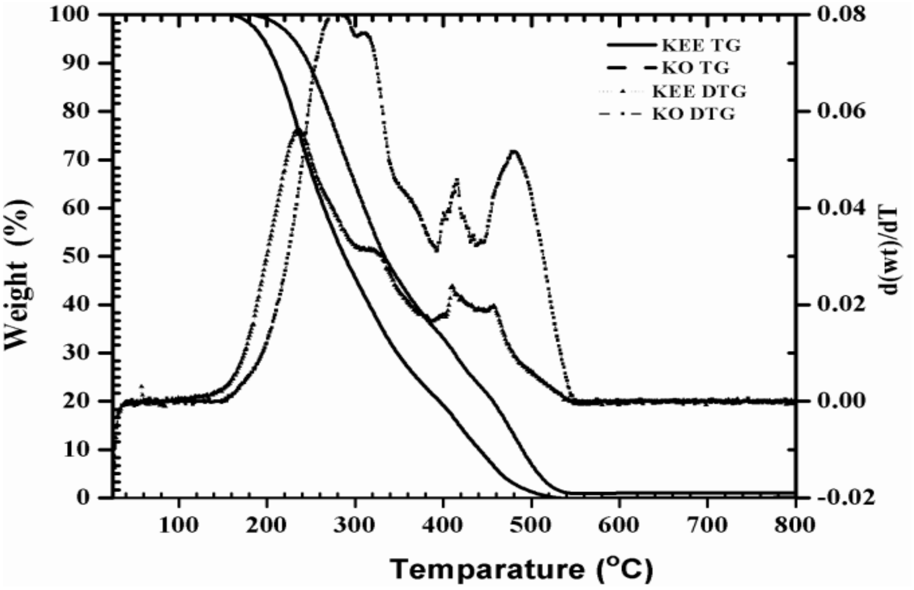

Fig. 7. TG and DTG curves of karanja oil, ethyl esters at heating rate of 10 °C/min in O_2 atmosphere.

Table 3. Mass loss data during thermal and oxidative degradation.

Oil /ester	Heating Rate (^{o}C/min)	Temperatures (^{o}C) of Mass Loss under N_2			Temperatures (^{o}C) of Mass Loss under O_2		
		10 %	50 %	90 %	10 %	50 %	90 %
KEE	10	226	341	416	210	289	441
KO	10	245	357	446	247	334	490

KEE: karanja ethyl ester; KO: karanja oil

Table 4. Onset temperatures of thermal and oxidative degradation.

Oil/ester	Heating Rate (^{o}C/min)	TOT* (^{o}C)	**OOT(^{o}C)
Karanja ethyl esters	10	178	160
Karanja oil	10	192	187

*TOT: Thermal Onset Temperature (N_2), **OOT: Oxidative Onset Temperature (O_2)

3.6 Cold Flow Properties

The estimation of low temperature properties of biodiesel is very important for its use in cold-climatic conditions. The properties of biodiesel are similar to diesel except the start up and performance problem when subjected to low temperature. This is because when a blended diesel fuel is used at low temperature, the biodiesel portion of the blend crystallizes and separates out from diesel fuel [23]. The formation of these crystals can create problems to engine flow system, undermine engine operation, and eventually cause engine to stop running. Therefore, suitable characteristics of biodiesel, low temperature properties such as cloud and pour point should be warranted before its commercial use. In this study DSC technique was used to determine the cold flow properties of ethyl esters. A typical DSC thermogram of ethyl esters sample heated from -30^{o}C to 40 ^{o}C is shown in Figure 8 and fatty acid compositions of karanja ethyl ester is shown in Table 2. It is well known that unsaturated ester crystallizes at temperature lower than saturated ester. The influencing factor is they have different three-dimensional conformations. As saturated ester molecules are in its minimum energy when fully extended and are well stacked, thereby strengthening intermolecular attraction force [24]. Unlike saturated ester, unsaturated ester molecules have weaker intermolecular interactions and therefore crystallize at a lower temperature. The saturation level of karanja oil used in this study was around 19 wt%. As a result, its ethyl ester possesses a pour point of -2^{o}C.

3.7 Fuel Properties of Karanja Ethyl Ester

The physico-chemical properties of karanja ethyl esters obtained after transesterification were estimated as per the ASTM specification and reported in Table 5. As evident in this table, the transesterification improved the fuel properties of the oil. Viscosity of the esters was found to be decreased (i.e. 6.07cSt) drastically after transesterification and was very close to that of diesel. This property supports very strongly in favour of biodiesel being used in a diesel engine without any engine modification. Acid value of ethyl ester was 0.85 mg KOH/g which was well below the maximum limit of 0.8 mg KOH/g according to ASTM D664 standards. The acid value is generally used as a guide in the quality control as well as monitoring oil degradation during storage [25]. Density and moisture content of ethyl esters were close to that of diesel and within the ASTM standard. Density of biodiesel is a key factor in fuel consumption and which can vary with fatty acid composition and its purity [26]. The saponification value indicates the average molecular weight of sample [27]. The saponification value of karanja ethyl ester was higher than the karankja oil. The unsaturation content in the samples was determined by iodine value [27]. *Encinar et al., (2007)* reported that biodiesel obtained from the same oil should have similar iodine value. There was no significant difference in the iodine value of karanja oil and prepared ester. The limited unsaturation is preferable since higher heating of unsaturated fatty acids cause polymerisation of glycerides [27]. The flash point of ethyl ester was found to be 182^{o}C, which was higher than that of conventional diesel. *Qi et al., (2010)* reported that fuels with flash point above 66^{o}C are considered as safe. Thus biodiesel is an extremely safe fuel compared to diesel [28]. Low temperature performance is one of the important considerations for usage of biodiesel [29]. The low temperature properties (i.e., cloud, pour and cold filter plugging points) indicate that the biodiesel with lower unsaturation content (double bonds) have better flow properties under low temperatures. The pour point of ethyl ester estimated in this work was -2^{o}C which was in the considerable limits of ASTM D664 standards [29]. The cetane number (*CN*) of ester was estimated by the empirical equation 2 proposed by Krisnangkura *et al.* [24].

$$CN = 46.3 + \frac{5458}{SV} - \left(0.225 \times IV\right) \tag{2}$$

Cetane number of biodiesel obtained from this equation was found to be 55.9 which meet the ASTM standard specification. This parameter gives the assurance of the good control of combustion and performance [27]. Altogether fuel properties of karanja ethyl ester were close to the ASTM standard specifications, although there were exceptions such as saponification value and flash point.

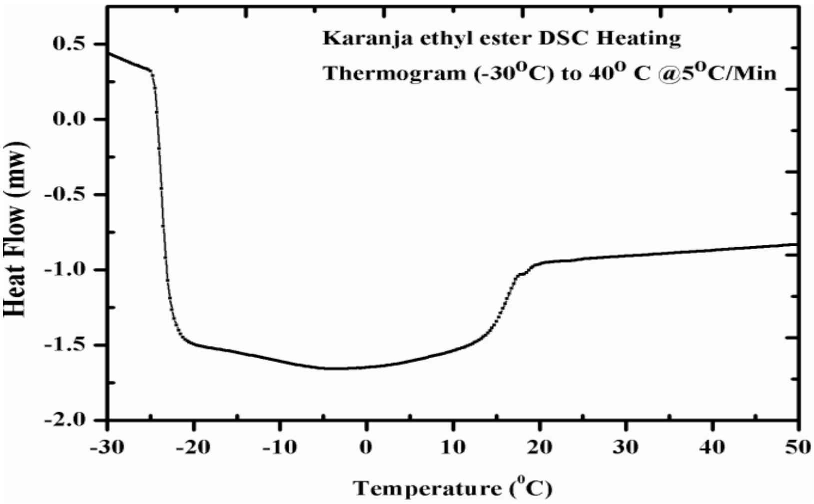

Fig. 8. DSC Thermogram of ethyl esters (biodiesel), at 5 ^{O}C/min in N_2 atmosphere

Table 5. Physicochemical properties of conventional diesel and Karanja ethyl ester.

Properties	Ethyl esters	Diesel	ASTM Biodiesel standard
Acid value (mgKOH/g)	0.85	-	0.8 max
Moisture (%)	0.07	-	0.5max
Density@ 24°C (g/cc)	0.902	0.85	0.860-0.9
Saponification value (mgKOH/g)	194	-	-
Iodine value (gI_2/100g oil)	80.08	-	120
Viscosity @24°C (cSt)	6.61	-	-
Viscosity@40°C (cSt)	6.07	2.86	-
Refractive index @ 27°C	1.46	-	1.9-6

5. CONCLUSIONS

The preparation of fuel quality biodiesel from low cost high FFA karanja oil was investigated in the present study. The optimum reaction conditions for ethanolysis of karanja oil was 1wt% KOH, ethanol to oil molar ratio 9:1, reaction temperature 75°C at 400 rpm. The yield of ethyl esters was 96-97 %. The oxidative and thermal degradation study specifies that decomposition of ethyl esters completed within a temperature range inferior to oil, which confirms that oil was thermally and oxidatively more stable compared to its ethyl esters. The acid value of the biodiesel was found to be 2.85 mg KOH/g, which unsatisfied the limit of ASTM specification.

NOMENCLATURE

FFA	Free Fatty Acid
KOH	Potassium Hydroxide
ASTM	American Society for Testing Materials
TGA	Thermo Gravimetric Analysis
DTA	Differential Thermal Analysis
DSC	Differential Scanning Calorimetry
FAEE	Fatty Acid Ethyl Esters
FAME	Fatty Acid Methyl Esters
NMR	Nuclear Magnetic Resonance Spectroscopy
$CDcl_3$	Deuterated Chloroform
TMS	Tetra Methyl Silane
TOT	Thermal Onset Temperature
OOT	Oxidative Onset Temperature
CN	Cetane Number

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