



Biodiesel from non-edible Karanja seed oil

M. J. Alam¹, S. M. S. Rana¹, M. A. Haque¹, M. Hossain^{2, 4}, S. M. A. Sujan^{2, 4} and M. S. Jamal^{2, 3*}

¹Department of Chemistry, Jagannath University, Bangladesh.

²Institute of Fuel Research and Development (IFRD), BCSIR, Dhaka, Bangladesh

³Solar Energy Research Institute (SERI), UKM, Malaysia

⁴Jahangirnagar University, Bangladesh

Abstract

The fossil fuel resources are dwindling day by day. Fuel has been a challenge for today's scientific works for increasing demand. The methyl esters of vegetable oils, known as biodiesel are becoming increasingly well known because of their low environmental impact. Methyl esters of *Pongamiapinnata* are derived through esterification and transesterification. Several processes of biodiesel fuel production has been developed, among which transesterification using alkali as a catalyst gives high level of conversion of triglycerides to their corresponding methyl ester in a short duration. Amount of solvent, catalyst, temperature and reaction time were optimized to estimates the conversion efficiency. The physical properties of Karanja seed oil (KSO) and biodiesel were studied and compared with standard. FTIR and TGA spectrums of KSO and KSO Biodiesel were studied for the confirmation of conversion.

Key words: Biodiesel; Free fatty acid,; Karanja seed oil; Esterification; Transesterification

Introduction

Vegetable oil was used as fuel during the period of Second World War when fuel availability became scarce. Now-a-days interest is growing on using vegetable oil as fuel (Shahid *et al.*, 2012). There has been renewed focus on vegetable oil and animal fats as an alternative to petroleum fuels due to limited resources of fissile fuels (Bobade and Khyade, 2012). *Pongamiapinnata* can grow in arid and wasteland which seeds contain oil is around 30-40% (Chandrashekar *et al.*, 2012). India has about 80-100 million hectares wastelands, which can be used for jatropha and pongamia plantation. Biodiesel has attracted considerable attention during the past decade as a renewable, biodegradable, eco-friendly and non-toxic fuel which is derived from triglyceride by transesterification and from the fatty acids by esterification (Bobade and Khyade, 2012). The thick oil from the seeds has been used as fuel in diesel engines, showing a good thermal efficiency and it is also having immense potential as a bio-diesel plant (Shrivastava and Kant, 2010). If we use edible oils for biodiesel production leads food oil crisis and the problem can be solved by using cheapest, low cost non-edible oils as feed stocks for biodiesel production (Mathiyazhagan *et al.*, 2011). Biodiesel almost completely eliminates lifecycle of carbon dioxide emissions and when compared with petrodiesel it reduces about half of the emission of particulate

matter, unburned hydrocarbons, and carbon monoxide; most part of the polycyclic aromatic hydrocarbons and entire sulphates on average (Haque *et al.*, 2010). *Pongamiapinnata* is one of the promising tree species suitable for providing oil for biodiesel production. The tree bears green pods, which after 10 to 11 months gets matured and changes to a tan color in the month of May-June. The fresh extracted oil is yellowish orange to brown and rapidly darkens on storage (Meher *et al.*, 2004). While feed stocks with a low level of free fatty acids (FFAs) can be used alkali catalyzed during the biodiesel production process, feedstock's with significant FFAs amount perform better in the presence of acid catalysts (Khayoon *et al.*, 2012). Methanol is the most commonly used alcohol because of its low cost and is the alcohol of choice in the processes developed in this study. In general, a large excess of methanol is used to shift the equilibrium far to the right. Further, the degree to which extensive propagation of *pongamiapinnata* and the extraction and processing of oil from seeds may contribute to the success of a sustainable biofuels industry is discussed (Scott *et al.*, 2008).

The main objective of this research work is the study of the regional basis characterization of biodiesel from Karanja seed oil. The Karanja seeds were collected from the district

*Corresponding author: e-mail: msjdubd@gmail.com

of Pirojpur. *Pongamia* has a varied habitat distribution and can grow in a widerange of conditions. The study of the production of biodiesel carried on specific region's Karanja seeds oil. Such studies would include the clonally propagation of high oil content and high yielding individual trees.

Materials and methods

Materials

Pongamia seeds (a source of non-edible oil) collected from Pirojpur (a district located in the southern part of Bangladesh) were used to produce biodiesel. The seeds of karanja were collected from their ripe fruits. After removing the coating of seeds, these were dried in the sun for a week. Then karanja oil was expelled from its kernel. The non-edible oil obtained from these, was used for the experiments involved in the current study.

The methods involved in the present study included the extraction, optimization and characterization of biodiesel.

Extraction of karanja seed oil

The solvent extraction method was used to extract oil from the kernel of karanja seeds. In this case, *n*-hexane was used as solvent. After extraction, the solvent was removed by distillation. The filtrated oil was used for the further experimental studies.

Optimization of acid value of crude karanja seed oil

Optimization is the first step on the way to produce biodiesel. The acid value of crude karanja seed oil was optimized through the esterification with an alcohol such as methanol (MeOH) in presence of an acid catalyst such as sulfuric acid (H_2SO_4). The main target of this step was to reduce the acid value of crude karanja seed oil. This reaction was carried out in a closed three-neck round-bottom flask by varying different parameters like oil to methanol ratio, oil to catalyst ratio, time and temperature. After completing the esterification, the reacted mixture was allowed to settle for an hour to separate the treated oil as bottom layer. In each case, the FFA (free fatty acid) was determined before and after the esterification.

Production of biodiesel through transesterification

Transesterification is defined as the reaction of a triglyceride with an alcohol in presence of an acid or alkali as a catalyst to form a mono alkyl ester i.e. biodiesel. In this study, the base catalyzed transesterification of the *pongamiapinnata* (karanja) seed oil was carried out with methyl alcohol in presence of sodium hydroxide. This reaction was also carried out in a closed three-neck round-bottom flask by using a standard agitator at 500 ppm speed. When the reaction was completed, then it was

allowed for settling for 10-12 hours in a separating funnel. Due to these separation two major products namely glycerin and biodiesel were obtained as bottom layer and upper layer respectively. The excess alcohol present in biodiesel was recovered through distillation and the alcohol-free biodiesel was washed gently with warm water for the removal of residual catalyst and soap. The water and other impurities present in biodiesel were removed completely by using rotary evaporator. The optimum condition for transesterification was estimated by varying the parameters like oil to methanol ratio, oil to catalyst (base) ratio and the time and temperature of reaction.

Analytical methods employed to characterized the properties of oil and biodiesel

The following analytical methods were employed to justify the characteristics of oil and biodiesel produced.

FTIR analysis

The functional groups present in KSO and KSO biodiesel were analyzed by FTIR analysis. An IR-Affinity-1 spectrometer, SHIMADZU, Japan (in the range of 500-4000 cm^{-1}) was employed to conduct the analysis.

Thermo gravimetric analysis (TGA)

A TG-DTA 6300 (exstar 6000), Seiko Instrument Incorporation, Japan was employed to examine thermal stability of KSO and KSO biodiesel.

Results and discussion

Extraction of karanja seed oil

Karanja seeds were well-dried, decorticated before to be powdered and screened to homogeneous size. Extraction of oil from these powders using *n*-hexane as solvent was then carried out in Soxhlet apparatus. The extracted oil from the Karanja seeds was (23-26) %.

H₂SO₄ catalyzed esterification

The major target of the acid catalyzed esterification was to reduce the acid value of crude karanja seed oil (KSO). The optimum condition for esterification was estimated by varying different parameters such as methanol to oil ratio, catalyst to oil ratio, and time and temperature of the reaction. The observations were listed on Table-I.

Acid value and FFA decreased from 9.87 mg KOH/g to 2.82 mg KOH/g with the increasing methanol proportion from 9g to 21g in oil to methanol ratio, from 6.72 mg KOH/g to 3.71 mg KOH/g with increasing catalyst proportion from 0.09g to 0.36g in oil to catalyst ratio, from 8.78 mg KOH/g to 3.35 mg KOH/g with increasing temperature 40°C to 80°C and from 9.93 mg KOH/g to 2.82mg KOH/g with the increasing time from 30 min to 90 min.

Table I. Variation of (a) methanol-to-oil ratio, (b) acid catalyst-to-oil ratio, (c) temperature and (d) time for the reduction of acid value and FFA

Id	Oil :MeOH	Oil : Catalyst	Temp, (°C)	Time (min)	Acid value (mg KOH/g)	FFA(%)
a	30 : 09	30 : 0.36	60	90	9.87	4.94
	30 : 12	30 : 0.36	60	90	8.87	4.44
	30 : 15	30 : 0.36	60	90	6.57	3.79
	30 : 18	30 : 0.36	60	90	5.57	2.79
	30 : 21	30 : 0.36	60	90	2.82	1.41
b	30 : 21	30 : 0.09	60	90	6.70	3.35
	30 : 21	30 : 0.18	60	90	5.52	2.76
	30 : 21	30 : 0.27	60	90	5.70	2.85
	30 : 21	30 : 0.36	60	90	3.71	1.86
c	30 : 21	30 : 0.36	40	90	8.78	4.39
	30 : 21	30 : 0.36	50	90	7.76	3.88
	30 : 21	30 : 0.36	60	90	5.57	2.79
	30 : 21	30 : 0.36	70	90	2.22	1.11
	30 : 21	30 : 0.36	80	90	3.35	1.68
d	30 : 21	30 : 0.36	70	30	9.93	4.97
	30 : 21	30 : 0.36	70	45	7.85	3.93
	30 : 21	30 : 0.36	70	60	6.53	3.27
	30 : 21	30 : 0.36	70	75	5.51	2.76
	30 : 21	30 : 0.36	70	90	2.82	1.41

NaOH catalyzed transesterification

Base-catalyzed transesterification process of crude KSO depends on different variables such as methanol to oil ratio, base to oil ratio, reaction temperature and time. The observations that were found during the transesterification are listed in Table-II.

The percentage of biodiesel increased from 30.23 to 76.92 with increasing methanol proportion from 6.01g to 18.03g, from 0.00 to 83.03 with increasing catalyst proportion from 0.09g to 0.36g, from 81.81 to 83.06 and then decreased with increasing temperature, from 30°C to 70°C and from 50.37 to 83.07 with increasing time from 30 min to 120 min.

Table II. Variation of (a) methanol-to-oil ratios, (b) base catalyst-to-oil ratios, (c) temperature, (d) time for the production of biodiesel.

Id	Oil :MeOH	Oil : Catalyst	Temp, (°C)	Time (min)	Yield% (Biodiesel)	Yield% (Glycerin)
a	30 : 6.01	30 : 0.36	60	100	30.23	69.77
	30 : 9.03	30 : 0.36	60	100	42.21	57.79
	30 : 12.02	30 : 0.36	60	100	74.12	25.88
	30 : 15.02	30 : 0.36	60	100	83.06	16.94
	30 : 18.03	30 : 0.36	60	100	76.92	23.08
b	30 : 15.02	30 : 0.09	60	100	0.00	0.00
	30 : 15.02	30 : 0.18	60	100	43.99	56.01
	30 : 15.02	30 : 0.27	60	100	58.72	41.28
	30 : 15.02	30 : 0.36	60	100	83.03	16.94
c	30 : 15.02	30 : 0.36	30	100	81.81	18.19
	30 : 15.02	30 : 0.36	40	100	82.53	17.47
	30 : 15.02	30 : 0.36	50	100	81.17	18.83
	30 : 15.02	30 : 0.36	60	100	83.06	16.94
	30 : 15.02	30 : 0.36	70	100	80.26	19.74
d	30 : 15.02	30 : 0.36	60	30	50.37	49.63
	30 : 15.02	30 : 0.36	60	60	72.76	27.24
	30 : 15.02	30 : 0.36	60	90	83.07	16.93
	30 : 15.02	30 : 0.36	60	120	83.07	16.96

Physicochemical properties of KSO and KSO biodiesel

The karanja seed oil and biodiesel obtained from it were characterized by the established methods. From the table -3, showed that kinematic viscosity of KSO biodiesel 4.70 which is not meet biodiesel standard but effectively decreased from seed oil value. Pour point and Flash point value were observed in -15°C and 170°C respectively which are easily achieved target value of biodiesel standard.

found in the FTIR spectrum of both KSO and KSO biodiesel. A smaller extent of unsaturation was estimated by the appearance of the peaks in the range of $1435\text{-}1456\text{ cm}^{-1}$. The basic difference between the two spectra (one for KSO and another for KSO biodiesel) was the presence of the peak at 1435.04 cm^{-1} corresponding to $-\text{OCH}_3$ groups. This peak was absent in the FTIR spectrum of KSO [Fig-1(a) and Fig-1(b)].

Table III: Proximate physico-chemical properties of crude KSO and KSO Diesel with standard biodiesel and Petro-diesel.

Name of the Parameter	Method	KSO	KSO Diesel	Biodiesel Standard (Rana <i>et al.</i> , 2015)	Diesel (Joshi and Pegg, 2007)
Density at 15°C , g/cc	IP-160/57	0.90	0.88	-	-
Kinematic viscosity, cSt	445-65 (40°C)	40.2	4.70	1.9-6.0	1.3-4.1
	D 445-65 (100°C)	4.93	2.10	-	-
Pour point, $^{\circ}\text{C}$	D 97-57	-14	-15	-1 to 10	-35 to -15
Flash point, $^{\circ}\text{C}$	D 93-62	232	170	100-170	60-80
Acid value, mg KOH/g	IP 1/58	9.87	2.23	0.08	-
Water content, %	IP-74/57	Nil	Nil	0.05% max.	161
Ash content, %	D 482-63	0.07	0.07	-	-
Carbon residue, wt%	D 189-65	1.51	2.36	-	-
Calorific value, J/Kg	IP-12/58	8318	11543	-	-
Sulphur content(g/g)	D 129-64	0.02	0.05	-	-

FTIR analysis of KSO and KSO biodiesel

For KSO and KSO biodiesel, FTIR shows main peaks at 1743.65 cm^{-1} and 1741.72 cm^{-1} respectively due to carbonyl($\text{C}=\text{O}$) groups present in ester. The peaks in the range of ($2922.16\text{-}2852.72\text{ cm}^{-1}$) are corresponding to C-H bending and stretching vibration present in alkanes was also

TGA Analysis

Thermo gravimetric analysis (TGA) which is an effective, inexpensive and fast technique to determine the boiling point of ester; was applied to measure the boiling point of KSO and KSO biodiesel (fig-2). The mass loss against temperature during the transesterification reaction was also

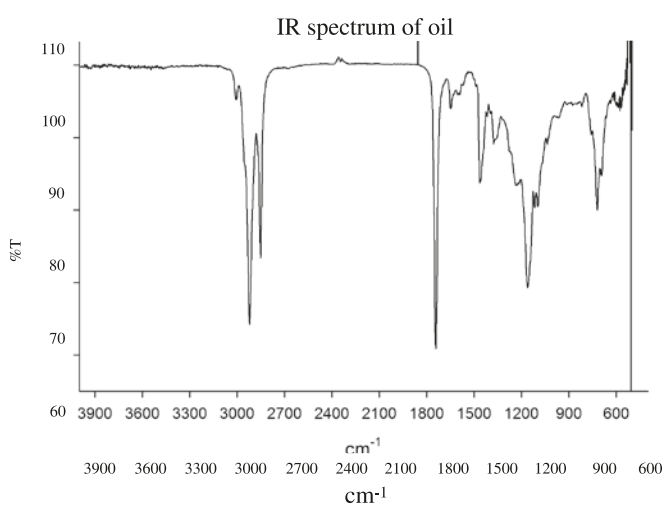


Fig. 1(a). FTIR spectra of crude karanja seeds oil

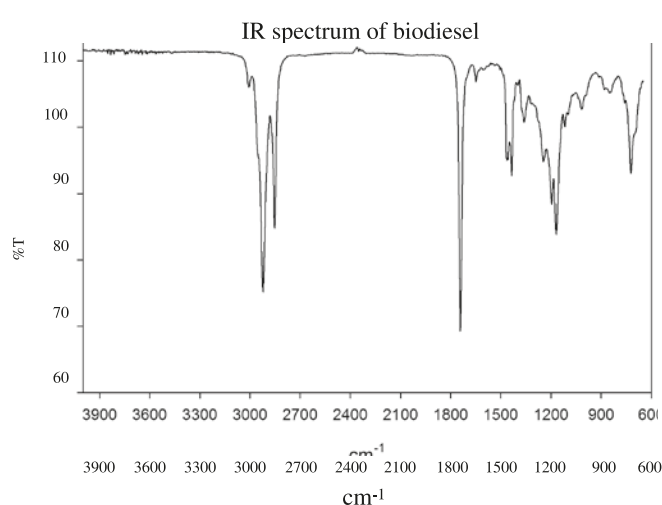


Fig. 1(b). FTIR spectra of karanja seeds oil biodiesel.

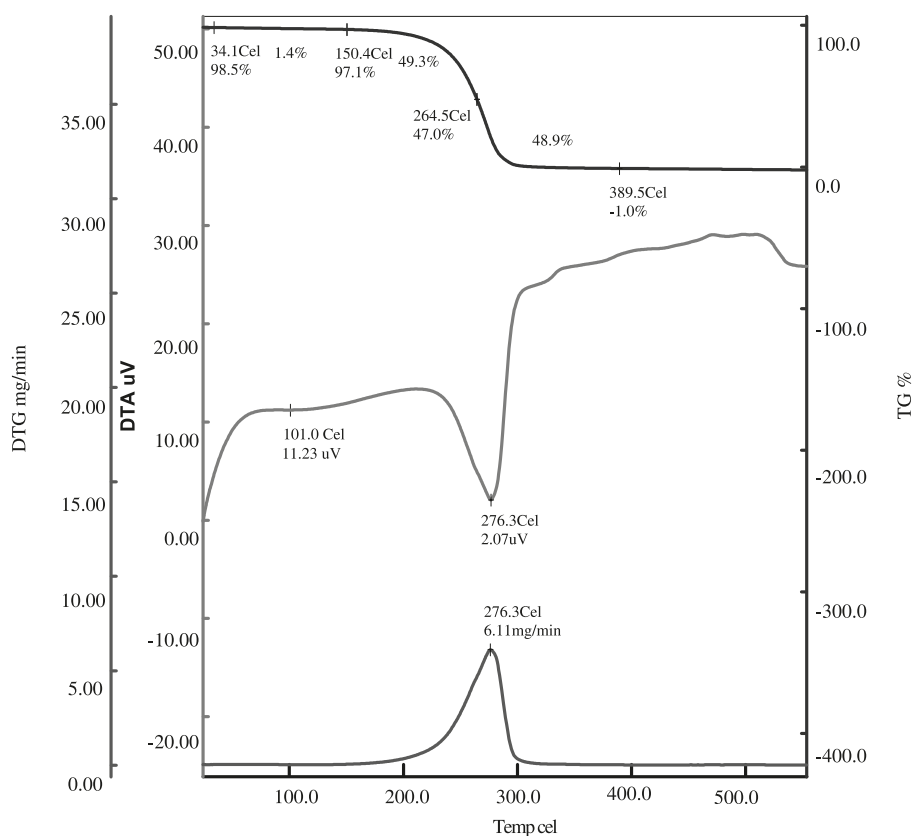


Fig. 2. Thermo gravimetric curves of MSO biodiesel.

followed by this technique to confirm the functional groups present in KSO and KSO biodiesel. In TGA curves of biodiesel the first weight loss at approximately 151.04°C represents the boiling point of biodiesel, the second weight loss at 264.5°C represents the boiling point of ester with unsaturated bonding and the third weight loss at 389.5°C probably represents the presence of KSO oil which was not transesterified.

Conclusion

One-step alkaline-catalyzed transesterification was found to be ineffective for biodiesel production from karanja oils extracted from karanja seeds due to high acid value (9.87mgKOH/g). Process was found to be effective, in which karanja oil was firstly pre-treated with an acid-catalyzed reaction yielding esters and reducing the acid value and then followed by transesterification using NaOH as the catalyst. The oil-to-catalyst (H_2SO_4) ratio (30: 0.36) was used as the acid catalyst in the first step and different oil-to-catalyst (NaOH) ratio (30: 0.36) were tested in the second step. A successful alkaline-catalyzed transesterification could be achieved with acid-pre-treated karanja oil having

an acid value 9.87mg KOH/g. The results show that a maximum yield of about 83.07% of the oil weight was obtained with NaOH of 1.2%. The physico-chemical properties of MSO biodiesel are comparable with that of standard diesel and biodiesel. The conversion of MSO to MSO biodiesel was confirmed by TGA and FTIR analysis.

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