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Biodiesel production from non-edible Mahogany seed oil by dual step process and study of its oxidation stability

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Abstract

Biodiesel derived from non edible sources is a potential eco-friendly substitute to petroleum fuel. Acid-catalysed esterification was applied to reduce free fatty acid (FFA) content of oil to zero followed by base-catalyzed transesterification to convert esterified product to its mono-esters and glycerol. The major factors affecting the conversion efficiency of these two processes such as amounts of solvent and catalyst, reaction temperature, and reaction time were optimized. The physical properties and heating value of Mahogany Seed Oil (MSO) and MSO diesel are evaluated and compared with that of commercial diesel. FTIR and 1H NMR spectrum of MSO and MSO biodiesel confirmed the conversion of MSO to biodiesel. The oxidation stability of MSO biodiesel oil was also studied. The study affirms the production of biodiesel from MSO as a renewable alternative to the diesel fuel.

Keywords: Biodiesel; Mahogany seed oil; Free Fatty Acid; Trans-esterification; Anti-oxidant

Introduction

The rapidly increasing prices and uncertainties concerning petroleum availability, a growing concern of the environment and the effect of greenhouse gases during the last decades, has revived more and more interests in the use of vegetable oils as a substitute of fossil fuel (Balat and Balat, 2008) Vegetable oils have long been promoted as possible alternatives of diesel. Besides animal fats, used cooking oil can be used to produce biodiesel which can be a good alternative to petroleum-based fuels. Vegetable oils are widely available from various sources, and the glycerides present in the oils can be considered as a viable alternative for diesel fuel (Balat and Balat, 2008). Depending upon the climate and soil conditions, different countries are looking for different types of vegetable oils as substitutes for diesel fuels. For example, soybean oil in South-east Asia (mainly Malaysia and Indonesia) and coconut oil in Philippines are being considered as raw materials for biodiesel. Biodiesel is receiving increased attention as a non-toxic, biodegradable, and renewable diesel fuel. Use of vegetable oil in diesel engines is not a radically new concept (Agarwal and Das, 2001; Recep *et al.,* 2001). It received attention only recently when it was conclusively realized that petroleum fuels are dwindling fast and environment- friendly renewable substitutes must be identified (Sahoo *et al.,* 2007). Several researchers have reported on the production of biodiesel from different seed oil (Canakci and Gerpan, 1999; Encinar *et al*., 2002; Pilar *et al*., 2004).

Transesterification is the chemical reaction between triglycerides and alcohol in the presence of catalyst to produce mono-esters (Sinha *et al*., 2008; Xu *et al.,* 2007). Most of the biodiesel produced worldwide is based on transesterification in homogeneous media with sodium methoxide as the reaction catalyst. The main difficulty for the production of biodiesel from vegetable oil is its high free fatty acid content. To reduce FFA, different pretreatment methods were applied previously. Among them steam distillation, utilization of solid base catalyst, extraction by alcohol and acid catalyst esterification were investigated (Morshed *et al*., 2011; Xu *et al.,* 2007). Comparing different aforementioned pretreatment methods, acid catalyst esterification is preferable one. Solid acid catalyst offers some advantages but the reaction rate is slow (Leung *et al*., 2010). Steam distillation is also not viable for high temperature operation. For the low solubility of FFA in alcohol, the alcohol extraction process is an expensive method (Morshed *et al*., 2011).

The presence of high levels of unsaturation in fatty acid methyl esters (FAME) makes biodiesel very susceptible to oxidation as compared to petroleum diesel (Domingos *et al*., 2007). The degree of unsaturation of MSO is very low. Oleic acid is the only unsaturated fatty acid in the composition of MSO and its relative percentage is less than 1% (Majid *et al.,*

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2004). Oxidative processes bring about increased viscosity as a result of condensation reactions involving double bonds, also leading to the formation of insoluble's, which can potentially plug fuel filters and injection systems (Monyem and Van, 2001). The increased acidity and increased peroxide value as a result of oxidation reactions can also cause the corrosion of fuel system components, hardening of rubber components, and fusion of moving components (Monyem and Van, 2001; Tao, 1995). To combat such problems, oxidation stability study is important.

The mahogany tree grows everywhere in Bangladesh. So the production of biodiesel from mahogany seed oil will be economical for the future energy consumption. The objective of this research work was to optimize the reaction condition for the production of biodiesel from mahogany seeds oil and study the oxidation stability of produced biodiesel. The properties of the MSO and MSO biodiesel such as viscosity, pour point, flash point, density and heating value are measured. According to our literature survey, this is the first approach in Bangladesh for the production of biodiesel from Mahogany *(Swietenia macrophylla)* seed.

Materials and methods

Materials

Mahogany *(Swietenia macrophylla)* seeds were used as raw material to produce biodiesel. The seeds were collected from Pirojpur and Jamalpur districts of Bangladesh. 99.8% Methanol was used in esterification and trans- esterification. NaOH and H_2SO_4 used as catalyst were purchased from Active Fine Chemicals Ltd., Bangladesh. AR grade solvents such as ethanol, diethyl ether, and n-hexane were used.

Extraction of oil

Crude MSO was extracted from Mahogany seeds (80 gm) by Soxhlet extraction for 30 minutes, using n-hexane as solvent. The Mahogany seeds were taken in the tube shaped filter paper which was placed into the Soxhlet with the powder of seeds and hot extraction of oil was done.

Experimental procedure

Fatty acid methyl ester (FAME) was prepared using two step reactions.

Acid-catalyzed esterification

The main objective of acid-catalysed esterification was to reduce the acid value of oils. In this step at first catalyst (H_2SO_4) was mixed with methanol using an agitator. Then the mixture of alcohol and catalyst was charged into a closed three-neck round-bottom flask with raw MSO. Reaction conditions selected for this optimization were 60 °C temperature, 400 rpm agitation rate and time of 90 min. After that, the treated oil was allowed to settle for at least 1 h in a separating funnel and the treated oil was collected as bottom layer.

Base catalyst transesterification

The base catalyst (NaOH) was added into methanol and was stirred until dissolved in the methanol under slight warm condition. Then the pretreated oil was added into the mixture. Reaction was carried out in apparently closed system to prevent the loss of methanol. The reaction mixture was kept below 65^0C (boiling point the methanol) at atmospheric pressure. The reaction time was varied from 30 to 120 min. The mixture was then allowed to settle overnight before separation of the glycerol layer to get FAME on the top. After separation of biodiesel, it was purified, dried and finally stored.

Analytical method

FTIR analysis

FTIR of the MSO and MSO biodiesel were conducted using iRAffinity-1 spectrophotometer, SHIMADZU, Japan in the range of 500-4000 cm^{-1}. The liquid sample was directly used for the analysis.

Elemental analysis

Elemental analysis was done by organic elemental analyzer (Reactor temp. 900 ^{0}C, He: 250 kPa, O_2: 250 kPa, TCD, Flash 2000, Thermo Scientific, USA). This instrument analyzes in accordance with the procedures stated in ASTM Standard D 5291-02.

^{1}H NMR analysis

The ^{1}H NMR spectra were recorded on a BRUKER, AVANCE-III 400 MHz FT-NMR instrument, with chemical shift data reported in ppm relative to the solvent used. The spectra were taken by using$CDCl_3$ solvent.

TGA analysis

TG-DTA 6300 (Exstar 6000), Seiko Instrument Incorporation, Japan was used for thermal stability analysis.

Oxidation stability analysis

The Rancimat 743 (Metrohm, Switzerland) was used to determine the oxidative stability of biodiesel in accordance with the EN14112. Analysis condition: Temperature 110 °C, Delta T 1.5, air flow rate 10L/h. The amount of sample and water used were 3 gm and 60 ml respectively. Tert-Butyl hydroquinone (TBHQ), Propyl-3,4,5-trihydroxy benzoate (PG) and Butyl hydroxyl anisol (BHA) were utilized as antioxidant for this experiment.

Result and discussion

Extraction of oil

Solvent extraction process used to extract the oil from Mahogany seeds. A commonly used solvent, n- hexane was used to carry out the experiment. About 52.08% oil can be extracted from Mahogany seeds.

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	100	4.57	2.29
	30 : 12	30 : 0.36	60	100	3.62	1.81
	30 : 15	30 : 0.36	60	100	0.91	0.46
	30 : 18	30 : 0.36	60	100	0.89	0.45
	30 : 21	30 : 0.36	60	100	0.00	0.00
b	30 : 21	30 : 0.27	60	100	1.80	0.90
	30 : 21	30 : 0.36	60	100	0.90	0.45
	30 : 21	30 : 0.45	60	100	0.50	0.25
	30 : 21	30 : 0.54	60	100	0.00	0.00
c	30 : 21	30 : 0.54	30	100	1.50	0.75
	30 : 21	30 : 0.54	40	100	0.90	0.45
	30 : 21	30 : 0.54	50	100	0.30	0.15
	30 : 21	30 : 0.54	60	100	0.00	0.00
	30 : 21	30 : 0. 54	70	100	0.20	0.10
d	30 : 21	30 : 0.54	60	45	1.60	0.80
	30 : 21	30 : 0.54	60	60	1.20	0.60
	30 : 21	30:0. 54	60	75	0.7	0.35
	30 : 21	30 : 0.54	60	90	0.0	0.00
	30 : 21	30 : 0.54	60	105	0.3	0.15

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	Tem.(°C)	Time (min)	Yield%(Biodiesel)	Yield% (Glycerin)
a	10 : 3	10 : 0.07	60	120	65.53	34.94
	10: 4	10 : 0.07	60	120	85.72	14.28
	10 : 5	10 : 0.07	60	120	92.67	07.33
	10 : 6	10 : 0.07	60	120	90.05	09.95
	10 : 7	10 : 0.07	60	120	80.23	19.77
b	10 : 5	10 : 0.05	60	120	85.75	14.25
	10 : 5	10 : 0.07	60	120	88.20	11.80
	10 : 5	10 : 0.09	60	120	95.21	04.79
	10 : 5	10 : 0.11	60	120	74.27	25.73
c	10 : 5	10 : 0.09	40	120	75.04	24.96
	10 : 5	10 : 0.09	50	120	84.44	15.56
	10 : 5	10 : 0.09	60	120	89.31	10.69
	10 : 5	10 : 0.09	70	120	84.45	15.55
	10 : 5	10 : 0.09	80	120	74.13	25.87
d	10 : 5	10 : 0.09	60	30	86.67	13.33
	10 : 5	10 : 0.09	60	60	93.67	06.33
	10 : 5	10 : 0.09	60	90	97.34	02.66
	10 : 5	10 : 0.09	60	120	69.10	30.90

Acid catalyzed esterification

To reduce the acid value of MSO, the acid catalyst esterification was done. To meet the optimum condition, different variables such as methanol to oil ratio, catalyst to oil ratio, reaction time and temperature were optimized which are shown in Table 2. At the conditions of 100 min of reaction time at 60^{0}C, acid value and FFA were decreased gradually with the increase of methanol percentage in the oil to methanol ratio and met to 0.00 at ratio of 30:21. Then acid catalyst was also varied as a result of which acid value decreased to the optimum range. At the same way the other variables were also varied and optimum conditions were fixed. The optimum reaction condition thus found was 30:21 of oil to methanol ratio; 30:0.54 of oil to catalyst ratio and reaction time of 60 mins at a temperature of 60^{0}C with moderate stirring.

Base catalyzed transesterification

To maximize the biodiesel yield, base catalyst transesterification was optimized. For this different variables such as methanol to oil ratio, catalyst to oil ratio, reaction time and temperature were considered which are shown in Table 3. As oil to methanol ratio was increased, the production of biodiesel was also increased and reached maximum yield (92.67%) at the oil to methanol of 10:5. In case of oil to catalyst ratio, maximum yield of 95.21% was observed at 10:0.09. At the same way the other variables were also varied and optimum condition were fixed. When temperature was employed above 60^0C during transesterification reaction, biodiesel production was seen to decrease. Since methanol's boiling point is 63.7 ^{0}C, at temperature higher than 60^0C reaction between oil and methanol to form sodium methoxide does not proceed efficiently. In addition, 97.34% biodiesel yield was observed for 90 mins reaction time while keeping other variables at their optimum levels. The optimum condition for transesterification was 10:05:0.09 of oil to methanol to catalyst ratio and reaction time of 90 mins at a temperature of 60^0C with moderate stirring.

Table III. Proximate physico-chemical properties of MSO, Jatropha, C. inophyllum Biodiesel with standard biodiesel and Petro-diesel

Name of the Parameter	Method	MSO Diesel	Biodiesel Standard[a]	Jatropha Biodiesel[b]	C. inophyllum Biodiesel[c]	Diesel[c]
Color index	D 1500-64	0.5	-	-	-	-
Density at 15°C, g/cc	IP-160/57	0.88	-	0.88	0.87	-
Kinematic viscosity,	D 445-65 (40°C)	4.18	1.9-6.0	4.8	4.0	1.3-4.1
cSt	D 445-65 (100°C)	4.16	-	-	-	-
Pour point, °C	D 97-57	7.0	-1 5 to 10	2	4.3	-35 to -15
Flash point, °C	D 93-62	120	100-170	135	140	60-80
Acid value, mg KOH/g	IP 1/58	0.02	> 0.08	0.4	1.62	-
Water content, %	IP-74/57	Nil	0.05%	0.025	0.005	0.016
Ash content, %	D 482-63	0.02	-	0.012	-	-
Carbon residue, wt%	D 189-65	0.34	-	0.2	-	-
Heating value, MJ/Kg	IP-12/58	40.13	-	39.230	41.397	-

[a] (Leung et al. 2010), [b] (Ong *et al.,* 2011), [c] (Joshi and Pegg, 2007)

Table IV. The elemental analysis of MSO biodiesel

Sample	N (%)	C (%)	H (%)	S (%)	O (%)
MSO biodiesel	0.00	73.94	11.46	0.00	14.60

Physico-chemical properties of MSO and MSO Biodiesel

The physic-chemical properties of MSO biodiesel was measured according to procedures mentioned in Table III. In conjunction, their values were also compared with that of biodiesel standard (Leung et al. 2010), Jatropha biodiesel (Ong et al. 2011), and C. inophyllum biodiesel and diesel (Joshi and peg, 2007). Kinetic viscosity, pour and flash point, and acid value of MSO biodiesel are well comparable with biodiesel standard as well as other two biodiesels. An exclusive property of MSO biodiesel is its water content, water content was found to be zero in biodiesel derived from Mahogany. Heating value and density (at 15 °C) show little deviation from biodiesel obtained from Jatropha and C.

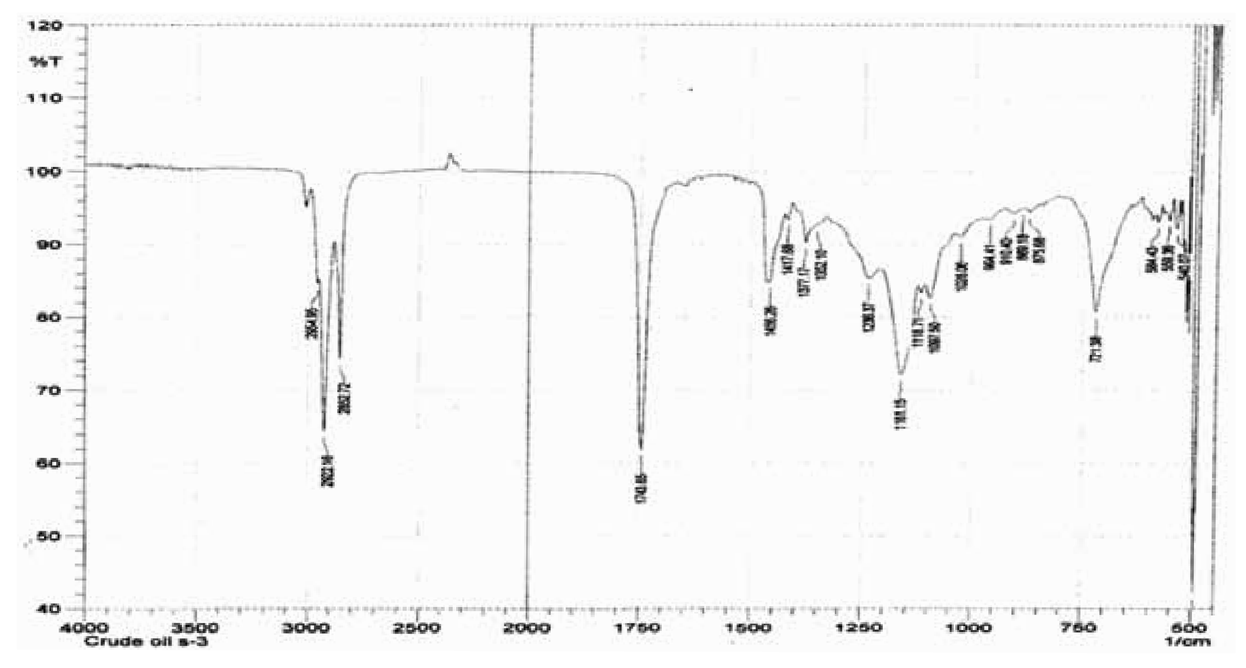

Fig. 1(a). FTIR spectra of crude mahogany seeds oil

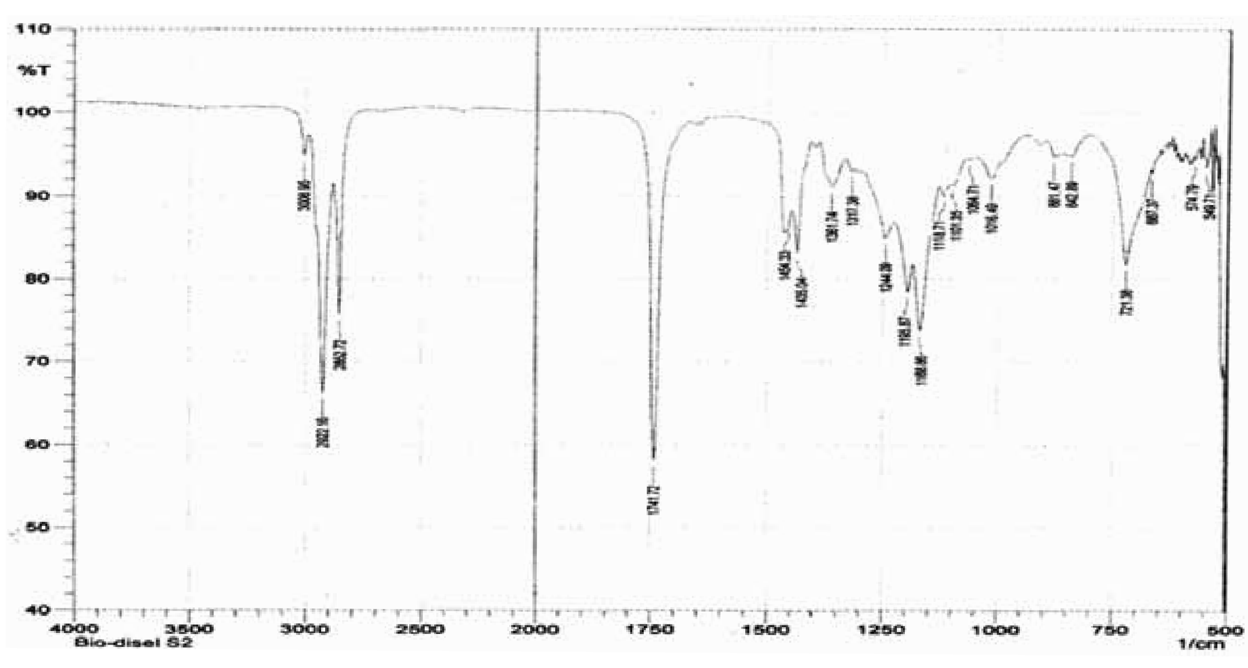

Fig. 1(b). FTIR spectra of mahogany seeds oil biodiesel

inophyllum. Carbon residue of MSO biodiesel is also found to be analogous with that of Jatropha biodiesel. I addition, kinetic viscosity at 40 °C of MSO biodiesel is within the range of diesel standard.

FTIR analysis

FTIR showing the main peaks of the MSO at 1743 cm^{-1} for the ester carbonyl (>C=O) groups (Fig. 1a) and for MSO biodiesel carbonyl peak appeared 1741 cm^{-1} (Sylvester *et al.,* 2013). The most characteristics peak for FAME appeared at 1435 cm^{-1} which represents methoxy (CH_3-O) group (Fig. 1b) (Sylvester *et al*., 2013). C=C double bonds absorption band appeared in the region 1435-1454 cm^{-1} (Sylvester *et al*., 2013).

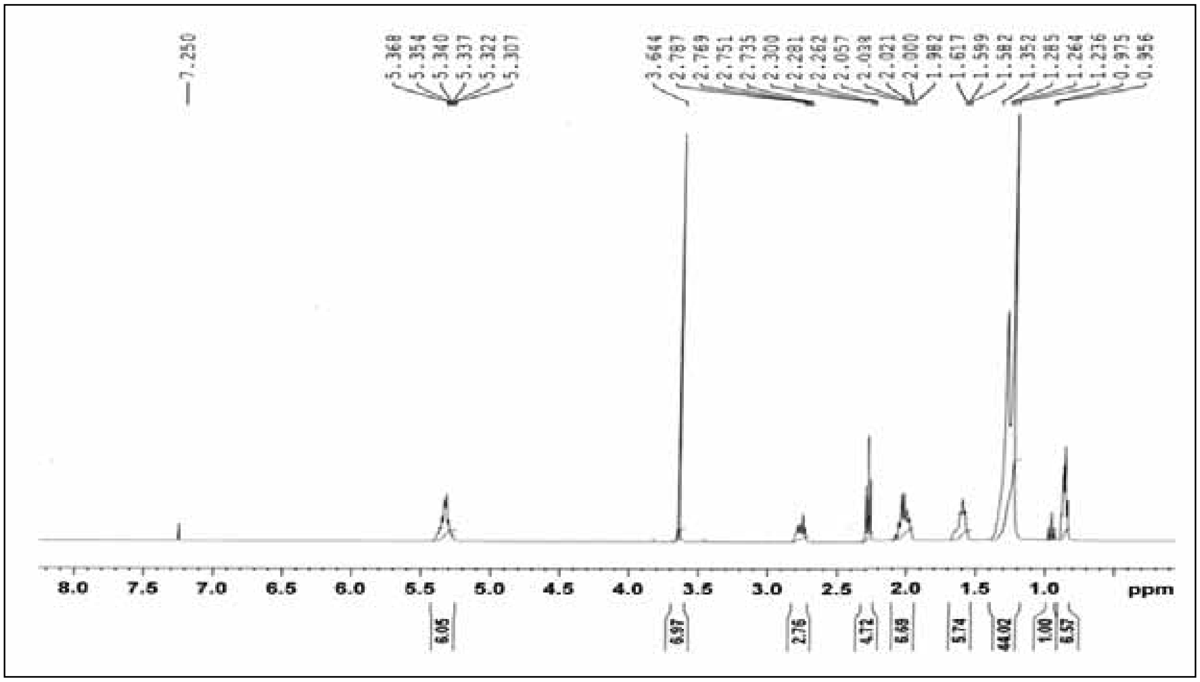

Fig. 2. Proton NMR of the MSO biodiesel

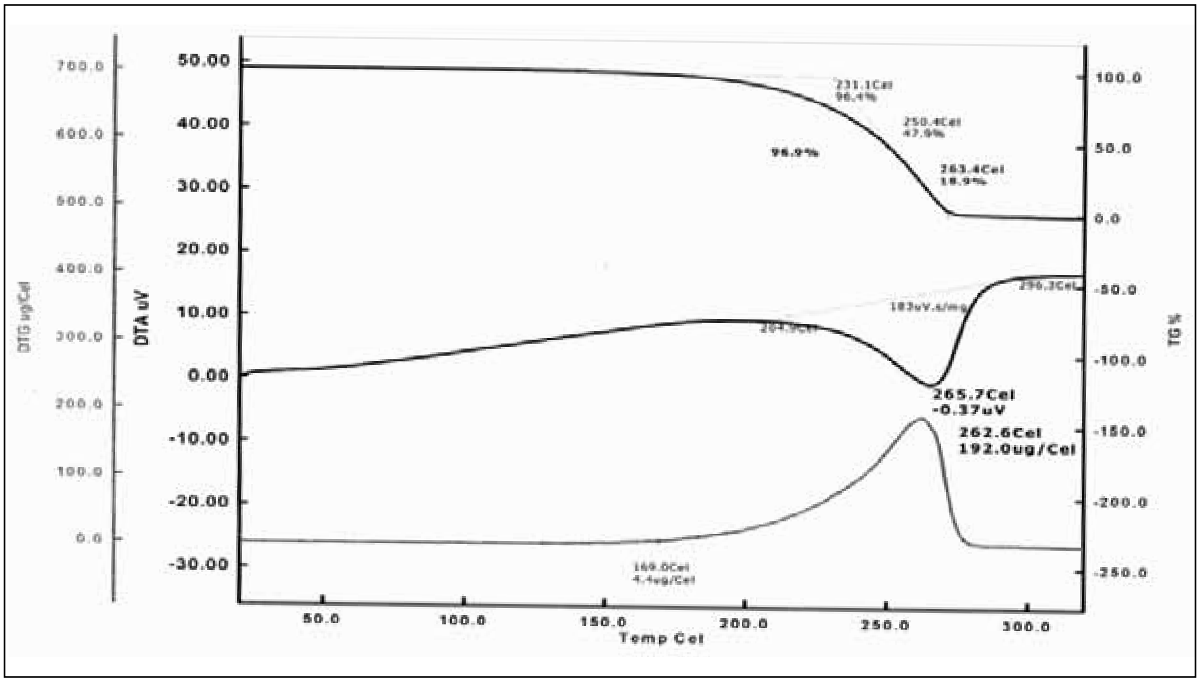

Fig. 3. Thermogravimetric curves of MSO biodiesel

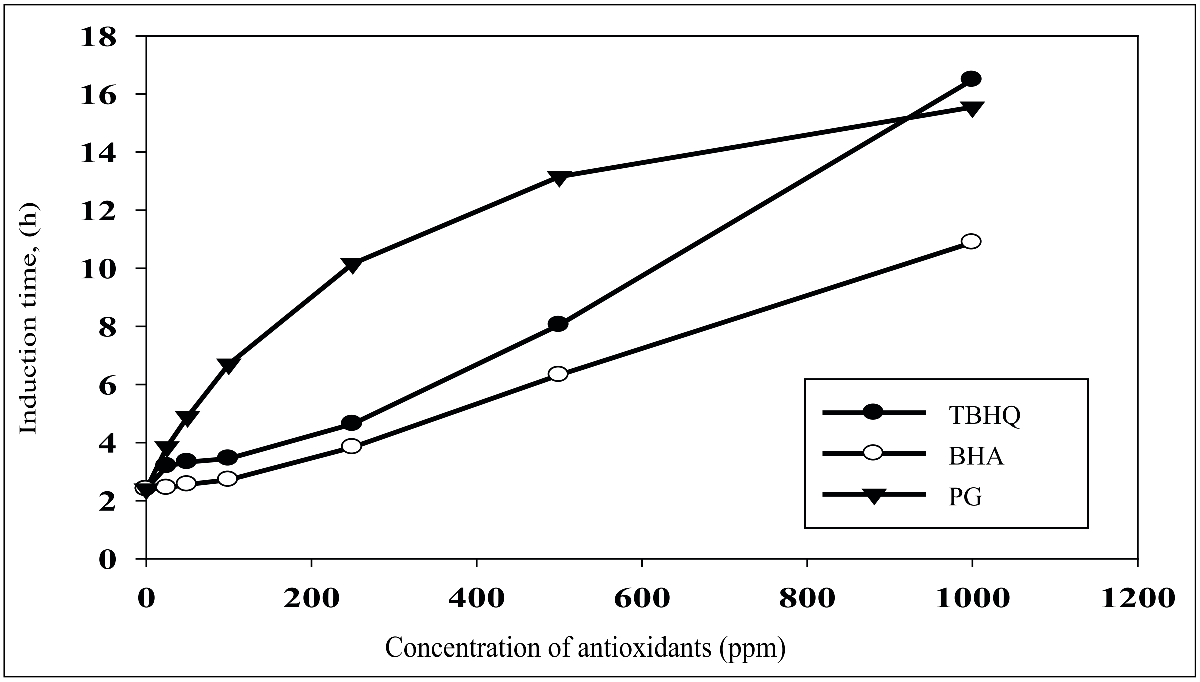

Fig. 4. Oxidation stability test by using phenolic antioxidant

Elemental analysis

The absence of sulphur and nitrogen in MSO biodiesel indicates it is to be an environmentally benign fuel (Table 4). As obtained in elemental analysis, carbon, hydrogen and oxygen presents were 73.94%, 11.46% and 14.60% respectively. This analysis leads to the empirical formula of MSO biodiesel as $C_7H_{13}O$.

Proton NMR analysis

The ^{1}H NMR spectrum of MSO biodiesel is shown in Fig-2. The multiplet at δ 5.31-5.36 ppm represents the olefinic protons (-CH=CH-). A singlet at δ 3.65 ppm is representing methoxy protons of the ester functionality of the biodiesel. The bis-allylic proton signal of polyunsaturated fatty acid (like linoleic acid) generally appears around at δ 2.8 ppm. So, the multiplet at δ 2.76 ppm indicates the bis-allylic protons ($-C=HC-CH_2-CH=C-$) of the unsaturated fatty acid chain. The triplet at δ 2.26-2.30 ppm represents the α-methylene protons of ester ($-CH_2-CO_2Me$). The α-methylene protons of double bond ($-CH_2-C=C-$) and β-methylene protons of ester (CH_2-C-CO_2Me) are both appear as multiplet at δ 1.99-2.05 ppm and δ 1.59-1.62 ppm respectively. The terminal methyl protons at δ 0.95-0.97 ppm appear as multiplet. The singlet at δ 3.65 ppm indicates the methoxy protons of the ester which is the evidence of conversion of biodiesel from mahogany oil.

TGA analysis of MSO biodiesel

TGA curves of biodiesel showed three steps, where the first weight loss started to decrease at approximately 231.1°C that attributed to a boiling point of biodiesel, the second one started to decrease at 250.4ºC and it was attributed to boiling point of the esters with unsaturated bonding, and the third step started to decrease at 263.4ºC, and it may be due to some Mahogany oil that was not transesterified (Fig. 3).

Oxidation stability

Fig. 4, shows that oxidation stability as induction period (IP) increased distinctly of FAME with the addition of phenolic antioxidants than blank FAME (IP = 2.4 h). BHA shows 6.0 h and 10.9 h oxidation stability at the concentration 500 ppm and 1000 ppm respectively which is met the EN and WWFC biodiesel standard. TBHQ shows better performance than BHA because TBHQ has two hydroxyl groups present in aromatic ring where as one hydroxyl group in BHA. 6.0 h oxidation stability reached in 350 ppm TBHQ concentration.

Especially, the addition of PG is very effective for improvement of oxidation stability in the lower concentration due to three hydroxyl group in the aromatic ring. PG achieved 6.0 hand 10.0 h oxidation stability as IP in the concentration 78 ppm and 240 ppm, respectively, which can easily met desired IP according to EN and WWFC standard. 16.49 h IP is shown by TBHQ in 1000 ppm concentration which is higher than BHA and PG in the same antioxidant concentration. In the higher concentration, TBHQ showed better results than BHA and PG. Because TBHQ contains two hydroxyl groups and only one tert-butyl group so there less steric hindrance was occurred than PG and BHA.

Conclusion

In this research work, by solvent extraction 52% oil was extracted from Mahogany seed. By comparing with other non-edible sources, the oil content is high. The FFA content of MSO is 3% which makes the pretreatment process easier for the reduction of acid value. The optimum conditions for transesterification reaction were oil to methanol and oil to catalyst (NaOH) of 10:5 and 10:0.09 respectively; reaction time of 90 min at a temperature of 60 °C with moderate stirring. About 89-97% biodiesel was seen to produce in these conditions. The physic-chemical properties of MSO biodiesel are comparable with that of standard diesel and biodiesel. The conversion of MSO to MSO biodiesel was confirmed by ^{1}H NMR spectrum, TGA and FTIR analysis. Elemental analysis shows the absence of sulfur and nitrogen which indicates eco-friendly biodiesel. TBHQ at 1000 ppm has shown the highest induction time of 16.49 hr at 110 °C. This study indicates that MSO is a potential source of biodiesel.

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