Available online at www.banglajol.info

Bangladesh J. Sci. Ind. Res. **50(2)**, 135-142, 2015

BCSIR

BANGLADESH JOURNAL OF SCIENTIFIC AND INDUSTRIAL RESEARCH

E-mail: bjsir07@gmail.com

Production of bio-diesel from Pithraj (*Aphanamixis polystachya*) seed oil

S. K. Banik[1], M. A. Rouf[1]*, M. Khanam[1], M. S. Islam[1], T. Rabeya[1], F. Afrose[2] and D. Saha[2]

[1]*Institute of Fuel Research and Development, BCSIR, Dr. Qudrat-i- Khuda Road, Dhanmondi Dhaka-1205.*
[2]*Department of Applied Chemistry and Chemical Engineering, University of Dhaka, Bangladesh.*

Abstract

The Pithraj seed has been collected from Gazipur district, Bangladesh. The oil from the seed was extracted by using Soxhlet apparatus using petroleum ether extraction method. Maximum yield of oil was found to be 50 % when the process was carried out for 2.5 hours. The physico-chemical properties of the extracted oil were studied. The properties of the oil reveal that the oil corresponds to diesel except acid value and sulphur content. The optimum conditions of the transesterification of the oil was 40% ethanol and 0.45% KOH at 75 ^{0}C for 1.5 hours. The optimum yield was more than 95 %.

Keywords: Pithraj seed; Biodiesel; Transesterification

Introduction

The current fossil fuel-based economy is not sustainable because of environmental impacts, economic dependence and energy security issues. Today 86% of the world energy consumption and almost 100% of the energy needed in the transportation sector is met by fossil fuels (Dorian *et al.*, 2006). The production and consumption of fossil fuels have caused the environmental damage by increasing the CO_2 concentration in the atmosphere (Westermann *et al.*, 2007). One-fifth of the global CO_2 emissions are created by transport sector (Goldemberg, 2008), which accounts for some 60% of global oil consumption (Anonymous, 2008). Around the world there were about 806 million cars and light trucks on the road in 2007 (Anonymous, 2007). These numbers are projected to increase by 1.3 billion by 2030 and to other 2 billion vehicles by 2050 (Anonymous, 2004). These growths will affect the stability of ecosystems and global climate as well as global oil reserves (Balat, 2009). There are active research programs to reduce on fossil fuels by use of

alternative and sustainable fuel sources and thus to increase the time over which fuel will still be available (Namasivayam *et al.,* 2010). As an alternative to petroleum based transportation fuels, bio-fuels can help to reinforce energy security and reduce the emissions of both green house gases (GHSs) and urban air pollutants.

At present bio-diesel is a suitable renewable substitute for petroleum based diesel. Pithraj seed oil is easily available in many parts of the world including Bangladesh and is very cheap compared to other sources. The non-edible renewable pithraj *(Aphanamixis polystacya)* oil can play a vital role in the cultivation of alternative substitute to diesel fuel. The climate and soil condition of Bangladesh is also suitable for the cultivation of this plant. Literature shows that the yield of oil from pithraj seed is about 40-45% which is higher compared to other non-edible seeds like rubber seed (31.8%) and others (Gui *et al.*, 2008). If the developed process is scaled up to commercial levels, then excellent business opportunity will be offered by the bio-diesel and could be a major step towards the creation of an eco-friendly transportation fuel. By increasing pithraj plantation in Bangladesh, we can meet our demand. Finally, the by-product of transesterification can also be used in the soap industry. The present investigation includes: preparation of bio-diesel from pithraj seed oil, optimization of different parameters for maximum bio-diesel production, determination of properties of pithraj seed oil and prepared bio-diesel and comparison of the fuel properties of conventional diesel with prepared bio-diesel.

Materials and methods

Oil Extraction

Pithraj seeds were purchased from local market of Gazipur, Bangladesh and dried properly in the sun for several hours and then grinded. Then ground powder was screened to separate the coarse ones and which was again grinded for homogeneous. Extraction of oil from the powders using petroleum ether as solvent was then carried out in Soxhlet apparatus at 60-80 ^{0}C and at reflux temperature of solvent. After extraction of oil, the solvent petroleum ether was separated and solvent-free oil was obtained. The oil was found to be viscous and dark brown in color. The oil was directly used as main raw material for bio-diesel production. The properties of the oil were then determined and recorded.

*Corresponding author. e-mail: roufmd@yahoo.com

Determination of the fatty acids and fats

The acid value of the reaction mixture was determined by a standard acid-base titration method using a standard solution of 1.0 M KOH solution. Biodiesel productions prior to transesterification, acid esterification of the oil was required to reduce (~57%) the free fatty acid. The ethanol and catalyst conc. H_2SO_4 mixture was then charged into a 2-neck closed reaction vessel and the raw oil was added. The reaction temperature was around 70 ^{0}C at agitation rate 400 rpm for 2 hours. After completion of transesterification, ethyl ester was separated from mixture of ethyl ester and glycerin. The mixture was taken in a separating funnel and left for 16 hours. The mixture was separated in two layers, bio-diesel as the top layer and glycerin as bottom layer. Glycerin layer was withdrawn and required product was obtained. Washing of bio-diesel is necessary to remove the soluble components. Hot water was sprayed on top of the bio-diesel. Then it was allowed to settle down. The product was dried using a vacuum evaporator at 80 ^{0}C and pressure was 180 atm. pressure. After drying the product became clear. After purification of bio-diesel, the fuel properties of bio-diesel were determined by laboratory method. To determine the properties of bio-diesel produced from Pithraj seed oil, different ISO standard methods were used.

Other parameters

All the parameters for fuel properties were estimated by ISO standard methods such as density at 15 ^{0}C by IP 131/57 method, colour index by ASTM & DIN 51900 method, kinematic viscosity by viscometer 73/53 method, pour point by ASTM D 97-57, IP 15/55 method, flash point by ASTM D 93-62 method, sulphur content by IP 61/59 method, water content by IP 74/57 method, carbon residue by ASTM D 189-65 method, ash content by IP 4/58 method, acid value by IP 1/58 method, calorific value by bomb calorimeter IP 12/58, corrosion by IP 154/59, fire point by IP 35/42 methods.

Results and discussion

Optimization to extraction of oil

After extraction of Pithraj seed oil by solvent extraction method, optimization of the method was performed. (Table I), it is clear that, higher percentage of oil per gram of sample was obtained when the extraction process was conducted with an excess of solvent. In addition, the extraction also requires an excess of time. An optimized point considering both amount of solvent and time for maximal yield of oil was obtained. when 600 mL of solvent was used and the process was carried out for 2.5 hours.

Table II. Properties of the pithraj seed oil

Parameters	pithraj seed oil
Color Index	0.5
Density @ 15 ^{O}C, g/cc	0.8473
Kinematic Viscosity @ 40 ^{O}C, cSt	2.0304
Kinematic Viscosity @ 100 ^{O}C, cSt	0.9676
Pour Point, ^{O}C	< -18
Flash Point, ^{O}C	30
Fire Point, ^{O}C	40
Sulfur Content, % (w/w)	8.091
Cetane Number	-
Water Content, % (v/v)	Nil
Carbon Residue, % (w/w)	0.0593
Ash Content, % (w/w)	0.00255
Acid Value, mg KOH/g	56.4
Calorific Value, kcal/kg	9368.3463

Table I. Extraction of pithraj seed oil by solvent extraction method

Sample weight (g)	Solvent (mL)	Solvent recovered (mL)	Oil extracted (g)	Oil volume (mL)	Oil content (wt %)	Time (minutes)
87.0030	800	420	21.6689	23.95	24.91	60
85.4241	800	345	28.1671	31.13	32.97	60
99.7364	600	320	44.2030	48.86	44.32	60
85.6348	600	235	43.1432	47.69	50.38	150
36.7771	500	370	14.7100	16.26	39.98	150
45.7945	400	355	21.9800	24.29	48.00	150
29.0465	300	170	14.1663	15.66	48.77	150

Physicochemical properties of Pithraj seed oil

After extraction of oil from Pithraj seeds, the physicochemical properties of the oil were determined according to the standard procedure. Table II. shows the properties of the Pithraj seed oil.

Effects of different factors on production of biodiesel

Bio-diesel was produced using Pithraj seed oil by transesterification process. The yield of bio-diesel depends on a number of factors which affect the transesterification reaction.

Effect of change of ethanol to product yield

The effect of change of molar ratio of ethanol to oil was optimized. The amount of catalyst KOH was kept constant at 1 % of oil. The temperature was fixed at 60-65 ^{0}C. Under this condition the percentage of ethanol was varied to get maximum yield of biodiesel (Table III).

Table III. The effect of variation of oil to ethanol ratio on product yield

pithraj oil (g)	Ethanol (% of oil)	KOH (% of oil)	Product (g)	Yield (%)
5.00	20	1	3.163	63.26
5.10	25	1	3.867	75.82
5.00	30	1	4.321	86.42
5.00	35	1	4.678	93.55
5.10	40	1	5.036	98.75
5.04	45	1	4.192	83.17

It is found that with the increase of ethanol on percent weight of oil, the percent yield of biodiesel also increases up to about 99 %. Further addition of ethanol the percent yield of biodiesel decreased. The optimum amount of ethanol to get maximum yield of biodiesel was about 40% of the weight of oil taken. The optimization of ethanol for maximum biodiesel yield is shown in (Fig. 1).

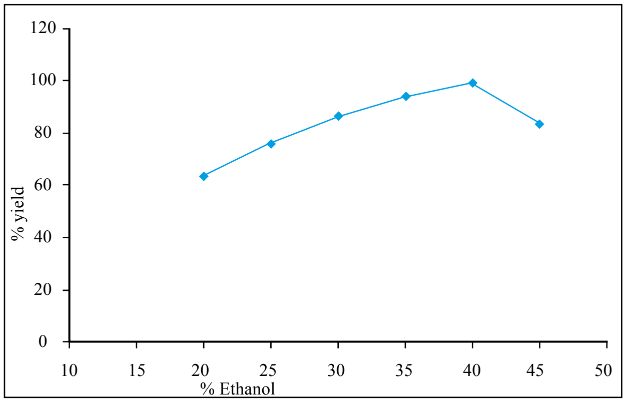

Fig. 1. Effect of variation of ethanol percent on product yield

Effect of variation of catalyst to product yield

To optimize the amount of KOH the percentage of ethanol was maintained at 40 % of ethanol on the wt % of oil taken. The temperature was also kept constant. In this condition, the reaction were carried out with KOH catalyst at concentrations 0.15, 0.25, 0.35, 0.45, 0.55, 0.65 and 0.75 % in order to determine optimum condition for the biodiesel production from the oil. The maximum yield of biodiesel was found to be at 0.45 % KOH concentration as shown in (Fig. 2).

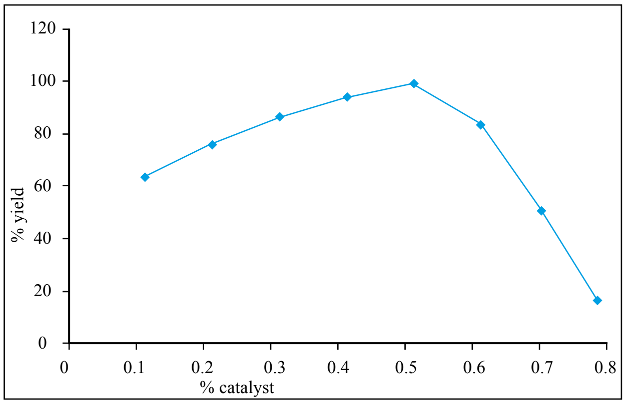

Fig. 2. Effect of change of catalyst percent on yield of Bio-diesel

Effect of variation of temperature on product yield

For the optimization of temperature, the percentage of catalyst and ethanol under maximum liquid condition considered constant and the temperature were found to be varied. The biodiesel production by transesterification was also studied at 55, 60, 65, 70, 75 and 80 ^{0}C. The maximum yield of bio-diesel was obtained when the temperature of reaction

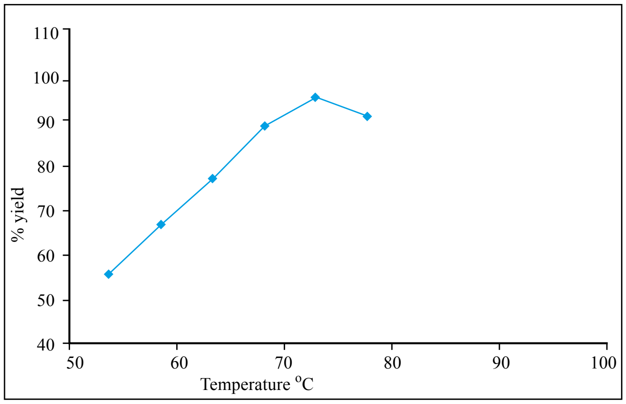

Fig. 3. Effect of Temperature on % yield of Bio-diesel

system was maintained at 75 ^{0}C which is just below the boiling point of ethanol as shown in (Fig. 3). Further increase of temperature caused the yield to decrease because the ethanol started to boil and became separated from the reaction system.

Effect of variation of reaction time on product yield

All variables except reaction time were kept constant in their optimum value. The transesterification reaction was continued for different period of time such as 30, 60, 90 and 120

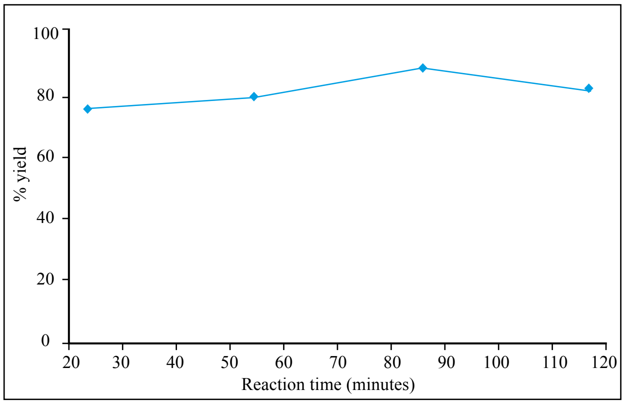

Fig. 4. Effect of Reaction time on the % yield of Bio-diesel

minutes respectively. Then the product yield was observed. The result of this optimization is shown in (fig. 4). It is found that with the increase of duration of reaction, the yield of bio-diesel shows increasing phenomena, eventually increase to give maximum yield about 94 %. when reaction took one 1.5 hours.

Although, further reaction time should raise the conversion percentage, it actually caused to decrease in yield %. The reason might be prolonged time of stirring, that cause problem in phase separation. Moreover, the longer duration of a reaction process was not considered feasible.

The optimum conditions for biodiesel production from pithraj seed oil can be summarized as follows: The overall transesterification reaction requires about 40% of ethanol on the basis oil taken; catalyst (KOH) with a concentration is 0.45% of the oil and a fair reaction time of 1.5 hours at a temperature of 75 ^{0}C with moderate stirring rate. The optimum yield is more than 95 %.

Characteristics of bio-diesel from Pithraj seed oil

The bio-diesel obtained was then characterized by the established methods. Table IV describes the fuel characteristics of bio-diesel from pithraj seed and also gives a comparison of obtained bio-diesel with conventional diesel fuel.

FTIR analysis

To determine the functional group of extracted pithraj seed oil, FTIR Spectroscopic analysis method was employed (Fig. 5.). Appropriate quantities of KBr and pithraj seed oil (in the ratio of 100:0.1) were mixed by grinding in an agate mortar

Table IV. Comparison of the fuel properties of obtained bio-diesel and conventional diesel

Test Parameter	Bio-diesel standard	Prepared bio-diesel	Commercial bio-diesel
Density at 15 °C g/mL	0.88	0.873	0.8445
Kinematic Viscosity @ 40 °C, cSt	1.9 - 6.0	2.416	6.06
Kinematic Viscosity @ 100 °C, cSt	-	1.764	-
Pour Point, °C	-15 - 16	-8	-10
Flash Point, °C	100 - 170	153	70
Acid Value, mg KOH/g	0.80 max	0.58	0.34
Sulphur Content, % (w/w)	0.5	1.5	0.905
Cetane Number	48 - 60	51	51
Water Content, % (v/v)	0.05	nil	Nil
Carbon Residue, % (w/w)	0.05 max	0.82	-
Ash Content, % (w/w)	0.02 max	Nil	-
Calorific Value, kcal/kg	9231	10027	10664

and pellets were made with about 100 mg mixture. FTIR spectra were recorded with FTIR 8400S Shimadzu Spectrophotometer in the range of 4000-400 cm^{-1}. Resolution was kept at 2 cm^{-1} and the no. of scan was 30 times. The major peaks are in the region of 1710.89 cm^{-1} and 2925.10 cm^{-1}. So FTIR spectroscopic analysis shows that the main functional groups of pithraj seed oil are carboxylic acid (C=O) appears as main peak in 1710.89 cm^{-1} region and alkanes (C-H) that appears in 2853.73-2925.10 cm^{-1} (Table V).

Functional group analysis of Pithraj seed oil bio-diesel

Functional group analysis of the obtained bio-diesel was determined by the same method (Fig. 6) which was performed for pithraj seed oil. The ratio of KBr and bio-diesel was 100:0.1. Major peaks are at 1743.68 cm^{-1}, 2854.70 cm^{-1} and 2929.06 cm^{-1}. So the main functional groups of pithraj seed oil biodiesel are ester (C=O) appeared in 1743.68 cm^{-1} and sp^3 alkyl (C-H) that appears in 2800-3000 cm^{-1} region (Table VI).

Thermo-gravimetric analysis

Thermo-gravimetric Analysis is a technique in which the mass of a substance is monitored as a function of temperature or time as the sample specimen is subjected to a controlled temperature program in a controlled atmosphere. An alternative definition of TGA can be stated as, TGA is a technique in which upon heating a material, its weight increases or decreases. A simple TGA ent. A TGA thermal curve is displayed from left to right (Fig.7). The descending TGA thermal curve indicates a weight loss occurred.

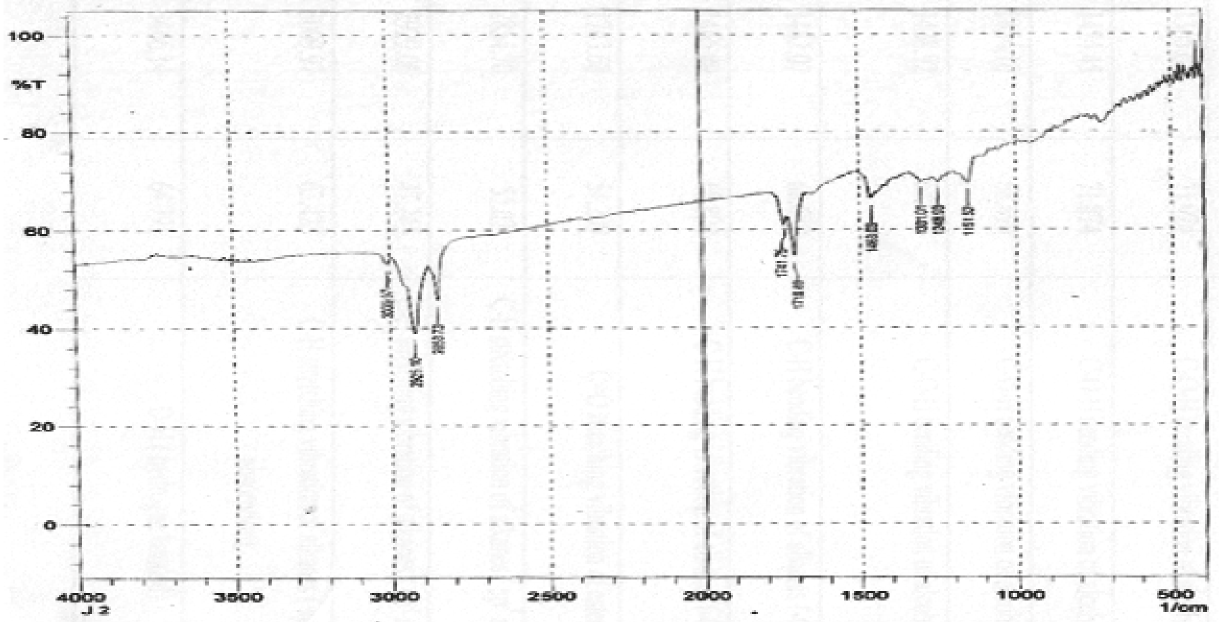

Fig. 5. FTIR spectra of pitraj seed oil

concept to remember is TGA measures a sample's weight as it is heated or cooled in a furnace. In TGA, a derivative weight loss curve is used to tell the point at which weight loss is most appar-

The results from TGA experiments of produced biodiesel are shown in the temperature vs. TGA % curve in a wide temperature range (40-600 ^{0}C). At higher temperatures

Table V. Analysis of peak obtained in FTIR of pithraj seed oil

Wave number of peak	Transmittance	Functional group
1151.52	69.503	C-O stretching vibration of ester
1248.93	69.791	C-O stretching vibration of ester
1301.01	69.861	C-O stretching vibration of ether
1463.03	66.183	C-H bending vibration of alkanes
1710.89	54.688	C=O stretching vibration of carboxylic acid
1741.75	61.068	C=O stretching vibration of aliphatic ester
2853.73	45.753	C-H stretching vibration of alkanes
2925.10	38.937	C-H stretching vibration of alkanes
3009.97	53.046	C-H stretching vibration of alkenes

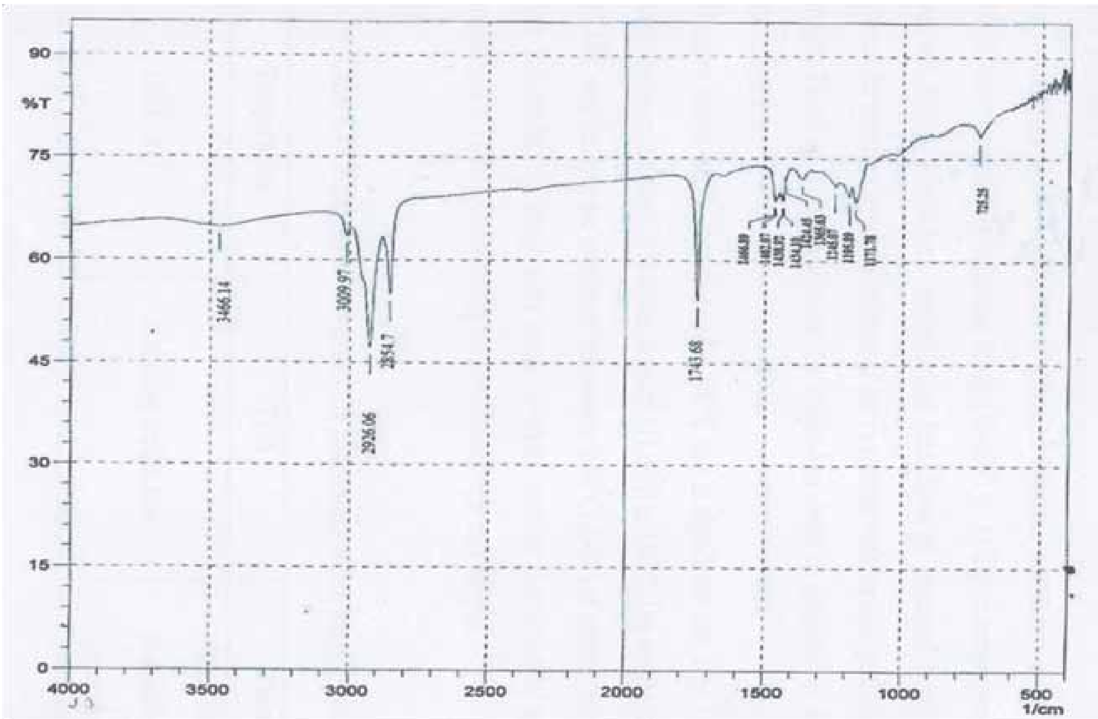

Fig. 6. FTIR spectra of produced bio-diesel from pitraj seed oil

Table VI. Analysis of peak obtained in FTIR of pithraj seed oil bio-diesel

Wave number of peak	Transmittance	Functional group
725.25	78.19	C-H aromatic bending vibration (for mono sub'd ring)
1171.78	68.552	C=O stretching vibration for alcohols
1195.89	69.364	C-O stretching vibration of esters
1245.07	70.834	C-O stretching vibration of esters
1365.63	71.924	C-O-H bending vibration of alcohols
1424.45	71.874	C-O-H bending vibration of alcohols
1434.10	68.699	C-O-H bending vibration of alcohols
1438.92	68.792	C-O-H bending vibration of alcohols
1462.07	68.682	C-H bending vibration of alkanes ($-CH_2-$)
1466.89	68.804	C-H bending vibration of alkanes ($-CH_2-$)
1743.68	54.209	C=O stretching vibration of esters
2854.70	55.02	C-H stretching vibration of alkanes (sp^3 absorption)
2929.06	47.245	C-H stretching vibration of alkanes (sp^3 absorption)
3009.97	63.423	C-H stretching vibration of alkanes (sp^2 and sp absorption)
3466.14	64.791	O-H (hydrogen bonded)

(>400 ^{0}C), all materials display weight-loss, involving the breakdown of structural bonds. The similarity between the onsets of structural collapse is put in contrast with variable positions of evaporation process. Therefore in this experiment the weight-loss could be attributed to the breakdown of structural bonds.

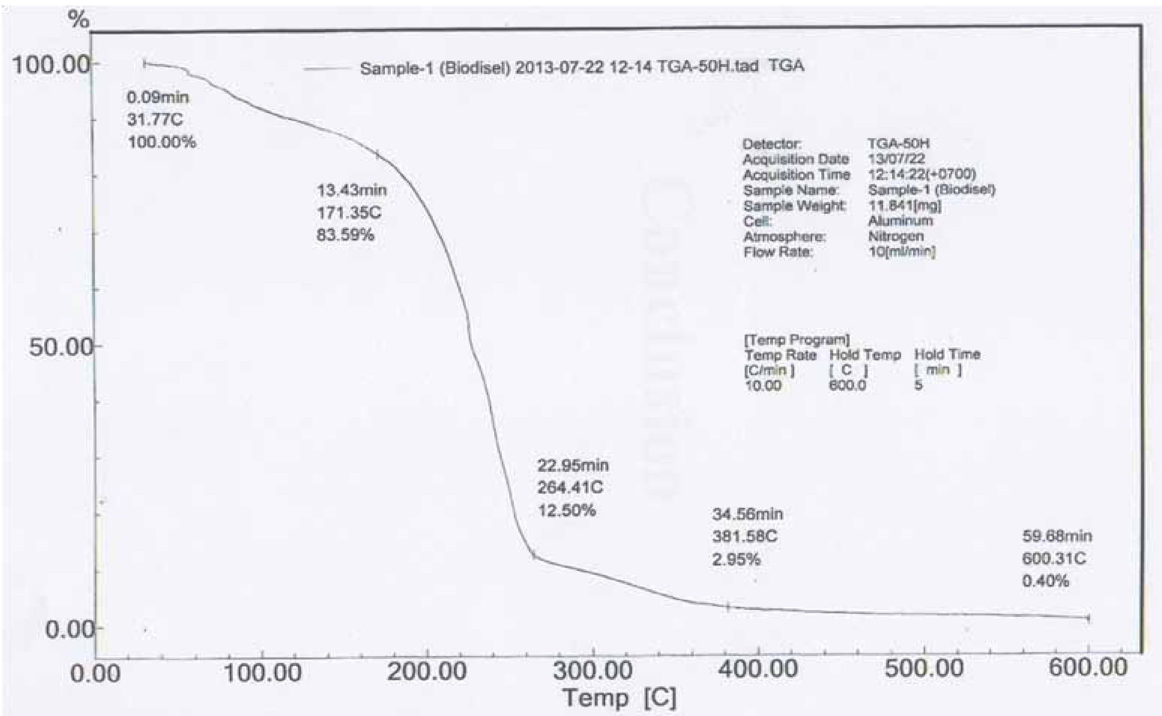

Fig. 7. Thermo Gravimetric Analysis (TGA) of produced bio-diesel

TGA curve (Fig. 8.) shows weight loss starts after 100 ^{0}C and in significant rate after 170 ^{0}C. Maximum weight loss occurs almost 71 % in the range of 171 ^{0}C to 264 ^{0}C. The weight becomes steady at 381 ^{0}C and finally at the maximum temperature (600 ^{0}C) 0.40 % of sample remains.

Conclusion

The Pithraj tree is available in different parts of Bangladesh. Particularly it abundantly grows in Bangladesh. The percentage of oil in its seed is higher (50%) compare to other non-edible seeds of bio-diesel such as rubber (31.8%) seed. The optimum condition for transesterification is 40 % ethanol and 0.45 % KOH catalyst and the reaction temperature and time is 75 ^{0}C and 1.5 hrs respectively. The physicochemical properties of the base oil are correspond to diesel except acid value and sulphur content. But after transesterification the oil became suitable to use as a substitute of diesel. Bangladesh does not have any petroleum resources, so this type of renewable fuel will be very helpful to solve our present fuel oil crisis.

References

Anonymous, Plunkett's automobile industry almanac (2008), Automobile, truck and specialty vehicle industry market research, statistics, trends & leading companies, Huston (Texas), Plunkett research Ltd.

Balat M and Balat H (2009), Recent trends in global production and utilization of bioethanol fuel, *App. Energy*, **86:** 769-778.

Balat M and Balat M (2009), Political economic and environmental impact of biomass based hydrogen, *Int. J. Hydrogen Energy*, **34:** 3589-3603.

Chhetri AA, Tango MS, Budge SM, Watts KC and Islam MR (2008), Non-edible plant oils as new sources for bio-diesel production, *Int. J. Mol. Sci.*, **9:** 169-180.

Demirbas A (2008), Bio-fuels sources, bio-fuel policy, bio-fuel economy and global bio-fuel projections, *Energy Convers. Manage*, **49:** 2106-2116.

Dorain JP, Franssen HT and Smbeck DR (2006), Global challenges in energy, *Energy Policy*, **34:** 1984-1991.

Goldemberg J (2008), Environmental and ecological dimensions of bio-fuels, *Int. Conference on the ecological dimensions of bio-fuels*, Washington (DC).

Gui MM, Lee KT and Bhatia S (2008), Feasibility of edible oil and vs non-edible oil vs waste edible oil as bio-diesel feed stock, *Energy,* **33:** 1646-1653.

International Energy Agency (IAEA) (2008), Key world energy statistics, OECD/IAEA, Paris.

Namasivayam AM and KorakianitisT, Crookes RJ, Bob-Manuel KDH and Olsen J (2010), Bio-diesel: Emulsified bio-diesel and dimethyl ether as pilot fuels for natural gas fuelled engines, *Appl. Energy*, **87:** 769-778.

Wstermann P, Jorgensen B, Lange L, Ahring BK and Christensen CH (2007), Maximizing renewable hydrogen production from biomass in a bio/catalytic refinery, *Int. J. Hydrogen Energy*, **32:** 4135-4141.

World Business Council for Sustainable Development (WBCSD) (2004), Mobility 2030: meeting the challenges to sustainability, The sustainable mobility project, Geneva (Switzerland).

Received: 08 January 2014; Revised: 15 December 2014; Accepted: 22 December 2014.