



***Pithecellobium monadelphum* Kosterm:
A non-edible feedstock for biodiesel production**

Sanjay Basumatary

Department of Chemistry, Bineswar Brahma Engineering College, Kokrajhar, Assam, India

ABSTRACT

Pithecellobium monadelphum seed oil was extracted and transesterification was carried out using methanol as the solvent in presence of a catalyst to produce biodiesel. The acid value of crude oil of *Pithecellobium monadelphum* Kosterm seed was estimated as 0.968 mg KOH/g and that of biodiesel was found to be 0.073 mg of KOH/g which is far below the specified maximum limit of ASTM D6751 and EN 14214. The value of refractive index and density decreases when the seed oil is converted to biodiesel. Predictions of three important chemical properties of biodiesel viz. iodine value, saponification number and cetane index were performed following theoretical calculation based upon fatty acid profile of *P. monadelphum* biodiesel and found to meet the necessary biodiesel standards of ASTM D6751 and EN 14214.

Key words: *Pithecellobium monadelphum* Kosterm, non-edible oil, *Musa balbisiana* Colla, transesterification, biodiesel.

INTRODUCTION

The conventional energies, meant for human activities, are mainly derived from fossil fuels which are depleting rapidly as energy consumption is increasing due to rapid population growth and economic development and consequently the prices of crude oils are becoming high. One potential alternative to fossil fuels is biodiesel that is derived from oils or fats containing triglycerides and can be converted to fatty acid methyl esters (FAME) by esterification or transesterification with methanol in presence of a catalyst (acid, base and enzyme) [1-7]. It can be obtained from a variety of feedstocks viz. edible and non-edible vegetable oils, animal fats, waste frying oils, waste cooking oils and microalgal oil [8-18]. Of these, non-edible oils have been attracted as cheaper and economically viable alternative feedstocks for biodiesel production. Therefore, searching alternative biodiesel feedstocks like non-edible vegetable oils is very attractive for biodiesel industries in near future.

Pithecellobium monadelphum Kosterm (called *Maj* in Assamese, **Fig. 1**) is a huge woody tree which grows as high as 50 metres or even more. The tree produces circular and flat seeds (**Fig. 2**) which are small in size but large in number. The seed has thin kernel covers which could not be dehusked easily and considered negligible. Oil content of the seeds with skiny cover is estimated at about 10 wt.% [5]. The chemical composition of biodiesel from *Pithecellobium monadelphum* seed oil determined by GC-MS analysis was reported [5] and the biodiesel consists of six fatty acid methyl esters and identified as 29.44 wt.% of methyl palmitate (C16:0), 38.91 wt.% of methyl linoleate (C18:2), 18.77 wt.% of methyl oleate (C18:1), 6.85 wt.% of methyl stearate (18:0), 2.87 wt.% of methyl arachidate (C20:0) and 3.13 wt.% of methyl behenate (C22:0). The linoleic acid is the major fatty acid followed by palmitic acid and oleic acid. Stearic, arachidic and behenic acids are present as minor constituents.

The present study deals with the synthesis of biodiesel from *Pithecellobium monadelphum* seed oil by transesterification with methanol using a catalyst and investigation of some properties of the biodiesel formed by employing some experimental and theoretical methods.



Fig. 1. *Pithecellobium monadelphum* tree



Fig. 2. *Pithecellobium monadelphum* seed

MATERIALS AND METHODS

Materials

Pithecellobium monadelphum Kosterm seeds were collected from Bongaigaon District of Assam, India during its availability of the season. The seeds were dried in sunlight and the kernel crushed using a grinder prior to oil extraction. Methanol used was of analytical grade (Merck, Mumbai, India). All other solvents and chemicals used were of analytical grade, and they were procured from commercial sources and used as such without further treatment.

Oil Extraction

Crushed kernel in petroleum ether (bp 40-60 °C, 10 mL/g) was magnetically stirred at room temperature (22-23 °C) for 3 h, filtered and solvent was removed at 45 °C using a rotary vacuum evaporator to yield the crude oil. The oil was purified prior to transesterification done, by column chromatography over silica gel (60-120 mesh) using a mixture of petroleum ether and ethyl acetate (20:1) as the eluent.

Transesterification of Seed Oil

The purified oil was transesterified to fatty acid methyl esters (FAME) using a heterogeneous catalyst derived from the trunk of *Musa balbisiana* Colla [8, 19]. A mixture of oil in methanol (10 mL/g of oil) and the catalyst (20 wt.% of oil) was magnetically stirred at room temperature (32 °C) and the conversion was monitored by TLC. The reaction mixture was filtered under vacuum pump and the residue washed with petroleum ether and the combined filtrate was partitioned between water and petroleum ether. The organic phase was washed with brine, dried over anhydrous Na₂SO₄ and the solvent was removed under vacuum to yield the crude product which was further purified by column chromatography over silica gel using 20:1 petroleum ether and ethyl acetate as the eluent. The purified product was further subjected to high vacuum to remove the last traces of solvents to yield pure biodiesel (FAME).

Calculation of Iodine Value, Saponification Number and Cetane Index

Iodine value (IV) of the oils was calculated from fatty acid compositions of the biodiesel using equation (1) suggested by Krisnangkura [20]:

$$IV = \sum (254 \times D \times A_i) / MW_i \quad (1)$$

Where, D = number of double bonds in the *i*th component

A_i = percentage of the *i*th component in the mixture

MW_i = molecular weight of the *i*th component.

Saponification number (SN) was similarly calculated from equation (2) suggested by Krisnangkura [20]:

$$SN = \sum (560 \times A_i) / MW_i \quad (2)$$

Where, *A_i* = percentage of the *i*th component in the mixture

MW_i = molecular weight of the *i*th component

For calculating Cetane Index (CI) of the biodiesel, the equation (3) of Krisnangkura was used [21]:

$$CI = 46.3 + 5458/x - 0.225y \quad (3)$$

Where, x = SN as determined by equation (2) and y = IV as determined by equation (1)

Determination of acid value

Acid values of oil and biodiesel were determined [8, 22, 23]. The required amount of test sample (1-10 g) was weighed into a dry conical flask of suitable size and dissolved in a (10 mL/g of oil) neutral solvent (1:1 mixture of 95% alcohol and diethyl ether). A few drops of phenolphthalein were added to the mixture and titrated against 0.1 N KOH solution with constant and vigorous stirring. The acid value was calculated as:

$$\text{Acid value (mg KOH/g)} = 56.1 \times H \times Y/G$$

Where, H = titre value (mL),

Y = normality of KOH solution (determined by standardizing KOH solution with oxalic acid),

G = weight of test sample taken in g.

Free Fatty Acid Determination

As free fatty acid is equivalent to half the value of acid value, hence the amount of free fatty acid (FFA) was calculated as:

$$\text{FFA (mg KOH/g)} = \text{AV}/2$$

Determination of refractive index and density

Refractive indices of purified seed oil and the transesterified product were determined by using the Abbe Refractometer (AW-24) at room temperature (28 °C). For determination of refractive index, only two or three drops of oil are required.

Densities of the purified oil and the transesterified product were determined at room temperature (32 °C). For this, a clean and empty plastic centrifuge tube was taken and weighed. Accurately 1000 μL (= 1 mL) of the liquid sample was transferred into the tube with the help of a syringe and then weighed again. Then the density is determined based on mass per unit volume of oil.

RESULTS AND DISCUSSION

Pithecellobium monadelphum Kosterm is a huge woody tree which grows as high as 50 metres or even more. The seed is circular, flat, small in size but large in number, contains 10 wt.% of oil. Free fatty acid from oil sample was removed by column chromatography before transesterification. Transesterification of *Pithecellobium monadelphum* Kosterm seed oil to biodiesel was carried out using methanol in presence of a catalyst derived from the trunk of *Musa balbisiana* Colla [8, 19] and reported a high yield of biodiesel (93 wt.%) at a reaction temperature of 32 °C within 3.5 h [5]. Some of the physicochemical properties of the seed oil extracted are shown in **Table 1**. The acid value of crude oil of *Pithecellobium monadelphum* Kosterm seed was estimated as 0.968 mg KOH/g (0.484 mg KOH/g of free fatty acid which is equivalent to half the value of acid value). The refractive index and density of the oil were measured at 1.468 (at 28 °C) and 0.903 g/cm³ (at 32 °C) respectively.

Table 1. Some physicochemical properties of *P. monadelphum* seed oil

Properties	Value
Oil content (wt.%)	10.00
Colour	Golden yellow
Physical state (at room temperature)	Liquid
Refractive index at 28 °C	1.468
Density at 32 °C (g/cm ³)	0.903
Acid value (mg KOH/g)	0.968
Free fatty acid (mg KOH/g)	0.484

Some properties of biodiesel from *P. monadelphum* Kosterm seed oil were presented in Table 2. It is observed that the value of refractive index (1.4455) and density (0.879 g/cm³ at 32 °C) decreases when the oil is converted to biodiesel. Acid number is a measure of acids in the fuel. A high acid value damages fuel pumps and fuel filters [24, 25]. The maximum limit of acid value specified in the biodiesel fuel standards such as ASTM D6751 and EN 14214 is 0.50 mg of KOH/g. The acid value of biodiesel obtained from *P. monadelphum* seed oil is 0.073 mg of KOH/g which is far below the specified maximum limit and the free fatty acid value is 0.037 mg of KOH/g. Predictions of three important chemical properties of biodiesel viz. iodine value [20], saponification number [20] and cetane index [21] were performed following theoretical calculation based upon fatty acid profile of *P. monadelphum* biodiesel [5].

Table 2. Some properties of biodiesel from *P. monadelphum* seed oil

Properties	Value
Refractive index at 28 °C	1.4455
Density at 32 °C (g/cm ³)	0.879
Acid value (mg KOH/g)	0.073
Free fatty acid	0.037
Iodine value (g I ₂ /100 g oil)	83.34*
Saponification number (mg KOH/g oil)	193.43*
Cetane index	55.76*

*Theoretical value

The iodine value is very important when biodiesel samples are analyzed as it is related to biofuel storage performance. The iodine value provides information about the unsaturation degree of the oil which directly affects its stability to oxidation. The reason for auto-oxidation occurrence is the presence of double bonds in the chains of

the fatty compounds. Higher unsaturated fatty acid on heating results in polymerization of glycerides. This can lead to the formation of deposits or deterioration of the lubricating property [26]. Hence, the limitation of unsaturated fatty acids in biodiesel is necessary. Theoretically, iodine value of biodiesel from *P. monadelphum* seed oil was calculated and found to be 83.34 g I₂/100 g which is far below the maximum limit of 120 prescribed in EN 14214.

The biodiesel standards such as ASTM D6751 and EN 14214 have no specification regarding the saponification number. The biodiesels obtained from soybean, sunflower, palm, canola, and *Jatropha curcas* oils have saponification numbers 201, 200, 207, 182 and 202 mg KOH/g respectively [27, 28]. In this study, saponification number of biodiesel is calculated theoretically and found to be 193.43 mg KOH/g which is comparable to the values of biodiesels obtained from soybean, sunflower, palm, canola and *Jatropha curcas* oils.

Cetane index (CI) is an important parameter and a prime indicator of fuel ignition quality in diesel engines. The minimum requirement of cetane number prescribed in biodiesel standards ASTM D6751 and EN 14214 is 47 and 51 respectively. The cetane index of biodiesel prepared from *P. monadelphum* seed oil is 55.76 (calculated) which crosses the minimum value specified in ASTM D6751 and EN 14214.

CONCLUSION

Biodiesel was produced from *Pithecellobium monadelphum* seed oil by carrying out transesterification reaction using methanol in presence of a catalyst. Some physicochemical properties of seed oil and biodiesel were determined. The acid value of crude oil of *Pithecellobium monadelphum* Kosterm seed was estimated as 0.968 mg KOH/g and that of biodiesel was found to be 0.073 mg of KOH/g which is far below the specified maximum limit of ASTM D6751 and EN 14214. The value of refractive index and density of biodiesel were found to decrease as compared to that of seed oil. Predictions of three important chemical properties of biodiesel viz. iodine value, saponification number and cetane index were performed following theoretical calculation based upon fatty acid profile of *P. monadelphum* biodiesel. Iodine value was found to be 83.34 g I₂/100 g which is far below the maximum limit of 120 prescribed in EN 14214. Saponification number of the present study is 193.43 mg KOH/g which is comparable to the values of biodiesels obtained from soybean, sunflower, palm, canola and *Jatropha curcas* oils. The cetane index of biodiesel is found to be 55.76 which crosses the minimum value specified in ASTM D6751 and EN 14214. *Pithecellobium monadelphum* Kosterm may be considered as a good non-edible feedstock for biodiesel production and further research needs to be done to explore its potential.

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