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Gmelina arborea and *Tabernaemontana divaricata* Seed Oils as Non-Edible Feedstocks for Biodiesel Production

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Abstract: *Gmelina arborea* and *Tabernaemontana divaricata* seed oils were extracted and transesterified using methanol as the solvent in presence of a catalyst to produce biodiesel. Predictions of four important chemical properties of biodiesel *viz*. iodine value, saponification number, cetane index and gross heat of combustion were performed following theoretical calculation based upon fatty acid profiles of *G. arborea* and *T. divaricata* biodiesels and found to meet the necessary biodiesel standards of ASTM D6751 and EN 14214.
Key words: *Gmelina arborea*, *Tabernaemontana divaricata*, non-edible oil, *Musa balbisiana* Colla, transesterification, biodiesel.

Introduction

Biodiesel, consisting of methyl esters of long chain fatty acids, is a renewable, biodegradable, non-toxic and environment-friendly fuel[1-3]. It is receiving more and more attention and is accepted as a strong candidate as an alternative to diesel fuel. Biodiesel has similar properties to conventional diesel fuel and can be used alone or mixed in ratio of 5-20% (B5- B20) with petroleum based diesel with no or very few technical adjustments[4,5]. Biodiesel is produced via transesterification of triglycerides present in biological resources such as vegetable oils *viz*. edible and non-edible, animal fats, microalgal oil or even used cooking oils by reacting with methanol in the presence of a catalyst (acid, base or enzymes)[6-9]. Non-edible oils from the plant seeds are the most promising alternative fuel for diesel engines as they are inexpensive and economically viable alternative feedstocks for biodiesel production.

Gmelina arborea Roxb. is a big forest tree popular for its wood used for making furnitures and as building materials. *Gmelina arborea* is a fast growing tree which grows to about 40 m in height. The tree is commonly planted as a garden and an avenue tree. Fruit contains very little kernel but the kernel is quite rich in oil (53 wt.%)[10]. Fatty acid profile (Table 1) of biodiesel from *Gmelina arborea* seed oil was determined by Basumatary *et al*. and reported[10]. The biodiesel consists of 15.09 wt.% of methyl palmitate (C16:0), 44.88 wt.% of methyl oleate (C18:1), 11.16 wt.% of methyl stearate (18:0), 15.95 wt.% of methyl gondoate (C20:1), 4.21 wt.% of methyl arachidate (C20:0) and 8.67 wt.% of methyl behenate (C22:0).

Tabernaemontana divaricata Linn is a small woody tree which grows to about 2 to 3 m in height and belongs to the *Apocynaceae* family. The plant flowers throughout the year in the climatic condition of Assam but heavy flowering can be seen only in autumn season. The oil content of the seed is about 24 wt.%[11]. The chemical composition of biodiesel (Table 1) from *Tabernaemontana divaricata* seed oil determined by GC-MS analysis was reported[11] and the biodiesel consists of 27.0 wt.% of methyl palmitate (C16:0), 10.54 wt.% of methyl linoleate (C18:2), 56.23 wt.% of methyl oleate (C18:1) and 6.20 wt.% of methyl stearate (18:0). The oleic acid is the major fatty acid followed by palmitic acid comprising of about 66 wt.% unsaturated and 33 wt.% saturated fatty acids.

The present study deals with the synthesis of biodiesel from *G. arborea* and *T. divaricata* seed oils by transesterification with methanol using a catalyst and investigation of some properties of the biodiesel formed by employing experimental and theoretical methods.

Table 1. Fatty acid profiles of biodiesel from *G. arborea* and *T. divaricata* seed oils

FAME		Composition (wt.%)	
		***G. arborea*[10]**	***T. divaricata*[11]**
C16:0	Methyl palmitate	15.09	27.00
C18:2	Methyl linoleate	--	10.54
C18:1	Methyl oleate	44.88	56.23
C18:0	Methyl stearate	11.16	06.20
C20:1	Methyl gondoate	15.95	--
C20:0	Methyl arachidate	04.21	--
C22:0	Methyl behenate	08.67	--

Materials and Methods

Materials

G. arborea and *T. divaricata* seeds were collected from Bongaigaon District of Assam, India during its availability of the season. The seeds were dried and crushed 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

Ground seed taken in petroleum ether (bp 40-60 ºC, 10 mL/g) was magnetically stirred for 2-3 h, filtered and solvent was removed at 45 ºC using a rotary vacuum evaporator to yield the crude oil. The oil was purified prior to transesterification 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 seed oil was transesterified to biodiesel (fatty acid methyl esters) using a catalyst derived from the trunk of *Musa balbisiana* Colla[1]. 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 ºC) 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 Na_2SO_4 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. Fatty acid methyl esters were determined using Perkin Elmer Clarus 600 GC-MS.

Determination of acid value (AV)

Acid values of oil and biodiesel were determined[12,13]. 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:

Acid value (mg KOH/g) = 56.1 x H x Y/G

Where, H = titre value (mL),

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

G = weight of the test sample taken in g.

Free fatty acid (FFA) 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:

FFA (mg KOH/g) = AV/2

Determination of refractive index and density

Refractive indices of purified seed oil and biodiesel 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 biodiesel 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.

Calculation of iodine value (IV), saponification number (SN), cetane index (CI) and gross heat of combustion (HG)

Iodine value (IV) of the oils was calculated from fatty acid compositions (Table 1) of the biodiesel using equation (1) suggested by Krisnangkura[14].

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

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) of Krisnangkura[14].

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

Where, A_i= percentage of the i^{th} component in the mixture.

MW_i= molecular weight of the i^{th} component.

For calculating Cetane Indices (CI) of the FAMEs, the equation (3) of Krisnangkura was used[15].

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

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

Lastly, the gross heats of combustion of both the triglycerides as well as FAMEs have been calculated using the equations (4) and (5) respectively[16].

HG of triglyceride

$$= 1{,}896{,}000/SN - 0.6IV - 1600 \quad (4)$$

Where, IV and SN are as calculated from equations (1) and (2) respectively.

HG of individual FAME

$$= 618{,}000/SN - 0.08IV - 430 \quad (5)$$

Where, $SN = (560/MW_i)100$ and

$IV = (254 \times D/MW_i)100$.

HG of the FAME mixture

$$= \sum (HG_i \times A_i)/100 \quad (6)$$

Results and Discussion

Transesterification of *G. arborea* and *T. divaricata* seed oils to biodiesel was carried out using methanol in presence of a catalyst derived from the trunk of *Musa balbisiana* Colla and reported a high yield of biodiesel (95 wt.%) at a reaction temperature of 32 °C[10,11]. Some of the physicochemical properties of both the seed oils are shown in Table 2. The acid values of crude oil of *G. arborea* and *T. divaricata* seed were estimated at 1.082 and 0.960 mg KOH/g and their free fatty acids are found to be 0.541 and 0.48 mg KOH/g respectively which are equivalent to half the value of acid values. The refractive indices of *G. arborea* and *T. divaricata* oils were measured at 1.468 and 1.463 respectively at 28 ºC and their densities at 32 ºC are 0.8977 and 0.902 g/cm^3 respectively. The calculated gross heats of combustion of *G. arborea* and *T. divaricata* oils are 40.3 and 38.2 MJ/kg respectively.

Table 2. Some physicochemical properties of *G. arborea* and *T. divaricata* seed oils

Properties	***G. arborea***	***T. divaricata***
Oil content (wt.%)	53[10]	24[11]
Colour	Golden yellow	Yellowish red
Physical state (at room temperature)	Liquid	Liquid
Refractive index at 28 ºC	1.468	1.463
Density at 32 ºC (g/cm^3)	0.8977	0.902
Acid value (mg KOH/g)	1.082	0.960
Free fatty acid (mg KOH/g)	0.541	0.48
HG (MJ/kg)	40.3[a]	38.2[a]

[a]*Calculated value*

Some properties of biodiesel prepared from *G. arborea* and *T. divaricata* seed oils were presented in Table 3. It is observed from Table 2 and Table 3 that the value of refractive indices and densities of both the samples 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[17,18]. 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 values of biodiesel obtained from *G. arborea* and *T. divaricata* seed oils are respectively 0.105 and 0.093 mg of KOH/g which are far below the specified maximum limit and the free fatty acid values are 0.053 and 0.047 mg of KOH/g respectively. Predictions of four important chemical properties of biodiesel *viz*. iodine value[14], saponification number[14], cetane index[15] and HG[16] were performed following theoretical calculation based upon fatty acid profiles of *G. arborea* and *T. divaricata* biodiesel[10,11].

Table 3. Some properties of biodiesel from *G. arborea* and *T. divaricata* seed oils

Properties	*G. arborea*	*T. divaricata*
Refractive index at 28 ºC	1.450	1.446
Density at 32 ºC (g/cm^3)	0.877	0.879
Acid value (mg KOH/g)	0.105	0.093
Free fatty acid (mg KOH/g)	0.053	0.047
Iodine value (g I_2 /100 g oil)	51.0^a	66.5^a
Saponification number (mg KOH/g oil)	185.7^a	194.1^a
Cetane index	64.2^a	59.5^a
HG (MJ/kg)	40.7^a	38.5^a

^{a}*Calculated 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 main reason for auto-oxidation 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[18]. Hence, the limitation of unsaturated fatty acids in biodiesel is necessary. Iodine value of biodiesel obtained from *G. arborea* and *T. divaricata* seed oils were calculated theoretically and found to be 51.0 and 66.5 g I_2 /100 g respectively which are 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[18,19]. In the present study, saponification numbers of biodiesels prepared from *G. arborea* and *T. divaricata* seed oils were calculated and found to be 185.7 and 194.1 mg KOH/g respectively which are 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[18]. The minimum requirement of cetane number prescribed in biodiesel standards ASTM D6751 and EN 14214 is 47 and 51 respectively. The calculated cetane index of biodiesel prepared from *G. arborea* seed oil is 64.2 and that of *T. divaricata* seed oil is 59.5 which are above the minimum value specified in ASTM D6751 and EN 14214 biodiesel standards.

The gross heat of combustion (HG), or the energy released when a compound undergoes complete combustion with oxygen under standard conditions, is an important parameter in the selection of a fuel for use in diesel engines. It is observed from Table 2 and Table 3 that HG value of the oil (40.3 MJ/kg for *G. arborea* and 38.2 MJ/kg for *T. divaricata*) and the corresponding biodiesel (40.7 MJ/kg for *G. arborea* and 38.5 MJ/kg for *T. divaricata*) are almost same which is expected because of unchange in atomic composition both qualitatively and quantitatively in the conversion of oil to biodiesel.

Conclusion

Biodiesels from *G. arborea* and *T. divaricata* seed oils were obtained by carrying out transesterification reaction using methanol in presence of a catalyst. Some properties of seed oil and biodiesel were determined. Calculations of four important chemical properties of biodiesel *viz*. iodine value, saponification number, cetane index and gross heat of combustion were performed based upon fatty acid profiles of *G. arborea* and *T. divaricata* biodiesels. Iodine values of biodiesel from *G. arborea* and *T. divaricata* seed oils were 51.0 and 66.5 g I_2 /100 g respectively which are far below the maximum limit of 120 prescribed in EN 14214 and saponification numbers were found to be 185.7 and 194.1 mg KOH/g respectively. The cetane index of *G. arborea* biodiesel is 64.2 and that of *T. divaricata* biodiesel is 59.5 which cross the minimum value specified in

ASTM D6751 and EN 14214. *G. arborea* and *T. divaricata* seed oils may be considered as potential non-edible feedstocks for biodiesel production and further research needs to be done.

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