

Composition of biodiesel from *Gmelina arborea* seed oil

Sanjay Basumatary^{1*}, Dinesh C. Deka² and Dibakar C. Deka³

¹Department of Chemistry, Bineswar Brahma Engineering College, Kokrajhar 783370, Assam, India

²Department of Botany, Birjhora Mahavidyalaya, Bongaigaon 783380, Assam, India

³Department of Chemistry, Gauhati University, Guwahati 781014, Assam, India

ABSTRACT

Composition of biodiesel prepared from *Gmelina arborea* seed oil was determined by IR, NMR and GC-MS analysis. Biodiesel from *Gmelina arborea* 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).

Key words: Biodiesel, non-edible vegetable oil, transesterification, *Musa balbisiana* Colla.

INTRODUCTION

Non-edible vegetable oils have very limited commercial use, and plants producing such oils are slowly disappearing because such plants are not taken seriously by the farmers. This is one of the reasons responsible for depleting plant diversity. Use of non-edible oil as feedstock in biodiesel industry will spare edible oils for uses in other industries of edible products [1]. Biodiesel is a renewable form of energy and our country desperately needs it as substitute for petrodiesel for self-reliance [2-4]. Therefore, there is an urgent need and the researchers are working hard to find a new energy resource that is renewable, clean, reliable and yet economically feasible as a substitution to the current fossil fuels.

Biodiesel, an alternative and renewable fuel for diesel engines, consists of alkyl esters of long chain fatty acids, more commonly methyl esters and is typically made from nontoxic, biological resources such as vegetable oils, animal fats or even used cooking oils by transesterification with methanol in presence of a catalyst [1, 5, 6]. Biodiesel has attracted considerable attention as a renewable, biodegradable, and nontoxic fuel and can contribute to solving the energy problems, significantly reducing the emission of gases which cause global warming [5, 7-9]. However, the cost of raw material escalates the production cost of biodiesel causing a major hurdle to its commercialization in comparison to petroleum-based diesel fuel. Therefore, alternative feedstocks like non-edible vegetable oils need to be explored to make production of biodiesel cost-effective [10-13].

Gmelina arborea Roxb., known as *Gomari* in Assamese, 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 on different localities and prefers moist fertile valleys with 750-5000 mm rainfall. The *Gmelina arborea* tree attains moderate to large height up to 40 m and 140 cm in diameter [14]. It is occurring naturally throughout greater part of India at altitudes up to 1500 m. It also occurs naturally in Myanmar, Thailand, Laos, Cambodia, Vietnam, and in southern provinces of China, and has been planted extensively in Sierra Leone, Nigeria and Malaysia [15]. This tree is commonly planted as a garden and an avenue tree; growing in villages along agricultural land and on village community lands

and wastelands. Flowering takes place during February to April whereas fruiting starts from May onwards up to June. The fruit is up to 2.5 cm long, smooth, dark green, turning yellow when ripe and has a fruity smell.

The present study deals with the synthesis of biodiesel from *Gmelina arborea* seed oil by transesterification with methanol and determination of composition of the biodiesel formed by employing various instrumental techniques.

MATERIALS AND METHODS

Materials

Gmelina arborea Roxb. seeds were collected from Bongaigaon District of Assam, India during its availability of the season. The seeds were dried in sunlight, deshelled 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

Extractability of oil was evaluated by solvent extraction of the crushed kernel. Crushed kernel in petroleum ether (bp 40-60 °C, 10 mL/g) was magnetically stirred at room temperature (22-23 °C) for 3 h, solvent was removed at 45 °C using a rotary vacuum evaporator to yield the crude oil. This process was repeated 2-3 times with the seed cake using fresh solvent each time in order to extract most of the 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 [16]. 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).

Analysis of FAME

Composition of FAME mixtures were estimated using Perkin Elmer Clarus 600 GC-MS. The column used was Elite 5 MS with dimension 30.0 m x 250 µm. The oven temperature was initially held at 140 °C for 5 min, increased to 240 °C at 4 °C/min, and then held for 5 min. The injector, transfer and source temperatures were 250 °C, 200 °C and 150 °C respectively. Carrier gas was helium and total scan time 35 min. Gas Chromatogram of the biodiesel is shown in Fig. 1. EI mode of ionization was applied and mass scan was from 20 to 400 Da. For identification of FAME library search was carried out using NIST, NBS and Wiley GC-MS library. Fatty acid profile of biodiesel from *Gmelina arborea* seed oil is reported in Table 1. The ¹H and ¹³C NMR spectra were recorded in CDCl₃ at 300 and 75 MHz respectively using Bruker Avance III 300 MHz/54 mm NMR spectrometer. IR spectrum was recorded with a Perkin Elmer RX I FT-IR spectrometer as a thin film on KBr plate. ¹H NMR (300 MHz, CDCl₃): δ 0.86-0.90 (m), 1.25 (s), 1.30 (s), 1.59-1.64 (m), 2.00-2.02 (m), 2.28-2.35 (m), 3.67 (s), 5.32-5.36 (m). ¹³C NMR (75 MHz, CDCl₃): δ 14.06, 22.63, 24.89, 27.10, 27.15, 29.03, 29.06, 29.09, 29.20, 29.26, 29.31, 29.40, 29.47, 29.54, 29.64, 29.71, 30.87, 31.85, 34.05, 51.41, 129.69, 129.93, 174.38. FT-IR (thin film): 737, 880, 1018, 1116, 1171, 1198, 1246, 1362, 1437, 1459, 1508, 1540, 1651, 1742, 2854, 2925, 3006 cm⁻¹. The ¹H and ¹³C NMR spectra of biodiesel from *Gmelina arborea* seed oil are depicted in Fig. 2 & 3.

RESULTS AND DISCUSSION

Gmelina arborea Roxb., *Gomari* in Assamese, is a big forest tree popular for its wood used for making furnitures. As the seeds possess hard outer shells which bear no oil, it was considered appropriate to first dehusk the hard and woody seeds before carrying out the estimation of oil content. Seeds with woody shell contains very little kernel (about 7 g kernel from 70 g seed, 10 wt.%) but the kernel is quite rich in oil (53.38 wt.% crude oil that loses 1.92 wt.% after chromatographic purification). Free fatty acid from oil sample was removed by column chromatography before transesterification. Transesterification of seed oil to biodiesel was carried out using methanol as the solvent in

presence of a catalyst derived from the trunk of *Musa balbisiana* Colla [11]. The yield of biodiesel from *Gmelina arborea* seed oil was 95 wt.% at room temperature (32 °C) within 3.5 h. The transesterified products were purified by column chromatography and analyzed. The ¹H and ¹³C NMR spectra were recorded in CDCl₃ at 300 and 75 MHz respectively using Bruker Avance III 300 MHz/54 mm NMR spectrometer. IR spectra were recorded with a Perkin Elmer RX I FT-IR spectrometer as a thin film on KBr plate. Composition of a FAME mixture was estimated using Perkin Elmer Clarus 600 GC-MS.

Analysis of FAME of biodiesel from *Gmelina arborea* seed oil

Fatty acid profile of the biodiesel prepared from *Gmelina arborea* seed oil was determined by GC-MS analysis. The individual peaks of the gas chromatogram (Fig. 1) were analyzed and the fatty acids were identified using MS database. Relative percentage of fatty acid esters was calculated from total ion chromatography by computerized integrator and results are presented in the Table 1. Biodiesel from *Gmelina arborea* 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). The oleic acid is the major fatty acid followed by gondoic acid and palmitic acid in *G. arborea* seed oil comprising of about 60.83 wt.% of unsaturated and 39.13 wt.% of saturated fatty acids.

Table 1. Fatty acid profile of biodiesel from *Gmelina arborea* seed oil

Retention time (min)	FAME	wt.%
18.27	Methyl palmitate	15.09
22.42	Methyl oleate	44.88
22.99	Methyl stearate	11.16
26.75	Methyl gondoate	15.95
27.30	Methyl arachidate	04.21
31.43	Methyl behenate	08.67

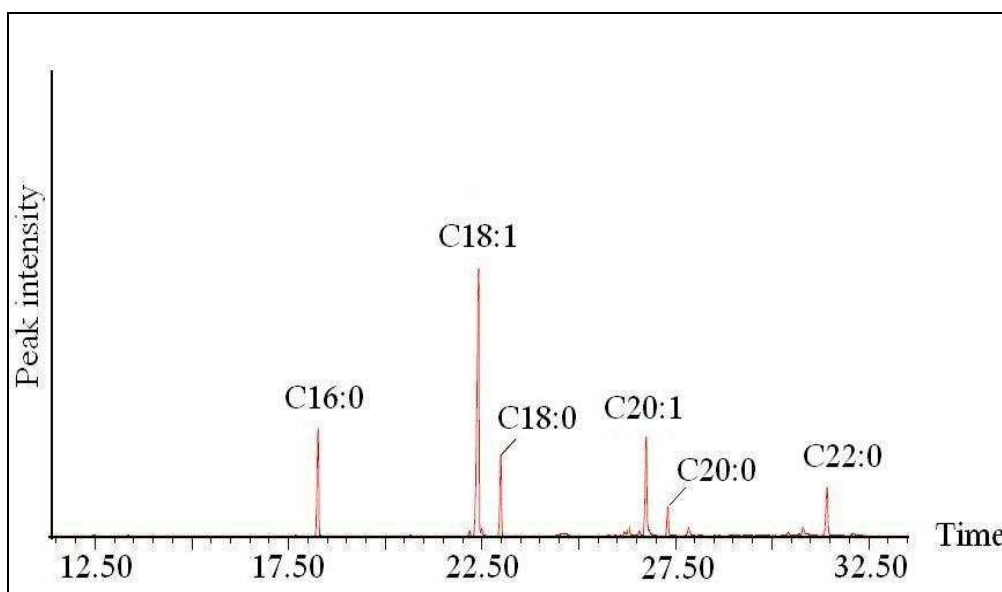


Fig. 1. Gas chromatogram of biodiesel from *Gmelina arborea* seed oil

The mass spectra of biodiesel from *Gmelina arborea* seed oil are shown in Figs. 1a to 1f. Molecular ion peaks and base peaks of the FAMES are shown in Table 2 and they are in the expected values. The molecular ion peaks of methyl palmitate, methyl oleate, methyl stearate, methyl gondoate, methyl arachidate and methyl behenate were observed at 270, 296, 298, 324, 326 and 354 respectively as expected. It is interesting to note that all the saturated FAMES detected in the biodiesel from *Gmelina arborea* (methyl palmitate, methyl stearate, methyl arachidate and methyl behenate) show CH₃OC(=OH⁺)CH₂ fragment and appears at m/z = 74 as the base peak (100%) which is the result of McLafferty rearrangement [17, 18] during the MS analysis due to a six-member ring structure of an

intermediate. Methyl oleate and gondoate show $[\text{CH}_2=\text{CHCH}_2\text{CH}_2]^+$ fragment which appears at $m/z = 55$ as the base peak (100%).

Table 2. Molecular ion and base peaks of FAME from *G. arborea* seed oil

FAME	Molecular ion peak (m/z)	Base peak (m/z)
Methyl palmitate	270	74
Methyl oleate	296	55
Methyl stearate	298	74
Methyl gondoate	324	55
Methyl arachidate	326	74
Methyl behenate	354	74

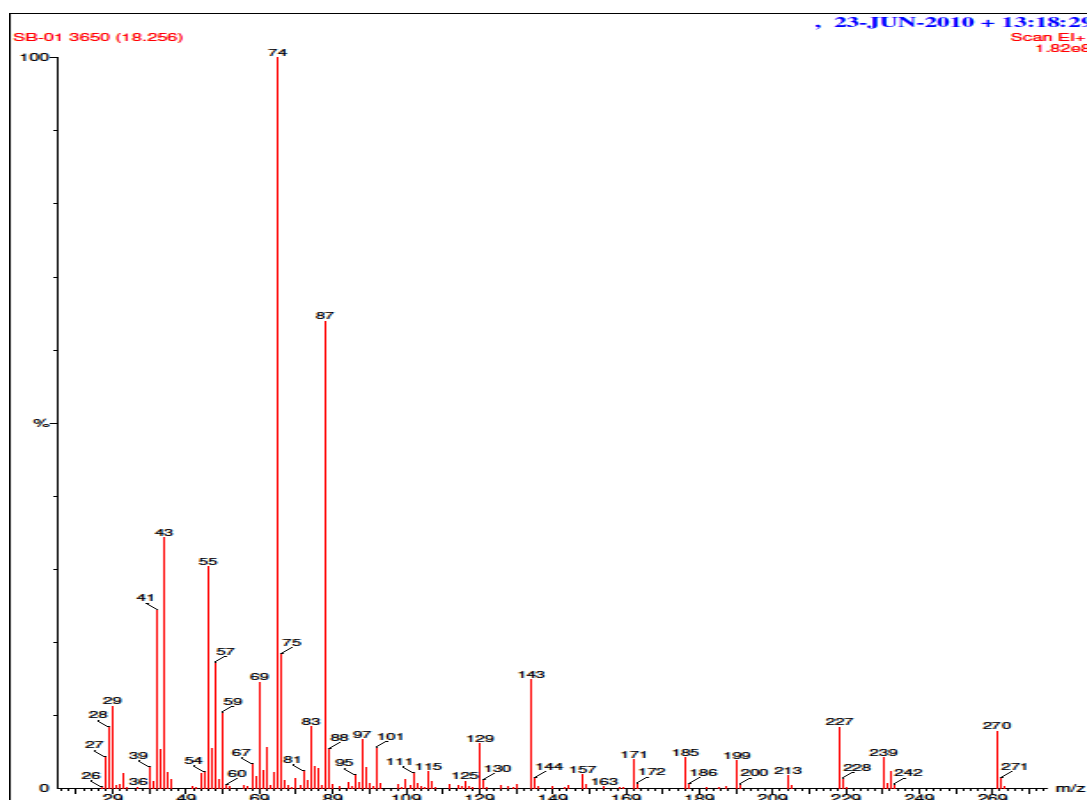


Fig. 1a. Mass spectrum of methyl palmitate

The ^1H NMR spectrum of biodiesel from *Gmelina arborea* seed oil is shown in Fig. 2. The multiplet at δ 5.32-5.36 ppm represents the olefinic protons ($-\text{CH}=\text{CH}-$). A singlet signal at δ 3.67 ppm is representing methoxy protons of the ester functionality of the biodiesel. It is interestingly observed that no signal is seen at about δ 2.8 ppm in the ^1H NMR spectrum of biodiesel from *Gmelina arborea* seed oil which indicates the absence of bis-allylic protons ($-\text{C}=\text{C}-\text{CH}_2-\text{C}=\text{C}-$) of the unsaturated fatty acid chain. The bis-allylic proton signal of polyunsaturated fatty acid (like linoleic acid) generally appears around at δ 2.8 ppm [19, 20]. The multiplet at δ 2.28-2.35 ppm may be due to the α -methylene protons to ester ($-\text{CH}_2-\text{CO}_2\text{Me}$). The α -methylene protons to double bond ($-\text{CH}_2-\text{C}=\text{C}-$) is seen as a multiplet at δ 2.00-2.02 ppm. The β -methylene protons to ester ($\text{CH}_2-\text{C}-\text{CO}_2\text{Me}$) also appear as a multiplet at δ 1.59-1.64 ppm. The singlet signals at δ 1.25 and 1.30 ppm are due to the protons of backbone methylenes of the long fatty acid chain. The terminal methyl protons ($\text{C}-\text{CH}_3$) at δ 0.86-0.90 ppm appear as a multiplet.

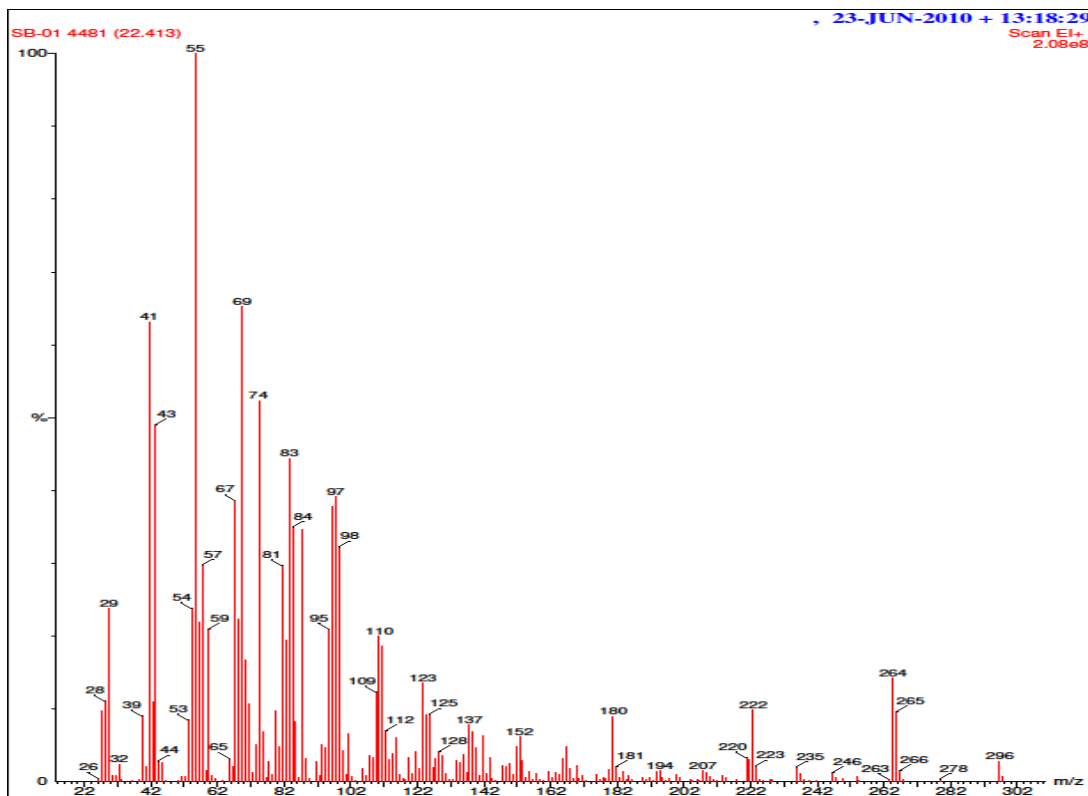


Fig. 1b. Mass spectrum of methyl oleate

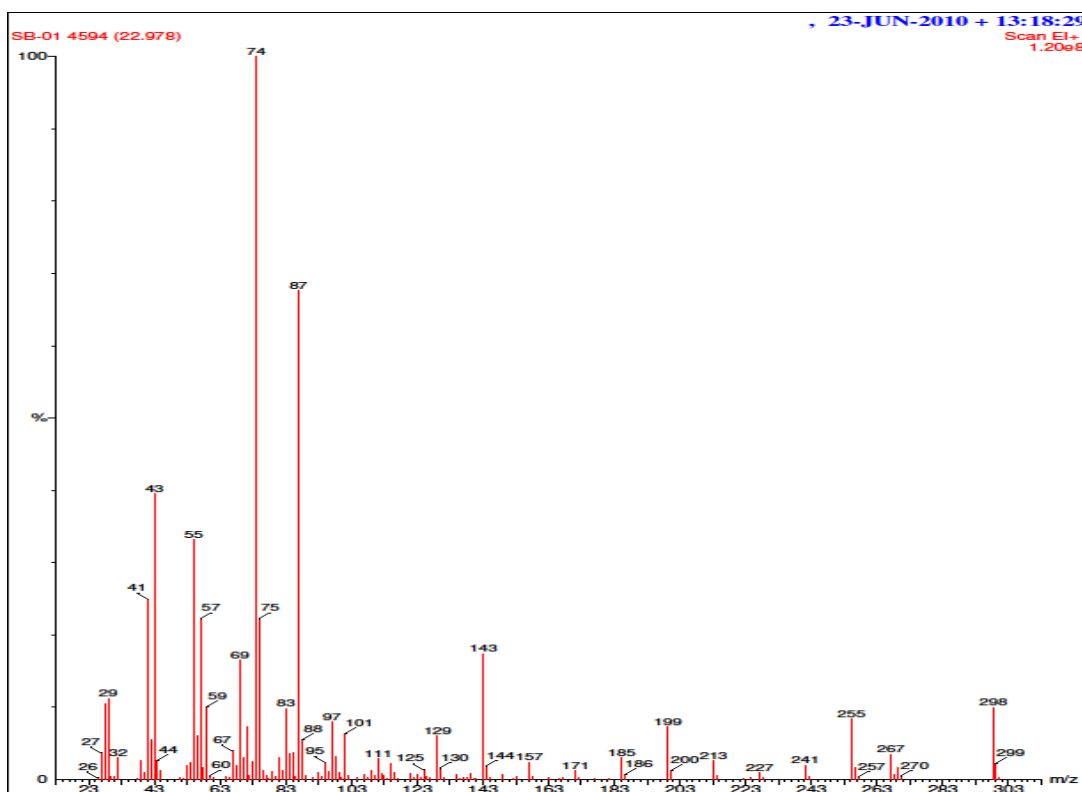
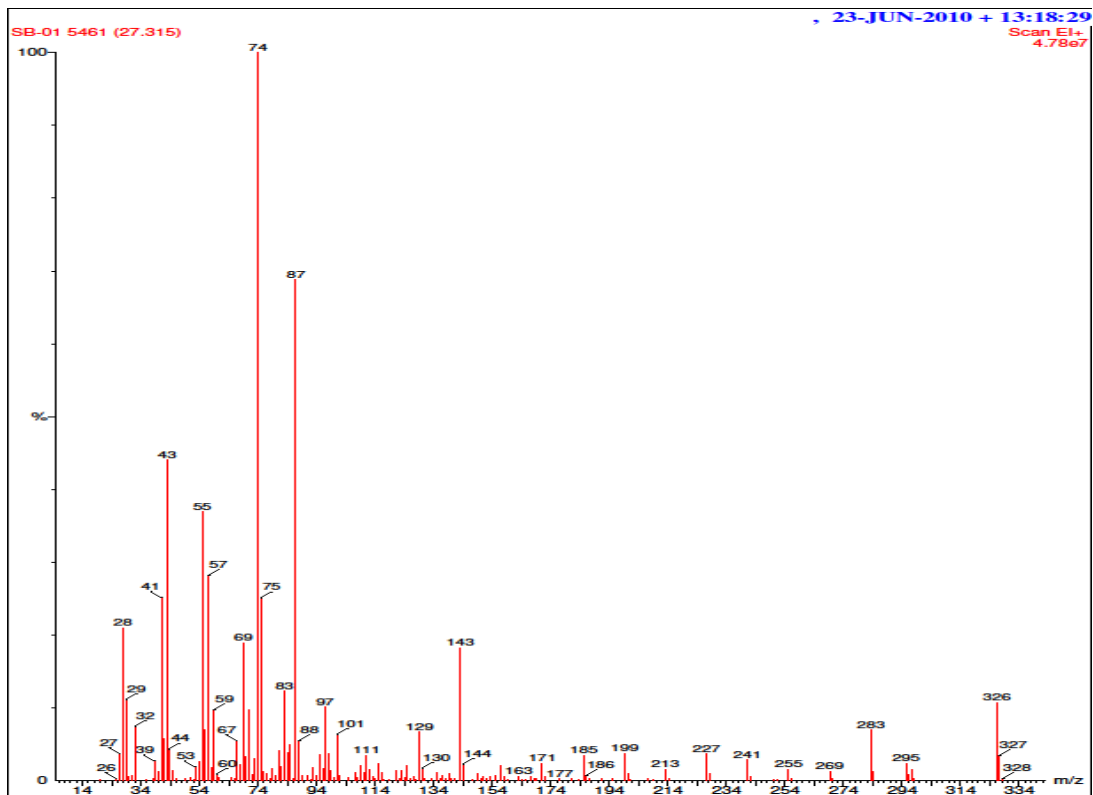
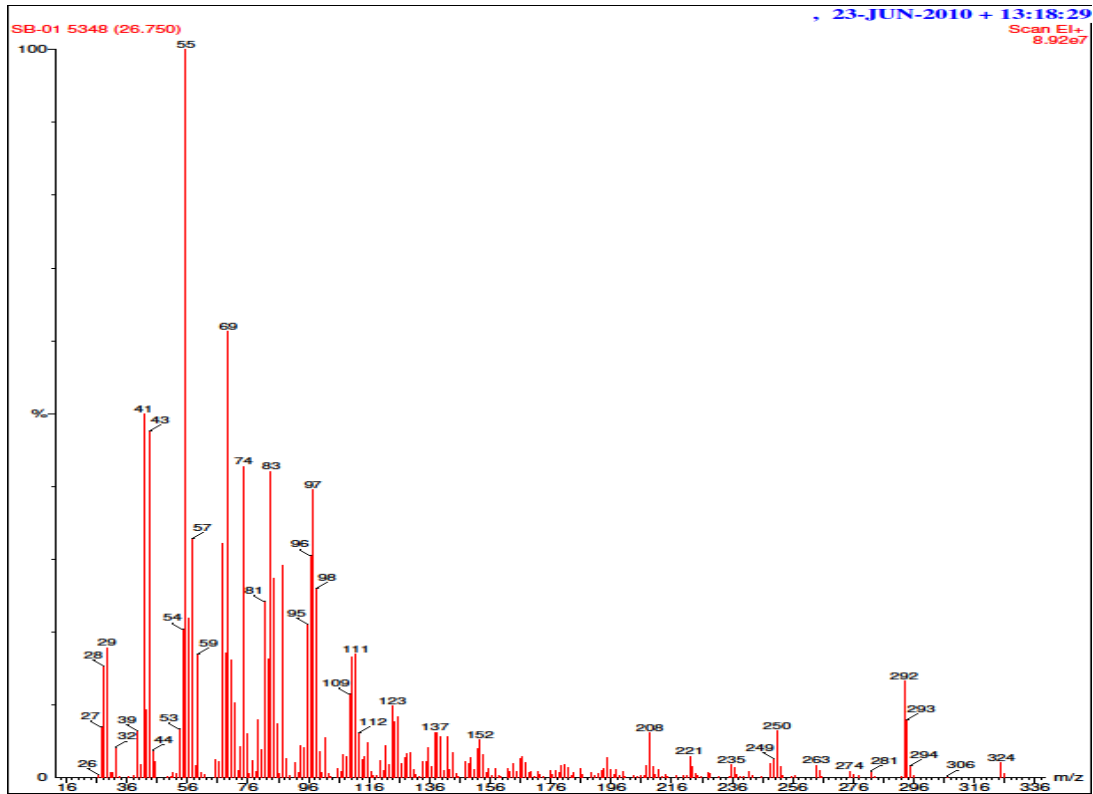


Fig. 1c. Mass spectrum of methyl stearate



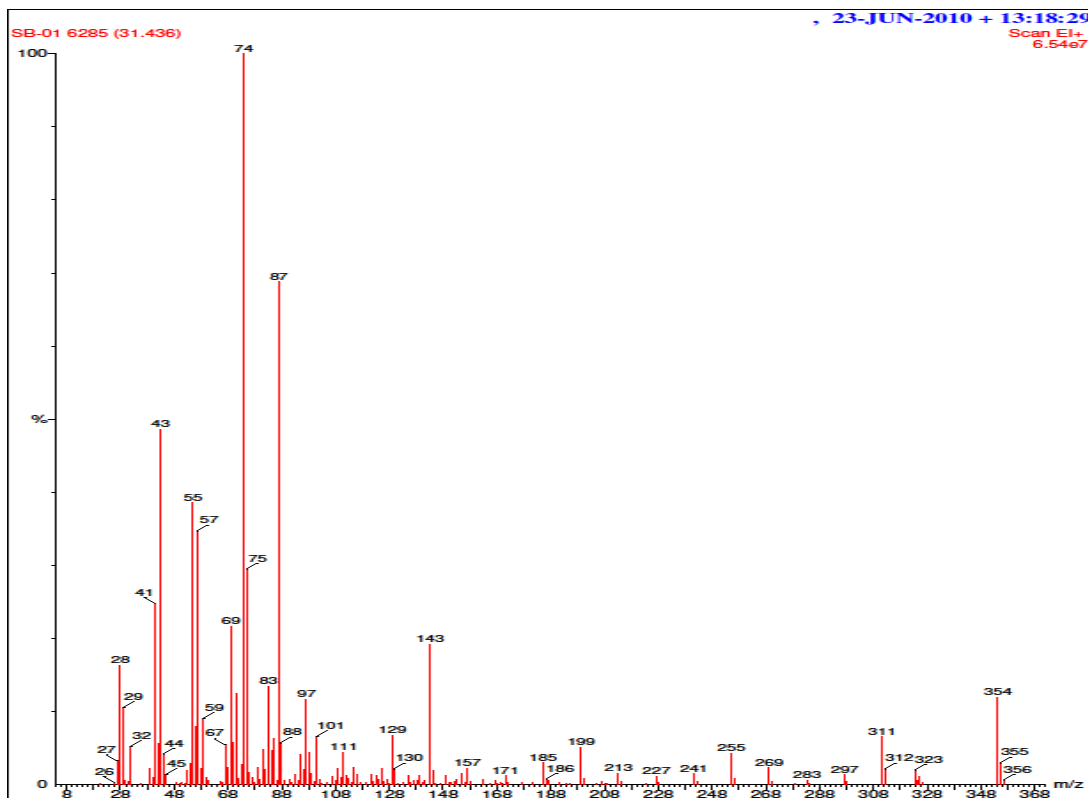


Fig. 1f. Mass spectrum of methyl behenate

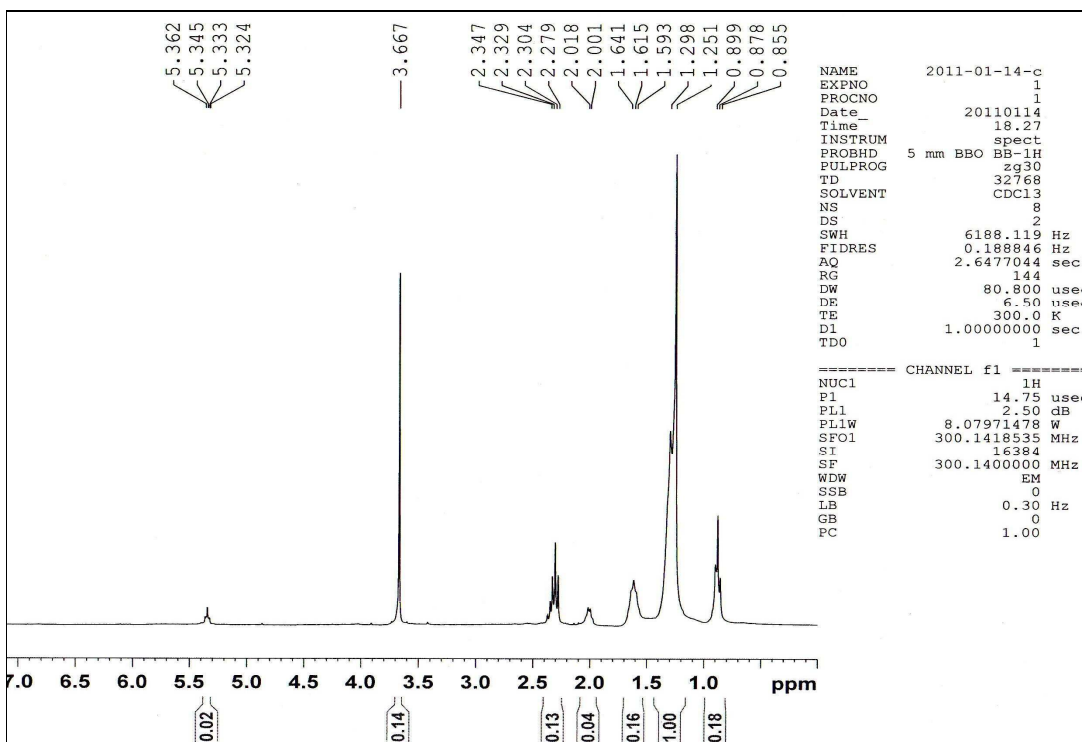


Fig. 2. ¹H NMR spectrum of biodiesel from *Gmelina arborea* seed oil

The ^{13}C NMR spectrum of biodiesel from *Gmelina arborea* seed oil is shown in Fig. 3. The signal at δ 174.38 ppm represents the carbonyl carbon of the ester molecules and the olefinic carbons appear at δ 129.69 and 129.93 ppm. The signal at δ 51.41 ppm in the ^{13}C NMR spectrum of biodiesel is due to methoxy carbons of esters. The methylene and methyl carbons of fatty acid moiety appear in the range from δ 14.06 to 34.05 ppm.

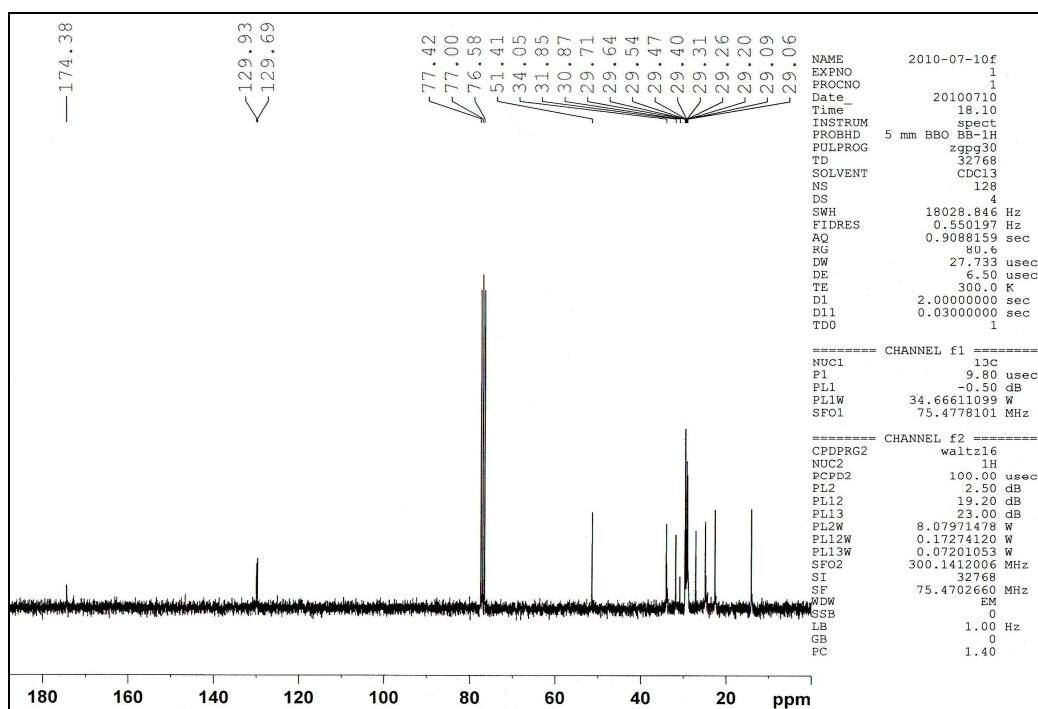


Fig. 3. ^{13}C NMR spectrum of biodiesel from *Gmelina arborea* seed oil

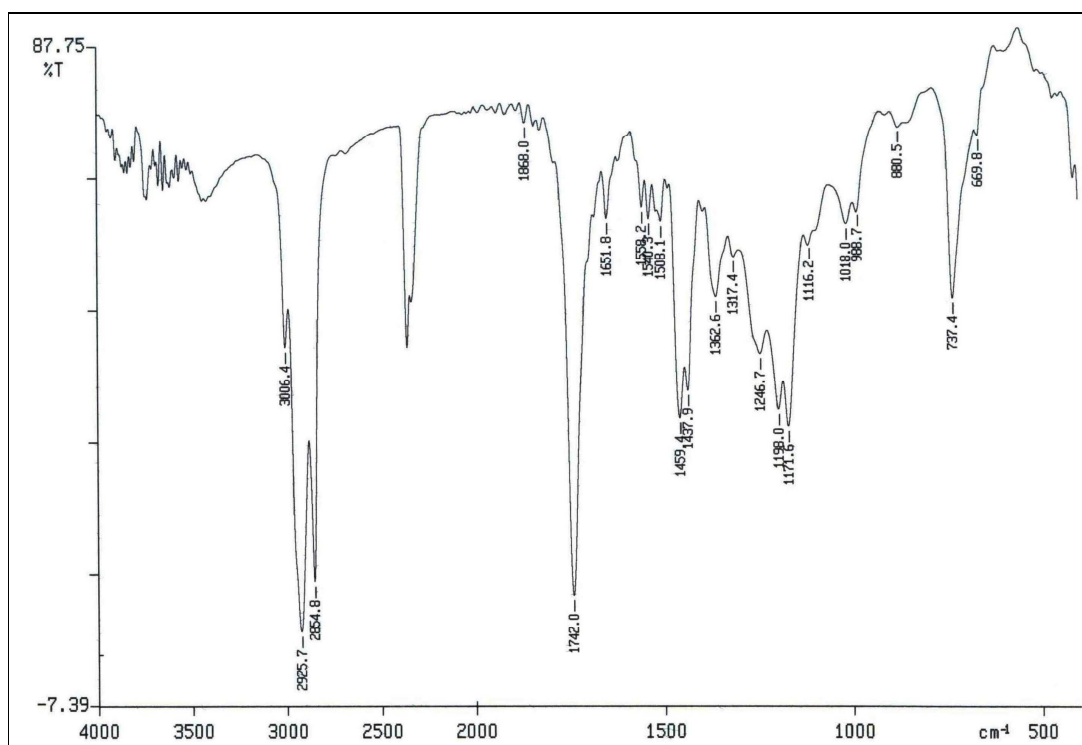


Fig. 4. IR spectrum of biodiesel from *Gmelina arborea* seed oil

In IR spectrum of biodiesel from *Gmelina arborea* seed oil (Fig. 4), a sharp signal at 1742 cm^{-1} is indicative of strong absorption by ester carbonyl stretching frequency. The weak signal at 1651 cm^{-1} may due to C=C stretching frequency. Strong and sharp signals at 2854 and 2925 cm^{-1} are due to C-H stretching frequencies. The absorbance at 3006 cm^{-1} indicates the =C-H stretching frequency. The bands at 1116, 1171, 1198 and 1246 cm^{-1} are expected for C-O-C stretching vibrations. The observation of an absorption peak at 737 cm^{-1} suggested the CH_2 rocking.

CONCLUSION

The *Gmelina arborea* seed oil biodiesel was synthesized by using a heterogeneous catalyst derived from the trunk of *Musa balbisiana* Colla with methanol and was confirmed by FT-IR, ^1H and ^{13}C NMR analysis. The chemical composition of biodiesel was determined by GC-MS analysis. The six fatty acid methyl esters were identified in the biodiesel from *Gmelina arborea* seed oil and 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). The oil may be useful as a source for the production of biodiesel or for other purposes. Therefore, more research is needed to explore its potentials for future industrial oilseeds crop.

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