



ORIGINAL ARTICLE

# Synthesis, spectroscopic and chromatographic studies of sunflower oil biodiesel using optimized base catalyzed methanolysis



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**Abstract** Methyl esters from vegetable oils have attracted a great deal of interest as substitute for petrodiesel to reduce dependence on imported petroleum and provide an alternate and sustainable source for fuel with more benign environmental properties. In the present study biodiesel was prepared from sunflower seed oil by transesterification by alkali-catalyzed methanolysis. The fuel properties of sunflower oil biodiesel were determined and discussed in the light of ASTM D6751 standards for biodiesel. The sunflower oil biodiesel was chemically characterized with analytical techniques like FT-IR, and NMR (<sup>1</sup>H and <sup>13</sup>C). The chemical composition of sunflower oil biodiesel was determined by GC-MS. Various fatty acid methyl esters (FAMES) were identified by retention time data and verified by mass fragmentation patterns. The percentage conversion of triglycerides to the corresponding methyl esters determined by <sup>1</sup>H NMR was 87.33% which was quite in good agreement with the practically observed yield of 85.1%.

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## 1. Introduction

In the last few decades energy needs have increased enormously and most of the energy needs are supplied through petrochemical sources (Vicente et al., 2007). In addition to rapid consumption, the rising costs, environmental problems and unavailability of the fossil fuel have led to look for the alternate sources of energy (Bajpai and Tyagi, 2006). The need of the hour is to have an alternative fuel which is technically feasible, economically competitive, environmentally acceptable and readily available (Demirbas, 2009). The most common fuel

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that is being focused upon and having brighter aspects is biodiesel. Biodiesel refers to a diesel-equivalent, processed fuel derived from biological sources.

Biodiesel is produced as a result of transesterification between a fat or oil and an alcohol (usually methanol) resulting in ester and a by-product, glycerol (Dorado et al., 2000; Angelo et al., 2005). Transesterification is a three step reaction with formation of mono and diglycerides as intermediate products (Vicente et al., 2007). Biodiesel is biodegradable, non-toxic, non aromatic and does not contain sulfur. Being plant based it does not emit CO on burning and is environmentally safe (Haq et al., 2006). Aromatic, ash, sediments, water, glyceride and methanol content if exist are less than 2% in biodiesel, in total showing that it has no waste products to be disposed off.

The commercial preparation of biodiesel from the oils of rapeseed (Komers et al., 2001), soybean (Candeia et al., 2009), rocket seed (Tariq et al., 2011), palm (Benjumea et al., 2008), sesame (Tariq et al., 2013), jojoba seeds (Mazloom et al., 2014), etc., has been reported in the literature. The present study deals with the synthesis of biodiesel from sunflower oil by base catalyzed transesterification with methanol to check the potential of this oil source for the commercial production of biodiesel. The importance of using base catalyzed transesterification is its economic process, less time for reaction, low temperature and high conversion rate. However, base catalyzed transesterification has limitations of hygroscopic nature of base catalyst, saponification, more washing and emulsion formation. The need of the present study is to find out an alternative renewable energy source in order to decrease dependence on crude oil and to check the potential of this oil source for the commercial production of biodiesel. Sunflower seeds contain about 42–50% high quality edible oil (Haq et al., 2006; Baksh et al., 1999). Sunflower has a high place in international agricultural market due to its varied uses. The biodiesel formed was characterized by different physico-chemical properties and its composition was determined by employing various instrumental techniques like FT-IR, NMR and GCMS.

## 2. Materials and method

### 2.1. Materials

Sunflower seeds were purchased from a local market. The seeds were washed with distilled water to remove the dirt and were oven dried at 60 °C till constant weight. The oil was extracted by using electric oil expeller (KEK P0015-10127), Germany. Methanol (99.9% purity), sodium hydroxide (NaOH) and anhydrous sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) were of analytical grade and were obtained from Merck (Germany) and used as such without any purification.

### 2.2. Analytical methods

The fuel properties of synthesized sunflower oil biodiesel were determined by ASTM methods. Sunflower oil biodiesel was characterized by FT-IR, using a Bio-Rad Excalibur Model

FTS3000MX in the range 4000–400  $\text{cm}^{-1}$ . The resolution was 1  $\text{cm}^{-1}$  and 15 scans. NMR analyses were performed using Avan CE 300 MHz spectrometer equipped with 5 mm BBO probes at 7.05 T. Deuterated chloroform ( $\text{CDCl}_3$ ) and tetramethylsilane (TMS) were used as solvent and internal standard, respectively (Ahmad et al., 2010). The  $^{13}\text{C}$  (75 MHz) spectra were recorded with a pulse duration of 30°, a recycle delay of 1.89 s and 160 scans. The fatty acid methyl ester (FAME) contents of sunflower oil biodiesel were determined by gas chromatography, model GC-6890 N coupled with mass spectrometer, model MS-5973 MSD (mass selective detector). Separation was performed on a capillary column DB-5MS (30 m  $\times$  0.32 mm, 0.25  $\mu\text{m}$  of film thickness). The mass spectrometer coupled with GC was set to scan in the range of  $m/z$  50–550 with electron impact (EI) mode of ionization.

### 2.3. Experimental procedure

#### 2.3.1. Transesterification

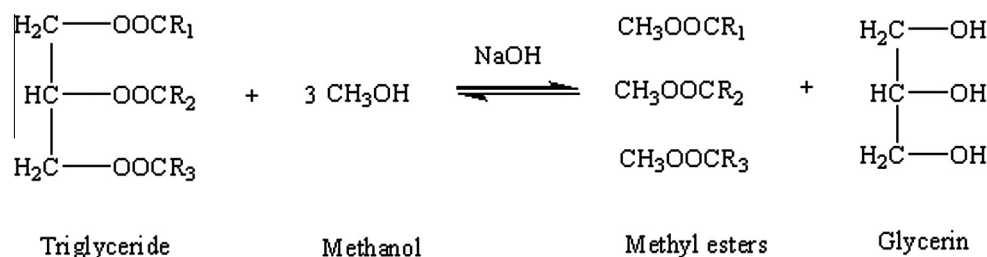
The transesterification was carried out using 2000 mL round bottom flask equipped with reflux condenser, magnetic stirrer, thermometer and sampling outlet. One liter vegetable crude oil was filtered and preheated up to 120 °C to remove moisture on a heating mantle. The transesterification of sunflower oil was carried out with a 6:1 M ratio of methanol/oil and 0.7% NaOH (as catalyst) w/w of the oil. Sunflower oil (500 mL) was transesterified with methanol (100 mL) in the presence of NaOH (3.25 g) as catalyst. The temperature of the reaction was maintained at 60 °C and the contents were stirred with a constant speed of 600 rpm for 1.5 h. The resultant mixture was cooled to room temperature for the separation of two phases. The upper lighter phase of biodiesel and lower denser phase of glycerin (by-product) were separated by simple decantation. Crude biodiesel contains the excess methanol, unused catalyst, soap formed, some entrained methyl esters and partially reacted glycerides. The remaining catalyst was removed by successive rinsing with distilled water followed by the addition of 1–2 drops of acetic acid to neutralize the residual catalyst and conversion of soap to free fatty acids (FFA). The residual water contents were eliminated by treatment with anhydrous  $\text{Na}_2\text{SO}_4$ , followed by filtration. A transparent yellow liquid was obtained as the final product.

The yield of biodiesel formed was calculated by using the expression

$$\% \text{Yield} = \frac{\text{Grams of methyl ester produced}}{\text{Grams of oil taken}} \times 100 \quad (\text{i})$$

## 3. Results

Biodiesel was synthesized from sunflower oil by using NaOH as catalyst for transesterification with methanol. The molar ratio of alcohol to oil (6:1) and temperature of 60 °C, used were selected on the basis of our earlier reports (Tariq et al., 2011; Mazloom et al., 2014) as well as other reported optimal conditions for the transesterification of vegetable oils (Meher et al., 2006). The general reaction of the base catalyzed transesterification can be represented as:



### 3.1. Characterization of sunflower oil biodiesel

The synthesized sunflower oil biodiesel was characterized for its fuel properties i.e., density, dynamic and kinematic viscosities, cloud point, pour point, flash point, acid number and sulfur contents, employing the methods of American Society for Testing and Materials (ASTM). The results are given in Table 1 along with recommended values for biodiesel (ASTM-D6751) and petrodiesel (ASTM-D975). The determined density of sunflower oil biodiesel at 40 °C, was 0.86 g cm<sup>-3</sup> which is comparable to the limits for petro-diesel and biodiesel (Table 1).

Viscosity is the most important property of biodiesel since it affects the operation of fuel injection equipment, particularly at low temperature when the increase in viscosity affects the fluidity of the fuel. High viscosity leads to poorer atomization of the fuel spray. The determined dynamic and kinematic viscosity of sunflower oil biodiesel at 40 °C was 5.321 cp and 4.719 mm<sup>2</sup>s<sup>-1</sup>, respectively, which are within the limits of ASTM D6751 of biodiesel and ASTM D975 values for petro-diesel (Table 1).

The pour point (pp) is the temperature at which the amount of wax, out of solution is sufficient to get the fuel, thus it is the lowest temperature at which the fuel can flow whereas cloud point (cP) is the temperature at which wax first becomes visible when the fuel is cooled. The determined values of pp and cP of sunflower oil biodiesel were -5.0 and 4.0 °C, respectively, which are within the prescribed ASTM limits for diesel fuels (Table 1). The flash point is a parameter which is considered in the handling, storage and safety of fuels and inflammable materials. The observed flash point of sunflower oil biodiesel (183 °C) is higher than the limits of ASTM D975 for petrodiesel and comparable to that of ASTM D6751 values for biodiesel (Table 1).

Acid number is the measure of free fatty acids in oil as well as in biodiesel. Acid number of oil and biodiesel was

determined by aqueous acid–base titration. The oil/biodiesel was titrated against standard KOH aqueous solution using phenolphthalein as an indicator. A blank titration was also carried out with isopropyl alcohol. The sample titration was carried out with 1 ml of sample. Acid number was calculated by using the following formula.

$$\text{Acid number} = \frac{(A - B) \times C}{V} \quad (\text{ii})$$

where

*A* = Volume of KOH used for sample (ml)

*B* = Volume of KOH used for blank

*C* = Concentration of KOH

*V* = Volume of sample (ml)

The determined values of acid number of sunflower oil and its biodiesel were found to be 3.22 and 0.07 mg KOH/g of sample, respectively (Table 1).

## 4. Discussion

### 4.1. Chemical parameters of sunflower oil biodiesel

#### 4.1.1. FT-IR spectroscopy

The esters have two characteristically strong absorption bands arising from methoxy carbonyl and CO stretching (Vivek and Gupta, 2004). The methoxy carbonyl group in sunflower biodiesel changed from 1743.71 cm<sup>-1</sup> in oil to a strong band at 1741.80 cm<sup>-1</sup> in biodiesel. The FT-IR spectra of sunflower oil and sunflower biodiesel are represented in Figs. 1 and 2, respectively. This slight shift in carbonyl frequency is due to the electron donating effect of methyl present in biodiesel along with the C=O group. The C–O stretching vibration in biodiesel showed two asymmetric coupled vibrations at 1168.65 cm<sup>-1</sup> due to ν C–C(=O)–O and 1016.32 cm<sup>-1</sup> due to O–C–C bonds. The methyl group stretching band appeared

**Table 1** Physical properties of sunflower oil biodiesel.

Fuel properties	ASTM method used	ASTM D6751	ASTM D975	Sunflower Oil Biodiesel
		Biodiesel	Petro-diesel	
Density (40 °C, g cm <sup>-3</sup> )	D5002	0.86–0.90	0.834	0.86
Dynamic viscosity (40 °C, cP)	D445	1.6–3.5	1.3–4.1	5.321
Kinematic viscosity (40 °C, mm <sup>2</sup> s <sup>-1</sup> )	D445	1.9–6.0	1.9–4.1	4.719
Pour point (°C)	D97	-15 to 16	-35 to -15	-5.0
Cloud point (°C)	D2500	-3.0 to 12	-15 to 5	4.0
Flash point (°C)	D93	100–170	60–80	183
Sulfur contents (%)	D4294	0.05	0.05	0.0029
Acid number (mg KOH g <sup>-1</sup> )	D664	0.5	0.5	0.07

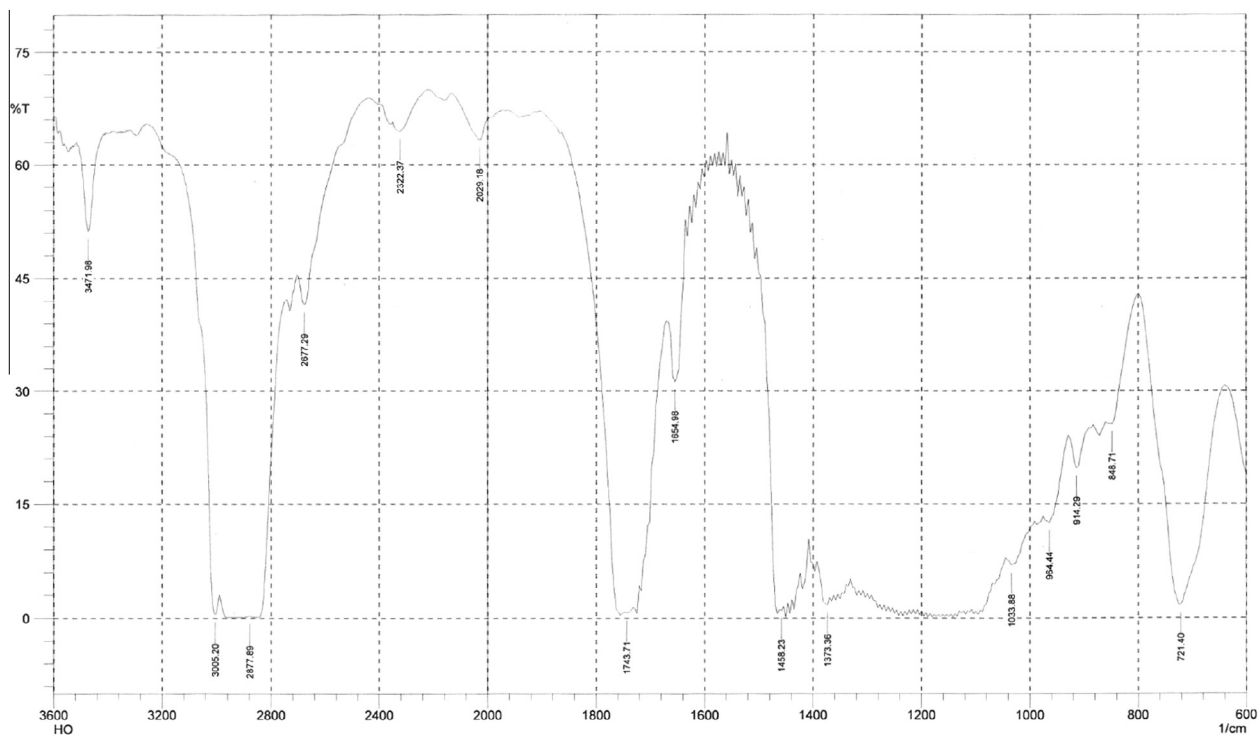


Fig. 1 FT-IR spectrum of triglycerides in *Helianthus annuus* oil.

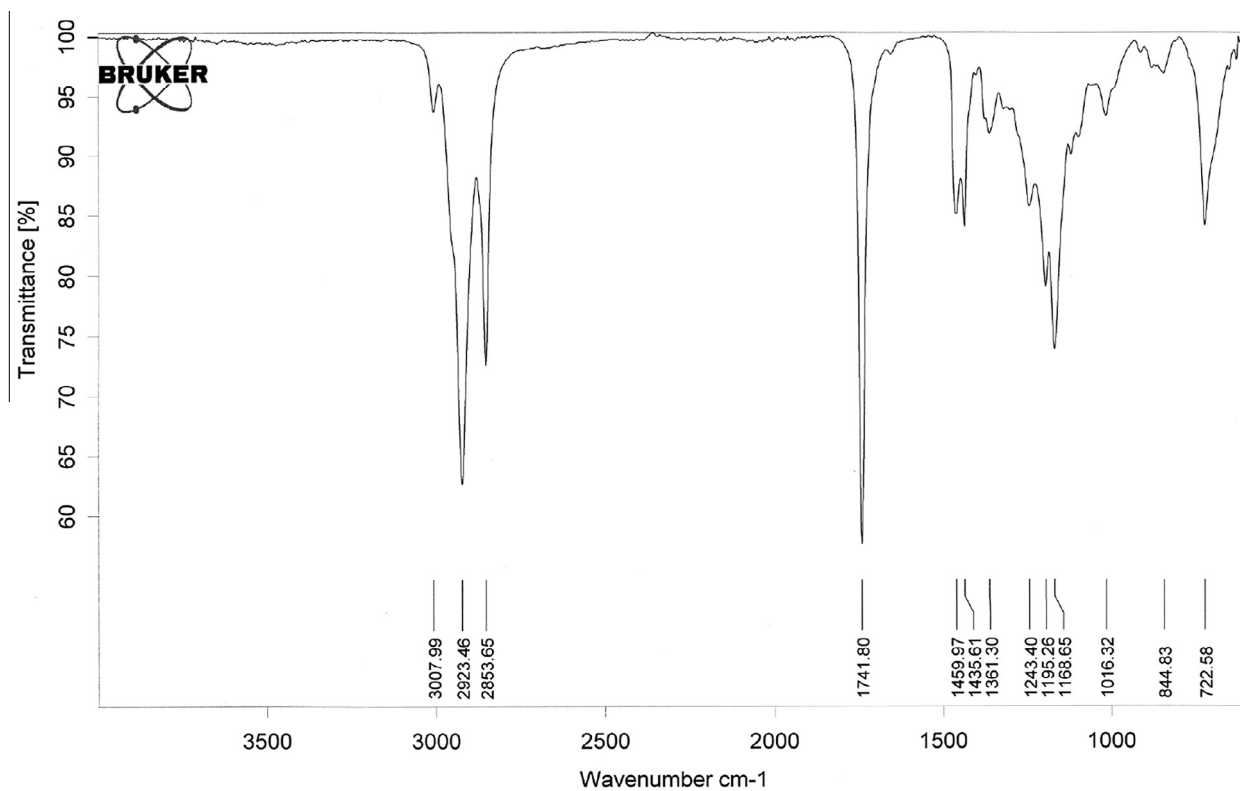


Fig. 2 FT-IR spectrum of methyl esters in *Helianthus annuus* oil biodiesel.

at  $2923.46\text{ cm}^{-1}$  while methylene stretching band appeared at  $2853.65\text{ cm}^{-1}$ . The bending vibrations of methyl groups appeared at  $1459.97$  and  $1361.30\text{ cm}^{-1}$  while methylene bending vibration appeared at  $1243.40\text{ cm}^{-1}$  and rocking (bending) vibration at  $722.58\text{ cm}^{-1}$ .

#### 4.2. Multinuclear NMR spectroscopy

##### 4.2.1. $^1\text{H}$ NMR study

The  $^1\text{H}$  NMR spectrum of sunflower oil biodiesel (B 100, meaning 100% biodiesel with 0% petrodiesel) is shown in Fig. 3. The characteristic intense peak of methoxy protons is observed at 3.622 ppm and  $\alpha$ -CH<sub>2</sub> protons signal at 2.240 ppm. These two peaks are the distinct peaks for confirmation of methyl esters present in the biodiesel. Other peaks were at 0.826–0.881 ppm of terminal methyl protons, a strong signal at 1.227–1.273 ppm related to methylene protons and 5.244–5.363 ppm assigned to olefinic hydrogens.  $^1\text{H}$  NMR can be used to quantify the conversion of vegetable oil in methyl esters by transesterification reaction. The relevant signals chosen for integration are those of the  $\alpha$ -carbonyl methylene protons at 2.240 ppm.  $^1\text{H}$  NMR can also be used to quantify the conversion of vegetable oil in methyl esters by transesterification reaction (Samios et al., 2009; Gelbard et al., 1995). The relevant signals chosen for integration were those of the methoxy group in the methyl esters at 3.622 ppm and of the  $\alpha$ -carbonyl methylene protons at 2.240 ppm. The equation used to quantify the yield of transesterification was:

$$C = 100 \times \frac{2A_{\text{Me}}}{3A} \quad (\text{iii})$$

where

$C$  = percentage conversion of triglycerides to the corresponding methyl esters

$A_{\text{Me}}$  = integration value of the methoxy protons of the methyl esters and

$A_{\text{CH}_2}$  = integration value of  $\alpha$ -methylene protons

The percentage conversion of triglycerides to the corresponding methyl esters by using Eq. (iii) was found to be 87.33% which is quite in good agreement with the practically observed yield of  $85.1 \pm 2.5\%$  through Eq. (i).

##### 4.3. $^{13}\text{C}$ NMR study

The characteristic peaks of ester carbonyl ( $-\text{COO}-$ ) and C–O are the distinct peaks for confirmation of methyl esters present in the biodiesel. In  $^{13}\text{C}$  NMR spectrum, the characteristic peaks of carbonyl ( $-\text{COO}-$ ) and C–O are observed at 174.13 and 51.29 ppm, respectively. The peaks at 127.84–130.05 ppm showed unsaturation in methyl esters. Other peaks around 14.01–14.05 ppm are related to terminal carbon of methyl groups and 22.56–34.09 ppm signals are related to methylene carbons of long carbon chain in FAMES (Ahmad et al., 2011).

##### 4.4. Gas chromatography and mass spectrometry

GC–MS was used to study the chemical composition of the synthesized sunflower oil biodiesel. Eleven major peaks were observed in GC spectrum of sunflower oil biodiesel (Fig. 4). Each peak corresponds to a fatty acid methyl ester and was identified from the library match software (NO. NIST 02).

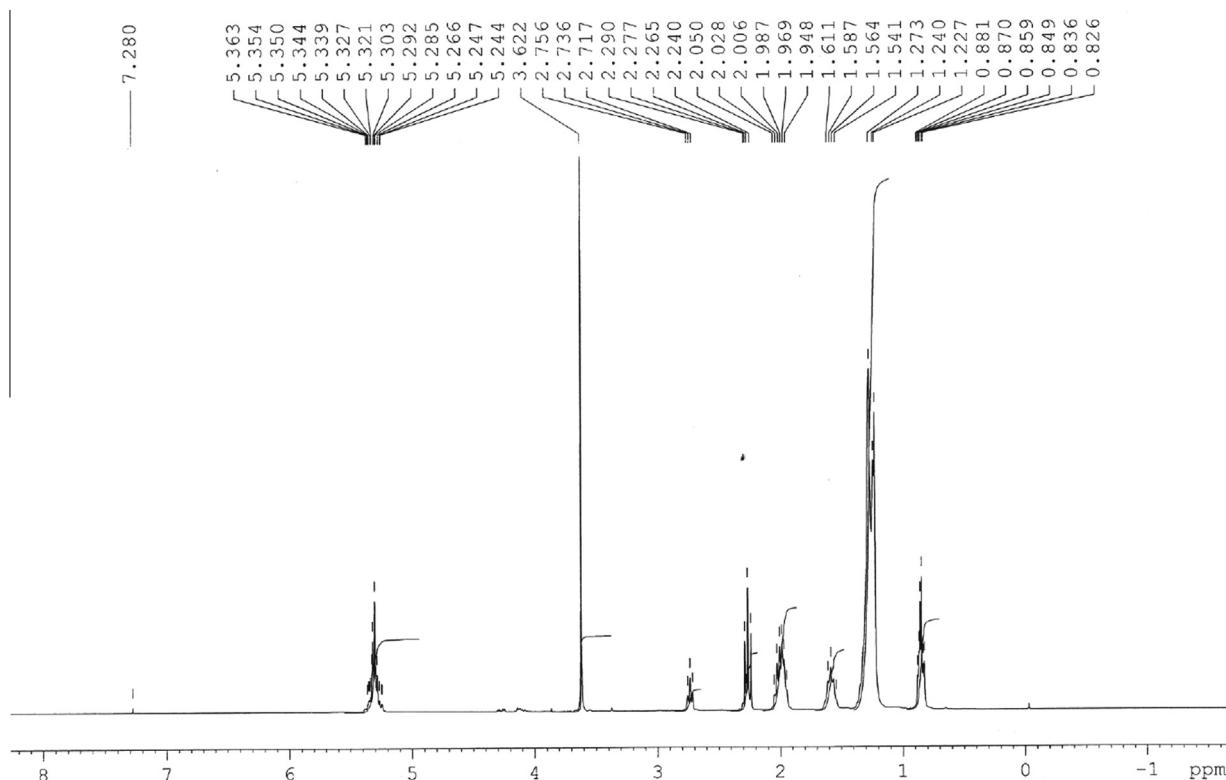


Fig. 3  $^1\text{H}$  NMR spectrum of sunflower biodiesel B100.

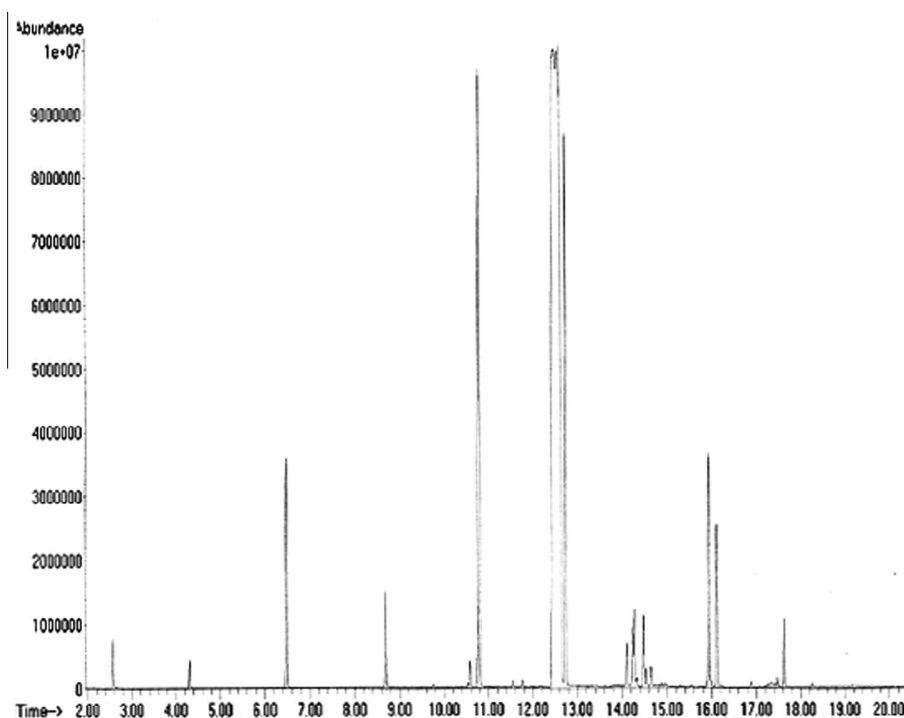


Fig. 4 Total ion chromatogram of sunflower biodiesel showing composition of fatty acid methyl ester.

**Table 2** FAME composition of sunflower oil biodiesel.

Peak no.	RT (min <sup>-1</sup> )	Identified compounds and their formulae
1	6.47	Methyl dodecanoate (C <sub>12:0</sub> ) CH <sub>3</sub> OOC(CH <sub>2</sub> ) <sub>10</sub> CH <sub>3</sub>
2	8.68	Methyl tetradecanoate (C <sub>14:0</sub> ) CH <sub>3</sub> OOC(CH <sub>2</sub> ) <sub>12</sub> CH <sub>3</sub>
3	10.79	Methyl hexadecanoate (C <sub>16:0</sub> ) CH <sub>3</sub> OOC(CH <sub>2</sub> ) <sub>14</sub> CH <sub>3</sub>
4	12.49	Methyl 8,11-octadecadienoate (C <sub>18:2</sub> ) CH <sub>3</sub> OOC(CH <sub>2</sub> ) <sub>6</sub> CH=CH-CH <sub>2</sub> -CH=CH(CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub>
5	12.58	Methyl 9-octadecenoate (C <sub>18:1</sub> ) CH <sub>3</sub> OOC(CH <sub>2</sub> ) <sub>7</sub> CH=CH-(CH <sub>2</sub> ) <sub>7</sub> CH <sub>3</sub>
6	12.74	Methyl octadecanoate (C <sub>18:0</sub> ) CH <sub>3</sub> OOC(CH <sub>2</sub> ) <sub>16</sub> CH <sub>3</sub>
7	14.27	Methyl 11-eicosanoate (C <sub>20:1</sub> ) CH <sub>3</sub> OOC(CH <sub>2</sub> ) <sub>9</sub> CH=CH-(CH <sub>2</sub> ) <sub>7</sub> CH <sub>3</sub>
8	14.47	Methyl eicosanoate (C <sub>20:0</sub> ) CH <sub>3</sub> OOC(CH <sub>2</sub> ) <sub>18</sub> CH <sub>3</sub>
9	15.93	Methyl 13-docosanoate (C <sub>22:1</sub> ) CH <sub>3</sub> OOC(CH <sub>2</sub> ) <sub>11</sub> CH=CH-(CH <sub>2</sub> ) <sub>7</sub> CH <sub>3</sub>
10	16.10	Methyl docosanoate (C <sub>22:0</sub> ) CH <sub>3</sub> OOC(CH <sub>2</sub> ) <sub>20</sub> CH <sub>3</sub>
11	17.62	Methyl tetracosanoate (C <sub>24:0</sub> ) CH <sub>3</sub> OOC(CH <sub>2</sub> ) <sub>22</sub> CH <sub>3</sub>

The identified FAMES with their retention time are shown in Table 2 which include seven saturated, three monounsaturated and one diunsaturated FAMES. The identity of FAMES was made by the retention time data and verified by mass spectrometric analysis. The chain length, number of double bonds and their positions were determined by mass spectrum. The mass spectrum was obtained by an electron impact (EI) ion source (Bano et al., 2014).

Seven saturated FAMES were identified in sunflower oil biodiesel by GC-MS. The electron impact spectra of saturated FAMES were very similar, having characteristic peaks of fragment ions. Each FAME was eluted out at the specific retention time by gas chromatography. The retention time of the eluted components help to identify, whereas the respective mass fragmentation patterns were used to confirm the FAMES. The base peak in all saturated FAMES was observed at  $m/z$  74 which



was a product of well-known McLafferty rearrangement process (McLafferty, 1959). Two other peaks i.e., a peak  $[M-31]^+$  due to  $\alpha$ -cleavage (loss of the methoxy group) and  $[M-43]^+$  due to rearrangement of the chain and one hydrogen atom, followed by expulsion of a propyl radical (carbon 2–4) were observed in the spectra of all the identified saturated FAMES. Other characteristic ions include at  $m/z$  87, the first member of the carbomethoxy ion series due to  $\beta$ -cleavage  $[CH_3OOC(CH_2)_n]^+$ , where  $n = 2, 3, 4, \dots$ ,  $m/z$  87, 101, 115, 129, 143... with a difference of 14 a.m.u., a hydrocarbon series of alkyl ions that were abundant in the low-mass region. Thus  $\beta$ -cleavage and alkyl series support the identification of saturated FAMES (Ahmad et al., 2014).

Three monounsaturated fatty acid methyl esters were observed in sunflower oil biodiesel. The retention time of GC and the fragmentation pattern of MS of the respective components helped to identify/confirm the monounsaturated FAMES. The identified unsaturated FAMES along with retention time and characteristic ions at various  $m/z$  values are shown in Table 2. Other components have very similar fragmentation pattern having characteristic peaks at  $m/z$  55 (base peak),  $[M-32]^+$  due to loss of methanol (the methoxy group plus hydrogen atom) and  $[M-74]^+$  due to loss of McLafferty ion. These three characteristic peaks help to identify monounsaturated FAMES. Other characteristic ions include hydrocarbon ions  $[C_nH_{2n-1}]^+$ ,  $[C_nH_{2n}]^+$ ,  $[M-88]^+$ ,  $[M-102]^+$ ,  $[M-116]^+$  etc. due to loss of a fragment containing the carbonyl group by cleavage between carbon (3, 4), (4, 5) and (5, 6) with addition of rearranged hydrogen atoms.

One diunsaturated FAME was also identified in sunflower oil biodiesel, methyl 8, 11-octadecadienoate (C18:2) whose fragmentation showed a characteristic base peak at  $m/z$  67  $[C_nH_{2n-3}]^+$ , a prominent ion at  $m/z$  263 ( $[M-31]^+$ ) due to loss of the methoxy group while an ion at  $m/z$  220 ( $[M-74]^+$ ) due to loss of McLafferty ion. Other characteristic ionic peaks of hydrocarbon with general formula  $[C_nH_{2n-3}]^+$  were observed in the lower range at  $m/z$  67, 81, 95, 109, 123 of mass spectrometry.

## 5. Conclusions

Sunflower oil biodiesel was synthesized by base catalyzed transesterification with methanol. The dynamic viscosity (5.321 cp) and kinematic viscosity ( $4.719 \text{ mm}^2\text{s}^{-1}$ ), density ( $0.86 \text{ g/cm}^3$ ), pour point ( $-5.0 \text{ }^\circ\text{C}$ ), cloud point ( $4.0 \text{ }^\circ\text{C}$ ), flash point ( $183 \text{ }^\circ\text{C}$ ) and acid number ( $0.07 \text{ mg KOH/g}$ ) of sunflower oil biodiesel met the ASTM standards after transesterification. Formation of FAMES was confirmed by FT-IR, NMR ( $^1\text{H}$  and  $^{13}\text{C}$ ) and GC-MS analyses. The chemical composition of sunflower biodiesel shows eleven types of FAMES as identified by retention time's data and verified by mass fragmentation pattern. The high percentage conversion of oil into biodiesel indicates that sunflower oil has great potential for commercial production of biodiesel.

## Conflict of interests

The authors certify that there is no conflict of interests with any financial organization regarding the material discussed in the paper.

## Author's contribution

R.N. carried out experimental work, M.T., S.A. and M.A. designed the experiments, M.A.A. conceived the project. All authors read and approved the final manuscript.

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