



CHARACTERIZATION AND IDENTIFICATION OF FAME'S IN CANOLA BIODIESEL USING SPECTROSCOPIC STUDIES

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ABSTRACT

Biodiesel was derived from canola seed oil, which was obtained through Expeller-Soxhlet extraction method, KOH as catalyst and methanol were used in single stage transesterification process at 65°C. Biodiesel was characterized using gas chromatography – Mass spectrometry, Fourier transform infrared spectrometry and nuclear magnetic resonance (^1H , ^{13}C) techniques were used to identify the various FAME's present in the biodiesel. Nine fatty acid methyl esters including lauric acid, myristic acid, palmitoleic acid, pentadecylic acid, linoleic acid, oleic acid, arachidic acid, gondoic acid and behenic acid were found in prominent compositions. The physio-chemical properties of canola seed biodiesel was also found to be with in ASTM standards.

Key words: Biodiesel, Transesterification, FAME's, NMR, GC-MS.

INTRODUCTION

Nowadays world is facing energy crisis due to rapid depletion of non-renewable energy such as crude petroleum, which mainly find its application in transportation sector (i.e.) spark ignition and compression ignition engines. On the other hand, environmental pollution has increased to a greater extent, which also affects global warming. Biodiesel derived from non-edible vegetable oils has proved itself to be a very promising alternative to the depleting fossil fuels, which has comparable physico-chemical properties with petrodiesel. The bio-degradability, non-toxicity, energy efficiency and performance ability are the added advantage of biodiesel to be used as fuel for SI and CI engines. Generally, two-stage trans-esterification process (acid catalysed and base catalysed trans-esterification) was

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employed to convert the triglycerides of vegetable oils into their respective mono-alkyl esters by using either ethanol and methanol and a catalyst in the trans-esterification reaction. Recent literature studies have also suggested the addition of oxygenates to the biodiesel in order to enhance their combustible properties. The main advantage of using biodiesel in an internal combustion engine is its self-lubricating characteristics, lesser emission of HC, CO, NO_x and oxides of sulphur.

Nabi et al.¹ investigated production and characterisation of biodiesel from *Pongamia pincata* and found it to be a promising source of alternative fuel. The maximum methyl ester was found to be 97%, which was conformed using chromatographic and spectrometric techniques like GC-MS and FTIR. The experimental analysis of karanja biodiesel on performance and emission characteristics proved to decrease the smoke NO_x and noise level to a greater extent. Naureen et al.² studied the characteristics of sunflower biodiesel using acid/base catalysed methanolysis. The chemical characteristics was carried out using Fourier transform infrared spectrometry supported by nuclear magnetic resonance (proton and carbon). Chromatographic–Mass spectrometry was employed to identify various methyl esters present in sunflower biodiesel gas. They revealed that conversion efficiency was more than 80% as confirmed by NMR & FTIR studies.

Samios et al.³ studied the double step trans-esterification process of sunflower and linseed oil, which has the conversion efficiency more than 90% and biodiesel yield up to 84%. Sharma and Singh⁴ optimized various parameters for preparation of biodiesel from *Schleichera triguga* (Kusum oil) since the acid value was found to be above 20 mg KOH g⁻¹. Two stage trans-esterification was adopted to reduce the acid value and to convert the oil into its biodiesel thereafter. The parameters like catalyst quantity, molar concentration and reaction period were optimised and higher yield of biodiesel was achieved, GC-MS and elemental analysis confirm the presence of FAME's with an optimized molar concentration¹⁹. Tariq et al.⁵ synthesized rocket seed biodiesel through single stage trans-esterification process with sodium hydroxide and methanol as catalyst and reaction medium, respectively. They noticed that eleven different types of methyl ester were present in rocket seed biodiesel through GC-MS analysis, which was confirmed by FT-IR and NMR studies also. The NMR characterization also reveal the conversion efficiency to be more than 88%. Monteiro et al.⁶ determined the blend levels of biodiesel in different sources of straight diesel. Soybean and castor oil were analysed using proton NMR studies and integrated calibration curves were determined with negligible effect in biodiesel quantification.

Present investigation deals with preparation, standardization and characterization of biodiesel from canola seed oil. Soxhlet extraction procedure with n-hexane as solvent is used to extract oil from crushed canola seeds. Base catalysed trans-esterification with KOH and methanol was employed to convert triglycerides into fatty acid methyl esters. The biodiesel extract was subjected to physico-chemical analysis and spectrometric/chromatography techniques for characterizing the canola seed biodiesel.

EXPERIMENTAL

Materials and methods

Dry canola seed were procured from a local vendor in Rajasthan, India. Seeds were washed in flowing water to remove dirt and impurities followed by drying in sunlight for 72 hrs. Canola seed were ruptured using mortar and pestle technique. Soxhlet apparatus was used to extract canola seed to extract canola seed oil. Thimbles filled with crushed canola seed was placed in the extraction chamber and n-hexane solvent was allowed to react with the cell wall membrane to dissolve and extract the canola seed oil. Followed by recovery of n-hexane, oil separation was done using separate condensation chamber. Single stage trans-esterification process using KOH and methanol was carried out to convert canola seed oil into biodiesel^{7,8}.

JOEL, GC MATE II, GC-MS was equipped with high resolution data system powered by double focusing spectrometer. Ion's source for electron impactment, chemical ionization, atom bombardment and elemental composition analysis with maximum resolution and calibrated mass of 6000 and 1500, respectively was employed to analyse the Gas Chromatography and Mass Spectroscopic studies in the presence of polar solvent, supported with NIST-2 library. Bruker AVANCE III 500 MHZ multi-nuclei solution NMR spectrometer equipped with magnet, RF console and probes was used to analyse ¹H-NMR, ¹³C-NMR data on Canola biodiesel with methanol D4 as a solvent medium. 11.7 tesla long hold magnet, actively shielded with 5 to 5.4 cm bore with built in cryo-shim and 34 channel room temperature shims. The RF console comprises of stable lock compatible with pulsed field gradient with low heat decapitation, automatic gradient shimming and deuterium lock. Broad band gradient probe head was 5 mm, BBO and quadruple inverse probe with gradients. Perkin Elmer spectrum and FTIR instrument equipped with globar and mercury vapour lamp as source and interfero chamber comprising of KBr and Mylar beam splitters followed by a sample chamber covering a region of 450-4000 cm⁻¹ was used to study the infrared spectrum of Canola biodiesel. The instrument also consists of signal enhancement and baseline correction systems with a resolution of 1.0 cm⁻¹.

The density of Canola biodiesel was found to be 872 Kg/m³ while rubber seed and Karanja biodiesel exhibited 896 Kg/m³ and 792 Kg/m³, respectively. The viscosity of Canola biodiesel was higher than rubber seed biodiesel. The calorific value and cetane number of Canola biodiesel was found to be 34.6 MJ/Kg and 57, respectively. Acid value of Canola was found to 0.01 mg/KOH/g, which is very much lower than rubber seed and karanja biodiesel, whereas flash point of Canola seed biodiesel was noticed to be higher at 158°C on comparison with other biodiesel⁹⁻¹¹.

Table 1: Comparison of physico-chemical properties – canola, rubber and karanja seed biodiesel

Properties/Biodiesel	Test method	Limits	Canola biodiesel	Rubber seed oil biodiesel	Karanja biodiesel
Density (Kg/m ³)	ASTM D6751	-	872	896	792
Viscosity (Cst)	ASTM D445	1.9 - 6	4.15	3.87	6.9
Calorific value (MJ/kg)	-	-	34.6	37.3	15.86
Cetane number	ASTM D613	47 Min	57	62	44
Flash point (°C)	ASTM D93	130 Min	158	128.6	92
Pour point (°C)	ASTM D6751	-15 -10	-12.8	-7	-9
Cloud point (°C)	ASTM D2500	-3 -12	-2.5	-11.5	-8
Acid value (mg/KOH/g)	ASTM D664	0.50 Max	0.01	0.76	0.52
Saponification value	-	-	172	201	186
Iodine value	ASTM D1959	112 Max	82	97	89

RESULTS AND DISCUSSION

Gas chromatography-mass spectroscopy analysis

Gas chromatography-mass spectrum analysis was employed to understand about the chemical composition of Canola biodiesel. The chromatogram revealed the presence of saturated and unsaturated fatty acid with major and minor composition. The GC-MS ion chromatography (Fig. 1) reveals the presence of a prominent fatty acids as peaks, which was identified by comparing the mass spectrum of individual esters with NIST MS – 1 library. It was identified that 9 major fatty acids like lauric acid, myristic acid, palmitoleic acid, pentadecylic acid, linoleic acid, oleic acid, arachidic acid, gondoic acid, behenic acid were present in the Canola biodiesel.

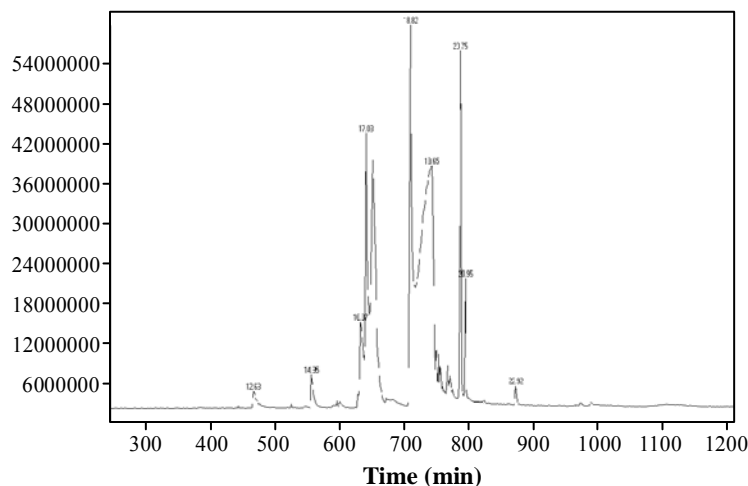


Fig. 1: GC/MS spectrum of Canola seed biodiesel

The Table 2 shows the presence of various fatty acids with respect to their retention time, number of ions and scans. The mass spectrum of all the nine fatty acid methyl esters reveals the base peaks at m/z 74, which is the product of McLafferty rearrangement process¹²⁻¹⁴.

Table 2: Fatty acid methyl esters in Canola seed biodiesel

Peak No.	Retention Time	Name of the ester	Name of the fatty acid	Corresponding acid	No. of ions	Scan
1	12.68	Dodecanoic acid, methyl ester	Lauric acid	C12:0	1677	466
2	14.95	Methyl tetradecanoate	Myristic acid	C14:0	1595	556
3	16.87	9-Hexadecenoic acid, methyl ester,	Palmitoleic acid	C16:0	1293	632
4	17.18	Pentadecanoic acid, 14-methyl-methyl ester	Pentadecylic acid	C15:0	1313	645
5	18.82	7,10 Octadecadienoic acid, methyl ester	Linoleic acid	C18:2	1056	710
6	19.65	8-Octadecenoic acid, methyl ester	Oleic acid	C18:1	1090	743
7	20.98	Eisanoic acid, methyl ester	Arachidic acid	C20:0	1588	796
8	20.78	11.Eicosenoic acid, methyl ester	Gondoic acid	C20:1	1040	788
9	22.92	Docosanoic acid, methyl ester	Behenic acid	C22:0	1574	873

Fourier transform infra-red spectroscopy

The Fourier transform infrared spectrum of Canola seed biodiesel is shown in Fig. 2. Bending and stretching vibrations between 1018 cm^{-1} to 1458 cm^{-1} , 1744 cm^{-1} and 2857 cm^{-1} to 3007 cm^{-1} confirms the presence of esters (carbonyl group; C=O]. Strong signal at 1720 cm^{-1} was shifted to 1744 cm^{-1} on comparison with Canola seed oil to biodiesel, which shows the presence of methyl ester. Stretching vibrations were identified between 1018 cm^{-1} and 1243 cm^{-1} . Between 2857 cm^{-1} and 3007 cm^{-1} , several strong absorbent peaks was identified, which is represented as C-H vibrations. At 1744 cm^{-1} a strong peak of carbonyl ion was identified, which also confirms the presence of methyl esters. Bending vibration between 1361 cm^{-1} and 1458 cm^{-1} indicates C-H bending vibrations¹⁵.

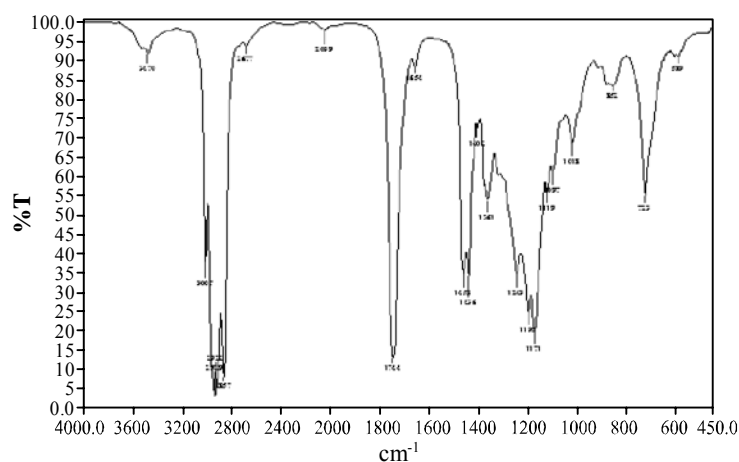


Fig. 2: FT IR spectrum of Canola seed biodiesel

Nuclear magnetic resonance

¹H-NMR: Characterization of Canola seed biodiesel was carried out through nuclear magnetic resonance techniques. A typical ¹H-NMR spectrum is shown in Fig. 3. At 3.67 ppm, a characteristic peak of methoxy proton as a singlet and at 1.63 ppm and 2.33 ppm a triplet of α -CH₂ proton was observed, which confirms the presence of methyl esters in Canola biodiesel. These characteristic peaks were mainly responsible to blend Canola seed biodiesel with commercial diesel with strong commercial viability. There were no peaks beyond 5.5 ppm, which confirms the absence of aliphatic and oleic hydrogens. A strong signal (singlet) at 3.37 ppm also shows the presence of methoxy groups. A weak signal at 4.87 ppm was also seen, which may be due to amines and hydroxy groups. The conversion

of methyl esters from triglycerides was estimated as 88.2%, which could be increased by employing process like chemical separation, centrifugation and ultrasonic separation method followed by prolonging the separation time¹⁶⁻²⁰.

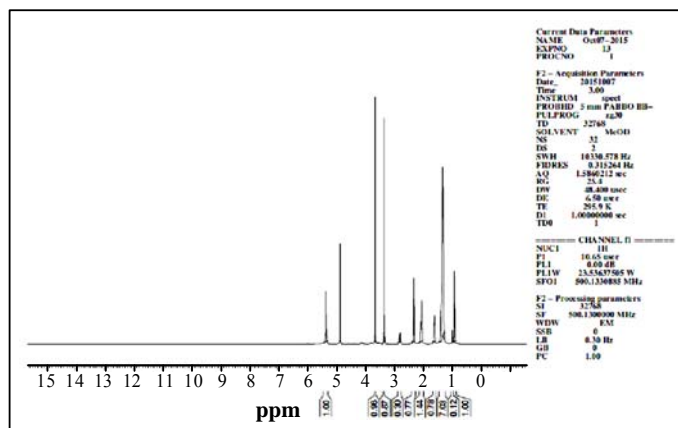


Fig. 3: ¹H NMR spectrum of Canola seed biodiesel

¹³C-NMR: The mass spectrum of ¹³C-NMR with respect to Canola seed biodiesel is shown in the Fig. 4 expressing the characteristic peak at 48.8 ppm. At 29.03 ppm, 67.77 ppm and at 174.03 ppm, esters of carbonyl group with (-COO) and (C-O) was identified, which confirms the presence of methyl esters. Long chain hydrocarbons with methylene group were also identified between 31.77 ppm and 28.75 ppm. One more characteristic peak was seen at 13 ppm, which may be due to methyl and methylene group terminal carbon^{6,21}.

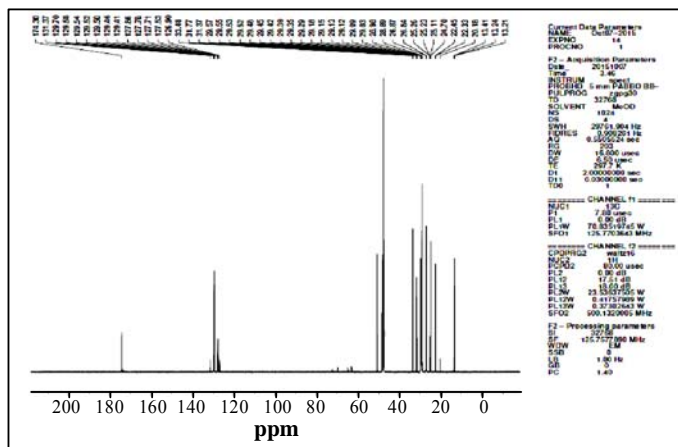


Fig. 4: ¹³C NMR spectrum of Canola seed biodiesel

CONCLUSION

In the present investigation Canola seed biodiesel was extracted and characterized with the help of spectroscopic studies and the following conclusion were arrived,

- (i) Canola seed oil was extracted using Soxhlet apparatus in extraction chamber with *n*-hexane.
- (ii) Base-catalysed transesterification with methanol and KOH as catalyst were employed. Transesterification efficiency of 88% was achieved.
- (iii) Gas chromatography – Mass spectroscopy analysis revealed the presence of nine major fatty acids namely lauric acid, myristic acid, palmitoleic acid, pentadecylic acid, linoleic acid, oleic acid, arachidic acid, gondoic acid and behenic acid.
- (iv) Fourier Transform Infrared Spectrum exhibited bending and stretching vibration between 1018 cm^{-1} to 2300 cm^{-1} indicated the presence of fatty acid methyl esters.
- (v) $^1\text{H-NMR}$ showed a strong signal at 3.37 ppm as a singlet and 1.63 ppm as triplet, which also confirms the presence of fatty acid methyl ester. The mass spectrum of $^{13}\text{C-NMR}$ showed characteristic peaks between 23.03 ppm to 174.03 ppm indicating the presence of carbonyl group.
- (vi) Physico-chemical analysis of Canola seed biodiesel was also found to be within ASTM standards.

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