Research Article

Synthesis and Characterization of Biodiesel from Soyabean, Coconut and Mustard oil

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Abstract

Rapid consumption, the rising costs, environmental problems and fast depletion of fossil fuels from earth have led to look for the alternate sources of energy. Now-a-days, biodiesel is considered as potential renewable energy resource to replace current petrol-derived diesel. The present study deals with the synthesis of biodiesel from *Soyabean oil (SO), Coconut oil (CO)* and *Mustard oil (MO)* via Transesterification by alkali-catalyzed ethanolysis and Characterisation of obtained biodiesel by FTIR. Some critical parameters like Saponification value (SV), Iodine number (IN) and Total Fatty acid (TFA) content from raw materials were also studied. The importance of using base catalyzed transesterification is its economic process, less time for reaction, low temperature and high conversion rate. The obtained yield of ethyl esters reached upto 82.7% wt/wt. where SV for SO, CO, MO was found 190.4±2, 170.8±2.3, 243.1±2.5 and for SOB, MOB, COB was 259.72±2.3, 125.3±2.1, 93±2. and IN for SO, CO, MO was 128.42±1.5, 138.57±2, 10.23±3 and for SOB, COB, MOB was 125.45±3.3, 140.5±2.3, 8±0.9 respectively and TFA for SO, CO, MO was 0.67±0.3, 2.24±0.5, 0.33±0.7 and for SOB, COB, MOB was 0.97±0.3, 1.8±0.3, 0.18±0.5 respectively. Comparison of Biodiesels (BD) showed clear difference in fatty acid composition; that very low iodine value (8.71) and absence of peak at 1650cm^{-1} to 1653cm^{-1} in IR spectra of CO indicates negligible amount of unsaturated fatty acid. Moreover slightly decrease from 1746 cm^{-1} to 1744cm^{-1} suggests the formation of ethyl ester. Appearance of some new peaks in BDs indicates that transesterification takes place. Similarity between IR Spectras of oil and biodiesel suggests no side reaction occurred.

Keywords: Vegetables oil, Biodiesel, IR Spectra, Ethanol, Iodine Number, Saponification value

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Introduction

Biodiesel derived from biological sources received increasing attention globally as it reduces the dependence on petroleum products, the energy crisis and in certain aspects it is environmentally safe e.g. 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 [1-4].

There are several advantages of Biodiesel i.e Biodegradability, Nontoxicity, does not contain sulfur. Moreover, being plant based it does not emit CO on burning [5]. Any types of feedstock which contains free fatty acids and/or triglycerides such as vegetable oils, waste cooking oil, animal fats, and waste greases can be converted into biodiesel [6].

Biodiesel (alkyl esters of fatty acids derived from biomass) is typically produced by acid- or base-catalyzed transesterification of oils and fats from vegetable or animal sources with ethanol or methanol where glycerol is the byproduct. BD also has several advantages over petroleum-based diesel fuel: depending on the engine its combustion generates between 50 and 78% less unburned hydrocarbons, NOx, particulate matter, and CO_2

We introduced a project on BD in 4CHMDEPR01 (Dissertation/Project) to our third-year chemistry students. The emphasis was on the synthesis and characterisation of BD from Mustard oil (MO), Coconut oil (CO) and soybean oil (SO).

Since FT-IR is vital in analysis of Biodiesel and is being employed as a modern analytical technique for detecting

the conversion of biodiesel because it is a fast and easy detection method. Raw oils and the ethyl esters are noted as fairly strong absorbers in the infrared region of the electromagnetic spectrum and this method is very valuable [7]. However, it is being used because spectral resolution is not needed for more specific analysis. A comparative study on biodiesel synthesis from different vegetable oils by infrared spectroscopy has been reported [8]. The ester carbonyl group stretching vibration at 1740 cm^{-1} is shown by strong bands, esteric –COC vibration at 1171 and 1207 cm^{-1} reveals medium intensity bands, and the presence of the $(CH_2)n$ group vibration band is seen at 724 cm^{-1}[9].

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. The present study deals with the synthesis and characterisation of biodiesel from *Soyabean oil, Coconut oil* and *Mustard oil* via Transesterification by alkali-catalyzed ethanolysis and characterisation of obtained biodiesel by FTIR. Some critical parameters like SV, IN and TFA content from raw materials and their ethyl esters were also studied. In contrast, usage of ethanol in place of methanol has the following advantages: mainly produced from biomass; easily metabolized by humans and generates stable fatty acid esters [10].

Methods

Chemicals

Soyabean, Coconut and Mustard oil purchased from local market Jammu, ethanol (99% purity, Merck), potassium hydroxide (99% purity, Merck), all other chemicals used in this study were of analytical grade. Biodiesel formation was also confirmed by FTIR analysis using a Bruker, Germany 3000 Hyperion Microscope with Vertex 80.

Synthesis of Ethyl Ester

Transesterification of oils were carried out by mixing preheated 5 g of each oil, 5 mL of ethanol and 200 mg of catalyst (sodium hydroxide) in a 50 ml round bottom flask separately on a magnetic stirrer. The system was under this condition for 30 min. then, few drops of hydrochloric acid was added drop wise to the reaction mixture, followed by soft heating until 80°C. After the heat was stabilized, the reaction resume on this condition for 2 h 30 min. then mixture was transferred to a separating funnel and kept for 3 h to separate the lighter phase (biodiesel) from the denser phase (glycerol). The ethyl esters (superior layer) are then separated from the raw glycerol (lower layer) with some traces of non reacted oil, and a small amount of ethanol. To remove the excess alcohol, the reaction mixture was concentrated using a water bath. After separation of two phases, ethyl esters (biodiesel) were mixed with sodium sulphate. The procedure was approximately performed during 4h and obtained biodiesel was analyzed by FTIR.

Total Fatty Acid content (TFA)

TFA 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 [11].

A blank titration was also carried out with ethanol. The sample titration was carried out with 1 ml of sample. Acid number was calculated by using the following formula.

$$\text{Acid value} = \frac{\text{Titre Value} \times \text{Normality of KOH} \times 56.1}{\text{Weight of Sample (g)}}$$

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)

Saponification Value

Saponification value (SV) was determined according to the AOAC method (920.160). A known weight of the oil or biodiesel sample (5 g) was heated with alcoholic potassium hydroxide (50 ml, 0.5%) for about 30 min. The reaction mixture was cooled down and then titrated with hydrochloric acid solution (0.5 N) using phenolphthalein as an indicator. A blank was performed where the same volume of alcoholic potassium hydroxide solution without oil was treated similarly as in the experiment. The saponification number is expressed as mg KOH required to saponify 1 g oil or biodiesel sample.

Formula

$$\text{Saponification Value} = \frac{28\,(\text{Titre Value of Blank} - \text{Titrant Value of Sample})}{\text{Weight of Sample}}$$

Iodine value (IV)

IV was determined using the Hanus method, as described in AOAC (920.158). A known weight of the oil or biodiesel sample (0.2 g) was dissolved in chloroform (20 ml), then Hanus iodine (I2 +Br/ACOH) solution (25 ml) was added and left in the dark for 30 min. Potassium iodide solution (10 ml, 15%) was added, followed by freshly distilled water (100 ml), and the excess iodine was titrated by sodium thiosulfate (0.1 N) until the yellow color of the solution had almost disappeared.

Titration was continued after adding a few drops of starch as an indicator until the blue color had entirely disappeared. A blank was conducted where the total halogen content of the Hanus solution (25 ml) was determined by sodium thiosulfate solution without the addition of oil. IV is expressed as grams of I_2 absorbed by 100 g oil or biodiesel sample.

Formula

$$\text{Iodine Value} = \frac{(B - S) \times N \times 12.69}{\text{Weight of the Sample (g)}}$$

Statistical analysis

Data are expressed as mean ± standard deviation (SD) of three replicates. The data were analyzed by analysis of variance by SPss software.

Result and Discussions

The results has shown the maximum yield of ethyl esters reached upto 82.7% wt/wt. Various physiochemical parameters such as Acid Value, Saponification Number and Iodine Number are presented in **Table 1.**

Table 1 Physicochemical properties of various oils and their biodiesels

Sample (Oils)	Saponification Value	Iodine value	Acid value
Soyabean oil	190.4±2	128.42±1.5	0.67±0.3
Mustard oil	170.8±2.3	138.57±2	2.24±0.5
Coconut oil	243.1±2.5	10.23±3	0.33±0.7
Biodiesel			
Soyabean	259.72±3	125.45±3.3	0.97±0.3
Mustard	125.3±3.2	140.5±2.3	1.8±0.3
Coconut oil	93±2	8±0.9	0.18±0.5

Total Fatty Acid (TFA)

Determination of TFA is an important test to assess the quality of a particular biodiesel. The TFA of the starting material can play an important role on the % FAEE of the final product. The maximum level of TFA for pure biodiesel, as specified in ASTM standard D6751 [12], is 0.8 mg KOH $g^{-1.}$ In our study the TFA for SO, CO, MO was 0.67±0.3, 2.24±0.5, 0.33±0.7 and for SOB, COB, MOB was 0.97±0.3, 1.8±0.3, 0.18 ±0.5 respectively. Since, the acid number increases as the fatty acid breaks down into shorter chain acids (ASTM D-664). The high FFA content (>1%; w:w) will cause soap formation, and the separation of products will be exceedingly difficult; as a result, it has a low yield of biodiesel product.

Saponification value (SV)

The SV indicates the amount of saponifiable units (acyl groups) per unit weight of oil. A high SV indicates a higher proportion of low molecular weight fatty acids in the oil or vice versa. The SV is used for measuring the average molecular weight of oil and expressed in milligrams of potassium hydroxide (mg KOH/g oil). Results are presented in Table 1.

Iodine value (IV)

The IV is the measure of degree of unsaturation in oil. It is constant for particular oil or fat. The IV is a useful parameter in studying oxidative rancidity and chemical stability properties of different oil and biodiesel fuels. A higher quantity of double bonds in the sample has greater potential to polymerize and, hence, lesser stability. Our results has shown that IV for SOB, COB, MOB was 125.45±3.3, 140.5±2.3, 8±0.9 and for SO, CO, MO was 128.42±1.5, 138.57±2, 10.23±3 respectively. Oils with an IV above 125 are classified as drying oils; those with an IV of 110–140 are classified as semidrying oils. Those with IVs less than 110 are considered as nondrying oils. IVs are useful for determining the overall degree of saturation of the oil, which is important for viscosity and cloud points. The lower the IV, the better the fuel will be as a biodiesel. IVs greater than 50 may result in decreased engine life but give better viscosity characteristics in cooler conditions

FTIR of Raw materials and their Biodiesel

Oils and their BDs were investigated using FTIR spectroscopy and the spectra are illustrated in **Figure 1a-f**. Relatively small differences observed between the spectra of raw materials and their BDs. The peaks in the region from 1800–1700 cm^{-1} ascribed to the stretching of C=O were observed in biodiesels as well as in oil. The peaks obtained in the range 1500–900 cm^{-1} is known as the fingerprint region which discriminates biodiesel from its source. Moreover the peak at 1033 cm^{-1} was absent in spectra of MO where as this peak is present in MOB. The esters have two characteristically strong absorption bands arising from methoxy carbonyl and CO stretching [13]. In our study a slight shift in carbonyl frequency is due to the electron donating effect of methyl present in biodiesel along with the CO group. The C–O stretching vibration in biodiesel showed two asymmetric coupled vibrations at 1168.65 cm^{-1} due to m C–C (O)–O and 1016.32 cm^{-1} due to O–C–C bonds. The methyl group stretching band appeared at 2923.46 cm^{-1} while methylene stretching band appeared at 2853.65 cm^{-1} (review). The bending vibrations of methyl groups appeared at 1459.97 and 1361.30 cm^{-1} while methylene bending vibration appeared at 1243.40 cm^{-1} and rocking (bending) vibration at 722.58 cm^{-1}. The glycerol group O–CH_2 (mono, di and triglycerides) stretching was attributed to the absorbance peak at 1377 cm^{-1} which was found in soybean biodiesel spectrum. The absorbance peak obtained at 1195 cm^{-1}, attributed to the stretching of O–CH_3, but this peak was absent in all studied spectrum. 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]. Stretching vibrations were identified between 1018 cm^{-1} and 1243 cm^{-1}. Between 2857 cm^{-1} and 3007 cm^{-1}, several strong absorbent peaks were identified, which is represented as C-H vibrations. Absence of peaks at 1600 cm^{-1} to 1500cm^{-1}in CO as well as as in COB indicates a very low unsaturation. Moreover, Mustard oil (MO) has about 60% monounsaturated fatty acids (42% erucic acid and 12% oleic acid); it has about 21% polyunsaturated fats (6% the omega-3 alpha-linolenic acid and 15% the omega-6 linoleic acid), and it has about 12% saturated fats as reported in literature.

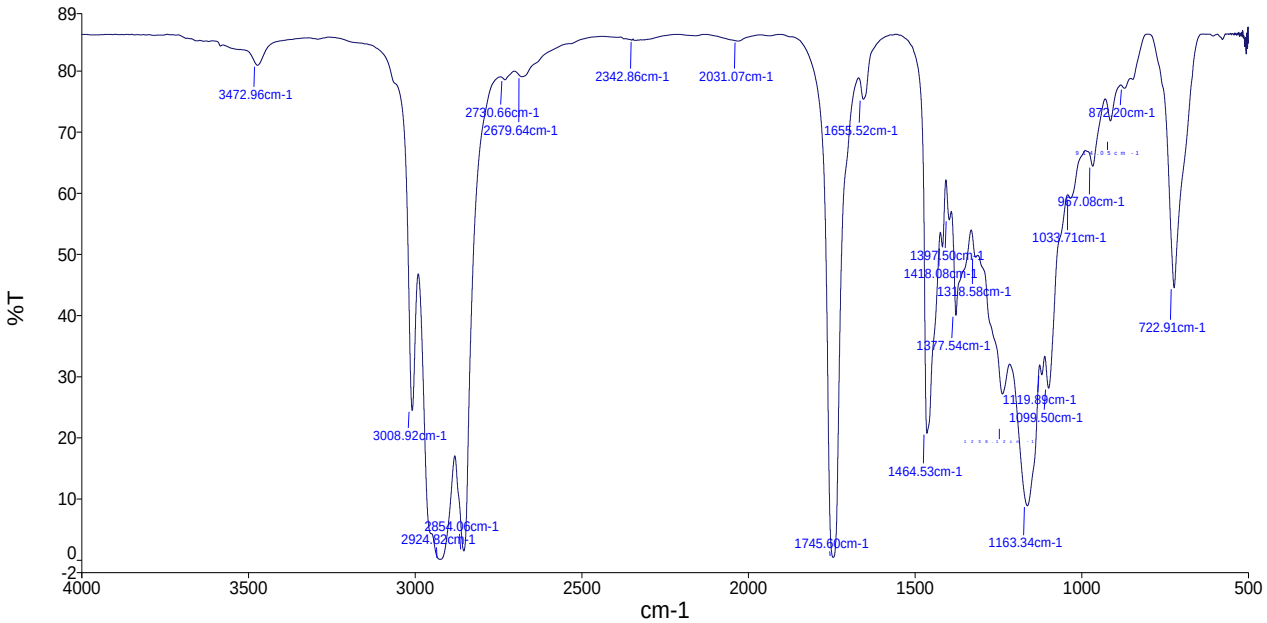

Figure 1 (a) FTIR Spectra of Soyabean Oil (SO)

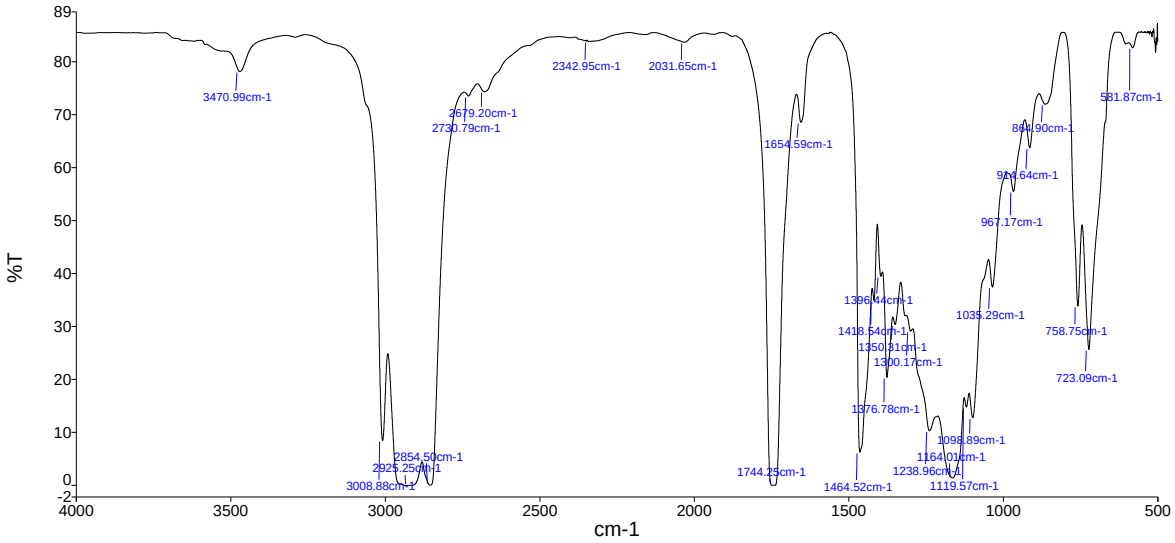

Figure 1 (b) FTIR Spectra of Soyabean Oil Biodiesel (SOB)

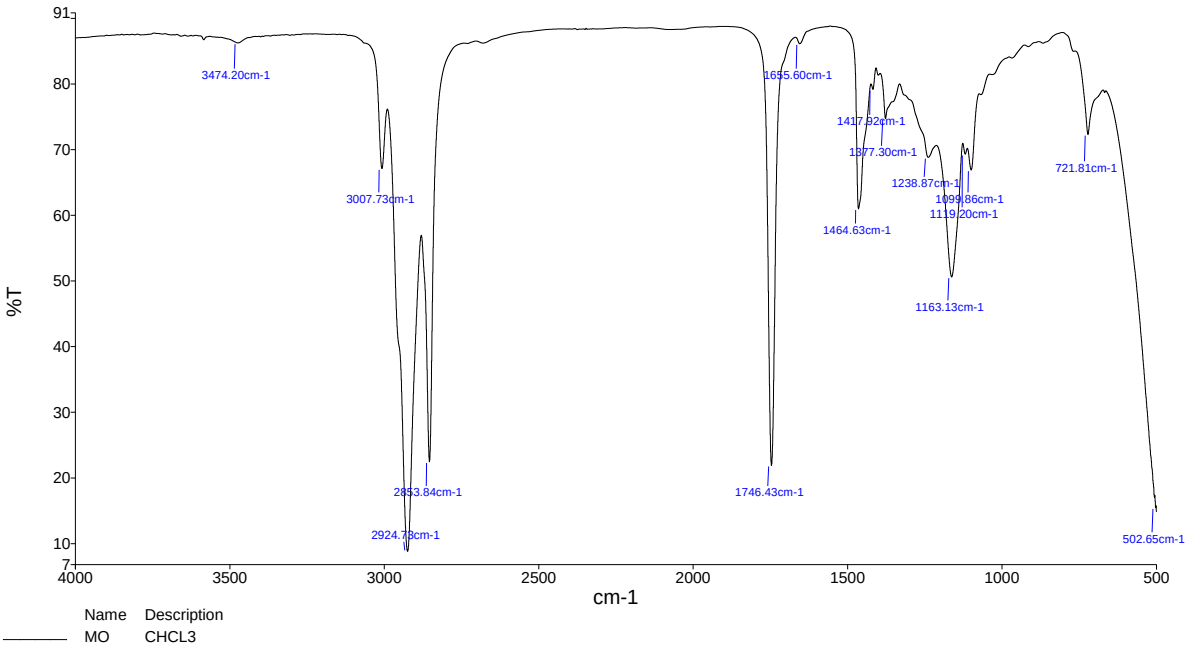

Figure 1 (c) FTIR Spectra of Mustard Oil (MO)

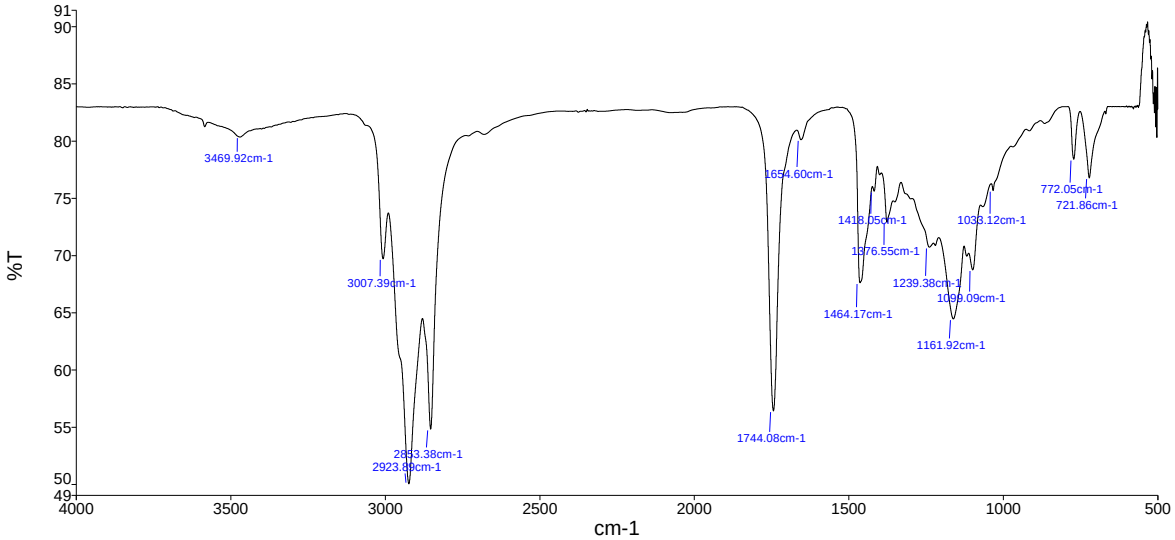

Figure 1 (d) FTIR Spectra of Mustard Oil Biodiesel (MOB)

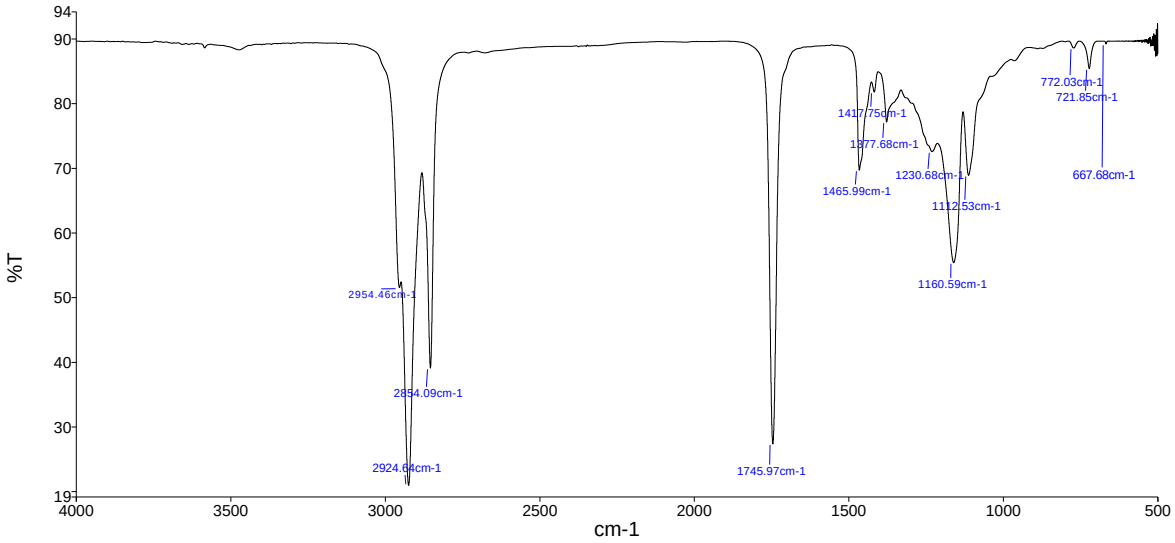

Figure 1 (e) FTIR Spectra of Coconut Oil (CO)

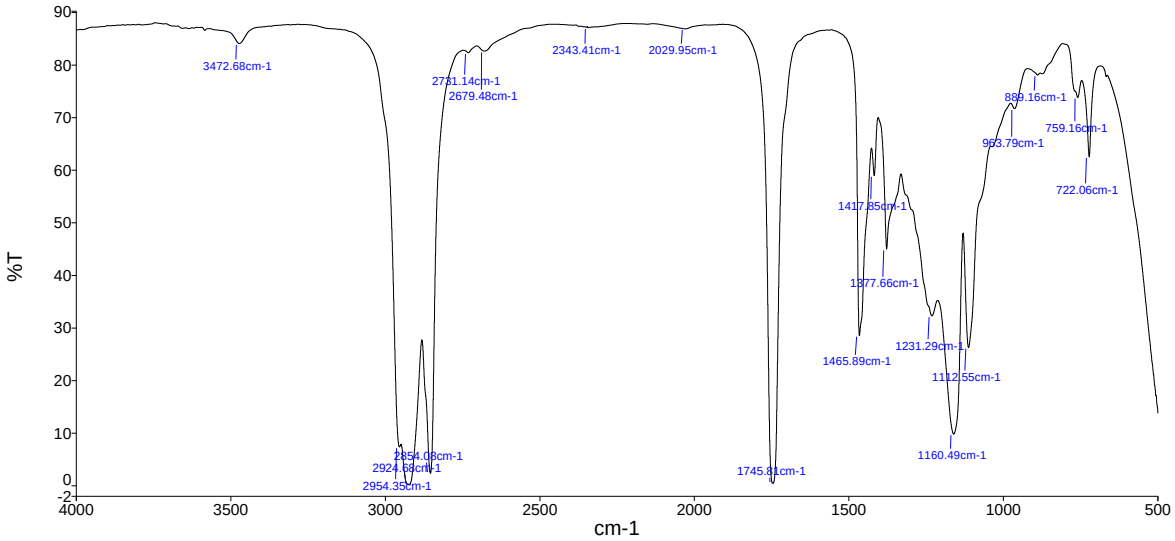

Figure 1 (f) FTIR Spectra of Coconut Oil Biodiesel (COB)

Conclusion

Highest yield of biodiesel was obtained from Soyabean oil. No statistically significant ($p \geqslant 0.05$) differences in the physicochemical parameters were found between biodiesel samples produced from various vegetable oils. Biodiesel with high amounts of saturates (which means low IVs) will have a higher cetane number (CN), while biodiesel from vegetable oils with high amounts of unsaturates (high IVs) will have a lower CN. Unsaturation in the fatty acid chain is the most significant cause of lower CNs. An important characteristic of CO is that it is composed of essentially saturated fatty acids, On the other hand, the fatty acids of SO are essentially unsaturated as this was further confirmed by their IR Spectras. Therefore, CO is much less prone to oxidation during deep-frying than SO.

Acknowledgement

The authors gratefully acknowledge the support and necessary facilities provided by Dr. Naveen Anand, Coordinator of Chemistry and Dr. Bopinder Singh, Dean, Academic Affairs, Cluster University of Jammu. We extend our thanks to Mr. Avinash Lab. Asstt. and Mr. Manohar, Lab. Bearer, who participated in this project. Special thanks to G.G.M Science College for providing required chemicals.

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Publication History
Received 19.03.2020
Revised 11.05.2020
Accepted 01.06.2020
Online 30.06.2020