

Qualitative analysis of biodiesel produced by alkali catalyzed transesterification of waste cooking oil using different alcohols

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The present study evaluates the nature of fatty acid methyl esters (FAMES) formed through alkali-catalyzed transesterification of waste cooking oil (WCO) using methanol, ethanol as well as in combination, where the sequential addition of ethanol followed by methanol is done keeping the molar ratio of alcohol to oil constant (5:1), with sodium hydroxide as catalyst. A substantial reduction in reaction time from 8 h to 20 min is seen in the latter case. Further, the gas chromatography/mass spectrometry (GC-MS) analysis of the transesterified oil show a significant presence of FAMES. Transesterified oil obtained from a combination of both the solvents show substantial quantities of unsaturated FAMES [linoleic acids (41.89%), palmitelaidic acid (7.97%)], saturated FAMES [stearic acids (4.62%), arachidic acids (2.54%)] and minor fraction of other acids. Hence, the utilization of WCO with the use of combined solvent system for transesterification, appear to have a great potential for replacing the conventional substrates that are being used for biodiesel production without much compromising on engine modifications.

Keywords: Biodiesel, GC- MS analysis, Resource Recovery, Transesterification, Waste cooking oil, Waste to Energy

Biodiesel has emerged as an attractive alternative fuel for sustainable development as the present era is endowed with problems of energy security due to depleting reserves of petroleum oil, their escalating prices, as well as concerns for environmental pollution. Biodiesel as an energy source derived from the alkali/acid catalyzed transesterification process using vegetable/animal fats have several advantages, being biodegradable, non-toxic and environmentally friendly, relieves the over-dependence on fossil fuel sources. In contrast to the fossil fuels based diesel, biodiesel has a more favorable combustion emission profile¹, producing much lower emissions of carbon monoxide, particulate matter and unburned hydrocarbons^{2,3}. Because of the higher flash point, it is much less volatile and comparatively easy to handle and transport. Further, it has better lubricating properties which provide extended engine life⁴. Biodiesel mixed with conventional diesel in some proportions has been successfully used in existing compression ignition engine⁵⁻⁷. In spite of the displayed advantages, the large scale commercial utilization of biodiesel is still lacking due to different constraints associated with the current feedstock which comprises of mostly the non-edible oilseed crops such as jatropha, pongamia and castor. Issues

like lower seed yield, limited availability of wastelands concomitant with the higher maintenance costs have made their use non-viable for building a sustainable biodiesel industry⁸. It is expected that India can supplement upto 41.14% of its diesel consumption if cost efficient resources were used as feedstocks⁹.

Waste fats or vegetable oil as feedstock for biodiesel production is expected to partially sort out the problems of higher production costs by 60-90% as prices of waste cooking oils (WCO) is 2-3 times cheaper than virgin oils¹⁰. WCO contains a significant amount of free fatty acids, thus can act as a promising source for biofuel^{3,4}. However, often frying results in a change in their physiochemical properties thus hindering their use as a fuel in engines¹. Several researchers have used different approaches of transesterification supplemented with alkaline catalysts^{11, 12}, acid catalysts¹³, heterogeneous catalysts¹⁴⁻¹⁶, enzymes¹⁷ along with supercritical treatment¹⁵, sonochemical treatment¹⁸ for converting WCO as fuel. Methanol and ethanol both with unique properties are most commonly used solvents in the process of transesterification¹⁹. In case of methanol, as the mass transfer is limited due to less solubility of oil, downstream processing and separation of transesterified oil is more comfortable. However, the reactive

intermediate methoxide makes equilibrium conversion faster²⁰. Ethanol, on the other hand, has better solvent properties than methanol, but the formation of an emulsion with oil during the process of transesterification makes the separation of ester very difficult. Thus to explore the advantages of both the solvents, a mixture of methanol/ethanol is used for the transesterification reaction. Higher yield of fatty acid methyl esters (FAMES) has been reported from a mixture of alcohols²⁰. Another advantage of using the mixture of alcohols is that since ethanol can be obtained from renewable sources, it causes less dependency on the synthetic sources for methanol, thus reducing the cost factor²⁰. Studies by Kulkarni *et al.*²¹, Kim *et al.*²²; have reported effective transesterification of vegetable oils with methanol/ethanol systems. Silva *et al.*²³ studied the effects of combined system of alcohols on the yield of alkyl esters from Babassu oil. Lin & Tsai²⁴, have used equal proportion methanol: ethanol (3:3) to carry out the transesterification of chicken fats. The use of methanol/ethanol system for transesterification of WCO under a milieu of parameters has also been investigated by few studies. Issariyakul *et al.*²⁰, studied the process of transesterification of waste fryer grease using methanol/ethanol system. Ma *et al.*²⁵ studied the influence of the use of methanol/ethanol system with heterogeneous catalysts like Mg/Al hydrotalcite. Very recently, Fadhil & Ahmed²⁶ reported the biodiesel yield of 97.30% with waste fish oil using mixed methanol/ethanol system with potassium hydroxide as catalyst. The potential of using the combination of alcohols has been well highlighted by the above studies. More such research under homogenous catalyst conditions is essential, to reduce the dependency on only methanol (prepared synthetically) replacing its proportion with ethanol (which can be prepared from agro-residues).

Various specifications that a biodiesel fuel must meet are contained in biodiesel standards, such as American Society for Testing and Materials (ASTM D6751) and Bureau of Indian Standards (BIS). Several properties of fuel like cetane number, kinematic viscosity, oxidative stability, and cold-flow properties in the form of the cloud point or cold-filter plugging point depends upon the fatty acid composition of the biodiesel²⁷. The nature of solvents used in the transesterification process also influences the biodiesel properties. Very limited studies^{20, 26} have reported the variation in FAMES with the combination of alcohol systems for WCO.

Therefore, the current paper aims to study the difference in properties of biodiesel obtained via the process of transesterification of WCO with methanol, ethanol and mixtures of both solvents in equal proportion. Properties of fatty acid alkyl esters prepared from different alcohols were analyzed using gas chromatography and mass spectrometry (GC-MS) with the perspective of use as fuel in compression ignition (CI) engine. Such studies are essential in establishing the promising potential of biodiesel from WCO as fuel in CI engines without going for expensive and time consuming engine modifications. The use of methanol/ethanol system would also reduce the proportions of synthetic methanol used, making the system more cost efficient and sustainable.

Experimental Section

Reagents and chemicals

WCO (1 L volume) was collected from the hostel mess of Vikram Sarabhai Hall of Residence (Hall-10) of NIT Rourkela in clean plastic bottles and were sealed till further use. Methanol and ethanol of analytical grade were purchased from Merck. Sodium hydroxide was purchased from Hi Media, India.

Analysis of properties of oil

Physical properties of WCO like cloud point, pour point, kinematic viscosity and density are measured. Cloud point and pour point are measured manually using the ASTM D2500-05 method. Kinematic viscosity and density were measured using capillary tube viscometer (Visco-88 Viscometer, Malvern Instrument) through falling ball method.

Conversion of waste cooking oil to biodiesel via transesterification

Transesterification reaction was carried out with 1:5 ratio of oil/alcohol with sodium hydroxide [2 % (w/v) of oil] as a catalyst. Freshly prepared sodium alkoxide solution (20 mL) was added to oil heated at 60°C with constant stirring at 250 rpm using a magnetic bead. The stirring continued for 120 min. The mixture was allowed to stand and settle into two separate phases. The denser layer of glycerol was separated from the upper layer of fatty acid methyl esters (FAMES). The reaction was carried out using two different alcohols (i.e., methanol and ethanol) as well as with the sequential addition of ethanol followed by methanol [20 mL each]. The reaction time in each case was analyzed.

GC-MS analysis of properties of biodiesel

For the quantification of biodiesel after transesterification reaction, samples were analyzed by a

Table 1 — Physical properties of waste cooking oil (WCO) compared to the standard limits of diesel and biodiesel

Properties	Experimental Values	ASTM Standard Limits	
		Biodiesel ^a	Diesel ^b
Physical state	Liquid	NA	NA
Colour	Deep, dark oily	NA	NA
Pour point (°C)	-20	-15 to -10	-35 to -15
Cloud point (°C)	-3	-3 to 12	-15 to 5
Density (g/cc)	0.87 (at 40 °C)	0.88 (at 15.5 °C)	0.85 (at 15.5 °C)
Kinematic viscosity (cST) at 40 °C	43.28	1.9 to 6	1.3 to 4.1

^a denotes standard limits of biodiesel as per ASTM D6751-07 (Wendy *et al.*²⁸)

^b denotes standard limits of diesel as per ASTM D975 (Wendy *et al.*²⁸; Aghel *et al.*²⁹)

gas chromatography-mass spectrometry (GC-MS) system incorporated with an Agilent 5977 A mass-selective detector (MSD). Approximately 1 μ L sample was injected into the GC. Helium was used as the carrier gas. The injection was performed in splitless mode. The parameters of the oven temperature program included a start at 80°C with 10°C min⁻¹ intervals up to 180°C (1 min) and up to 255°C with 15°C min⁻¹ intervals (2 min).

Results and Discussion

Physical properties of waste cooking oil

Physical properties of WCO as enlisted in Table 1 are measured using different analytical and manual methods, and compared to the ASTM standards for diesel and biodiesel. Pour point and cloud point of WCO were found to be -20 °C and -3 °C respectively. Dynamic viscosity at 40 °C of oil was found to be 37.65 mPa s as calculated from the shear stress versus strain graph (obtained from the viscometer) illustrated in Fig. 1. The density was found to be 0.87 g cm⁻³. The kinematic viscosity of oil 40 °C was found to be 43.28 cSt. The kinematic viscosity of WCO as reported in the literature ranges between 37 to 43 cSt, which is higher comparatively because of the oxidations and polymerization reactions occurring during the process of frying⁹. The physical properties of oil especially some of the essential parameters like kinematic viscosity affects the fuel injection strategy due to fuel atomization³⁰. The high viscosity oil reduces the fuel amount before combustion. WCO due to frying has higher viscosity which makes them unsuitable as fuel⁴ thus there is a need to convert the fatty acids in oil to fatty acid alkyl esters via transesterification.

Effect of alcohol on reaction time during transesterification reaction

The distinct, clear phase of fatty acid alkyl esters and glycerol was obtained in 8 h for oil treated with sodium methoxide as catalyst, whereas no distinct

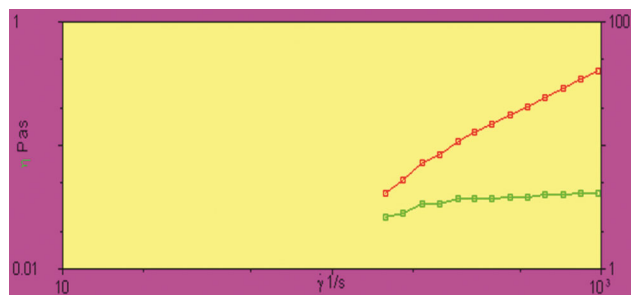


Fig. 1 — Shear stress versus strain graph obtained for measuring the viscosity of WCO at 40 °C.

phase separation was seen even after 48 h in case of oil treated with sodium ethoxide (Fig. 2a and 2b). However, the phase separation was seen instantaneously in 20 min with the combined usage of methanol and ethanol in equal quantity (Fig. 2c). Transesterified oil in both the cases was yellow in color. Sanli & Canakci³¹ reported methanol is the best alcohol for transesterification and other alcohols like ethanol require longer reaction times. It has been postulated by different studies^{32, 33} that the base catalyzed transesterification with only ethanol is inefficient and difficult, while compared to methanol based reactions. Due to higher solubility of oil in ethanol, the formation of stable emulsion is problematic as the oil and ethanol-glycerol layer are not distinctly formed³². Though the emulsion is formed during reaction, it does not break down quickly to separate as the upper alkyl ester layer and lower glycerol layer³³. It clearly justifies the failure in obtaining the ethyl esters even after 48 h of the reaction with ethanol. Musa¹⁹ have discussed that in case of oils with higher viscosity, the increase in molar ratio of alcohol: oil preferably in the range of 6:1 to 30:1 might favour a faster breaking of glycerin fatty acid linkages during the process of transesterification¹⁹. It justifies the requirement of maintaining a higher molar ratio to further bring down

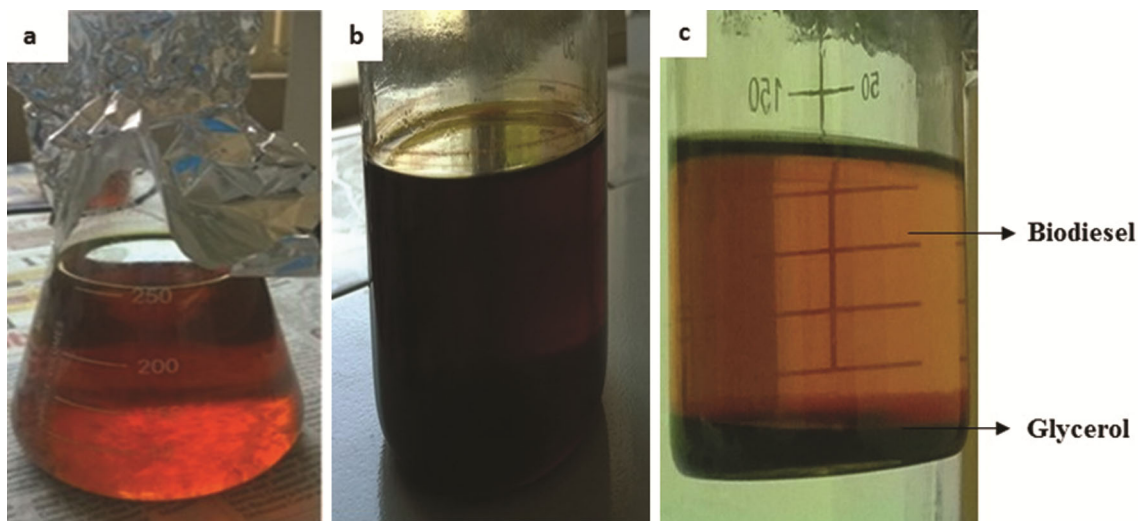


Fig. 2 — (a) WCO obtained after frying from hostel mess; (b) Oil after transesterification with ethanol showing no distinct phases; (c) Oil after transesterification with methanol and ethanol showing distinct phases of biodiesel and glycerol

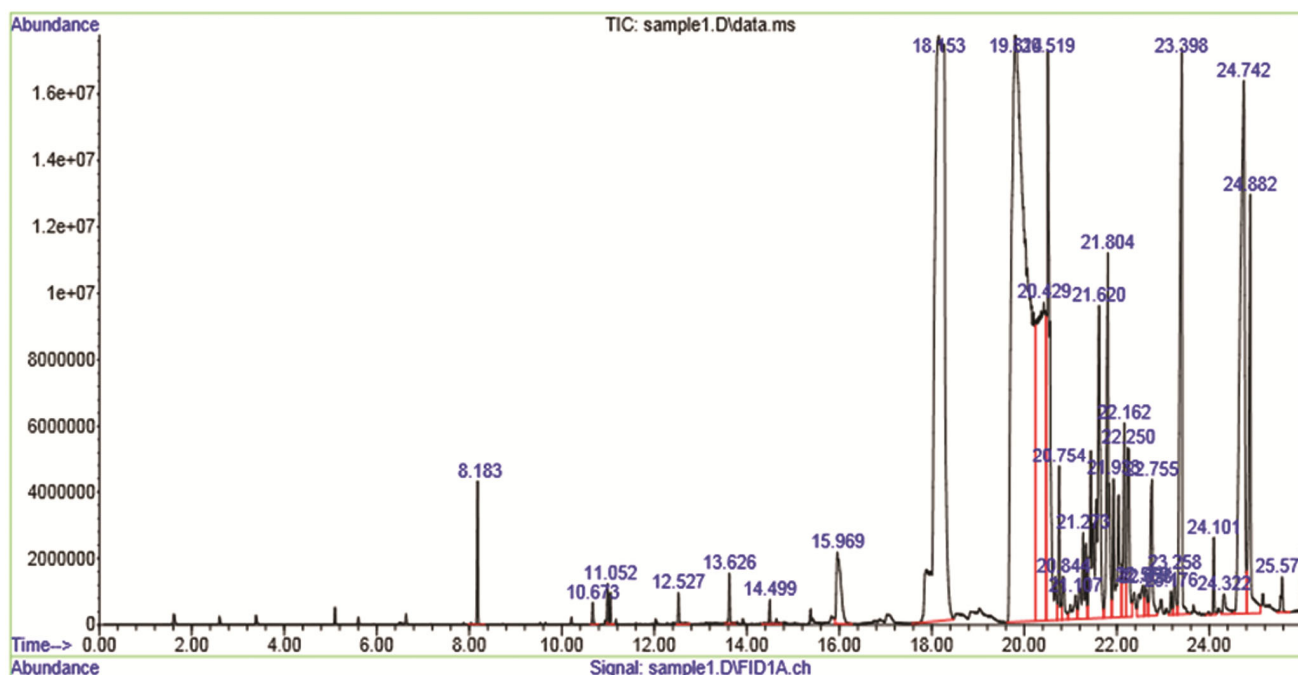


Fig. 3 — Chromatogram obtained via GC-MS analysis of transesterified WCO obtained using methanol

the reaction time in case of using only methanol, but this would add up the cost of the process. However, as methanol provides a faster reaction intermediate and ethanol provides better solvent properties²⁰, the reaction would be faster when both alcohols were used together at lower concentrations.

GC-MS analysis of FAMES formed with methanol

Compositions of the transesterified oil using sodium methoxide as a catalyst, analyzed by GC-MS have been shown in Table 2 & the chromatogram obtained is

given in Fig.3. Transesterified oil using sodium methoxide as catalyst showed the presence of only two fatty acid methyl esters [Decanoic acid methyl esters ($t_R=11.05$ min with an area of 0.22%) and Tetradecanoic acid methyl ester ($t_R= 15.07$ min with an area of 1.05%)]. All other compounds detected in the biodiesel has been enlisted in Table 2. Results obtained indicate the influence of reaction time on product yield. More extended reaction enhanced the hydrolysis of esters leading to reverse of transesterification that

Table 2 — Compounds obtained via transesterification of WCO with methanol

Sl. No.	Compound Name	Retention time (min)	Area (%)
1	Decanoic acid methyl esters	11.05	0.22
2	Tetradecanoic acid methyl esters	15.07	1.05
3	2-(2-methylpropyl) thiazolidine	18.15	20.28
4	Cyclododecanol	19.81	30.77
5	Propenaldimethylhydrazone	20.43	9.41
6	Pentanoic acid, 4-oxo-, trimethylsilyl ester	20.52	5.41
7	N-Cyclohexyl-N-ethyl acetamide	21.62	4.51
8	2,2-Dimethyl-1-dimethyl(dichloromethyl) silyloxypropane	21.80	2.68
9	N-(4-Quinolonyl)-1,2-ethanediamine monochloride	21.94	1.69
10	1H-Isoindole-1,3(2H)-dione, hexahydro- 1,2-Cyclohexanedicarboximide	22.17	1.17
11	Benzene	22.25	1.49
12	(Trimethylsilyl)(methylthio)butadiyne	22.75	1.12
13	Schizopeltic acid	23.40	4.28
14	Lysergic acid	24.74	8.22
15	cis-Ditolylanthracene	24.88	2.75

Table 3 — FAMES obtained from transesterification with ethanol and methanol mixture

Sl. No.	Compound Name	Retention time (min)	Area (%)
1	Octanoic acid methyl ester (C8:0)	7.33	0.21
2	Dodecanoic acid methyl ester (C12:0)	8.97	0.07
3	Nonanoic acid 9-oxo methyl ester (C9:0)	11.91	0.09
4	Pentadecanoic acid methyl ester (C15:0)	15.96	0.12
5	9-Hexadecenoic acid methyl ester (C16:1)	17.27	7.97
6	9,12-Octadecadienoic acid methyl ester (C18:2)	19.08	41.89
7	Octadecanoic acid methyl ester (C18:0)	19.71	4.62
8	Eicosanoic acid methyl ester (C20:0)	21.11	2.54
9	Docosanoic acid methyl ester (C22:0)	22.72	3.50
10	Tetracosanoic acid methyl ester (C24:0)	24.91	0.39

resulted in a significant loss of esters³⁴. Similar to the above findings, Eloka-Eboka *et al.*³⁵ reported that increase in reaction time decreases the yield of methyl esters due to the reversible nature of transesterification reaction. Further, the molar ratio of methanol: oil often determines the rate of conversion of oil into FAMES¹⁸. Aghel *et al.*²⁹ postulated that the appropriate amount of methanol: oil in the presence of co-solvent is essential, to prevent the hydrolysis of fatty acid methyl esters in order to achieve an optimum yield. It signifies the fact that optimum ratio of methanol: oil is essential to decrease the reaction time and thereby achieve the desired yield.

GC-MS analysis of FAMES formed with ethanol and methanol mixture

The biodiesel obtained with the sequential addition of methanol followed by an equal quantity of ethanol as a solvent with a reaction time of 20 min showed the substantial presence of FAMES as enlisted in Table 3. The chromatogram obtained along with the different compounds and retention time of each components has

been shown in Fig. 4. The presence of more FAMES is due to the fact that the methoxide ion has higher reactivity compared to the ethoxide ion, however, ethanol is essential as it provides a stable reaction equilibrium²². Significant quantities of unsaturated FAMES of linoleic acids (41.89%) and palmitelaidic acid (7.97%), along with saturated FAMES of stearic acids (4.62%), ara chidic acids (2.54%), and minor fractions of other acids were found. Martinez-Gueera & Gude³⁶ also reported a higher biodiesel yield using mixture of alcohols. The amount of 9,12 octadecanoic acid methyl ester was found to be highest in the biodiesel obtained via transesterification with alcohol mixtures. Significant amount of fatty acid alkyl esters were also obtained in the study by Issariyakul *et al.*²⁰ and Fadhil & Ahmed²⁶ with waste fryer grease and waste fish oil respectively. Presence of only one major component in high concentration is advantageous for fuel properties of biodiesel^{21,37}. Yuan *et al.*³ also observed the presence of six different FAMES and significant presence of 9,12 octadecanoic acid methyl

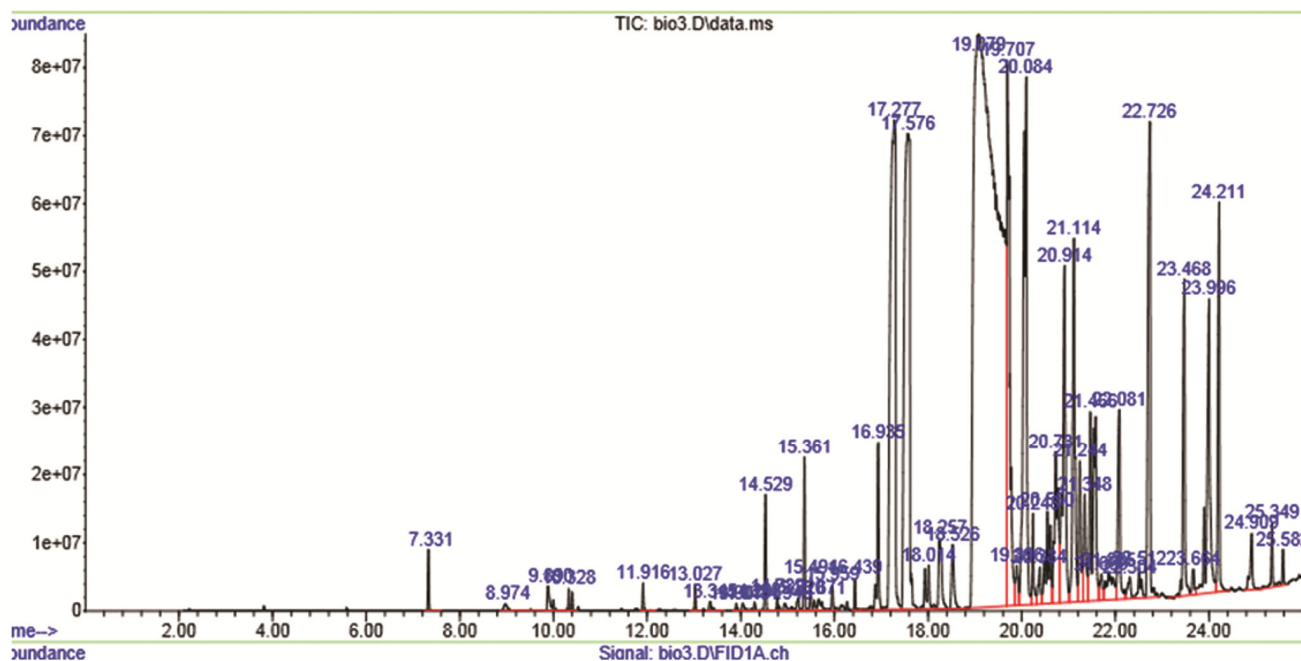


Fig. 4 — Chromatogram obtained by GC-MS analysis of transesterified WCO using methanol and ethanol mixture

ester from waste cooking rapeseed oil using methanol: oil ratio of 6:1 with a reaction time of 65 min. Knothe²¹ have reported that the presence of methyl oleate, methyl palmitoleate and esters of decanoic acid are strong candidates for improving fuel properties like combustion ignition and cold flow. These studies portrays the overall possibility of WCO as a promising feedstock for biodiesel in future.

Conclusion

The production of biodiesel with desirable fuel qualities from WCO has been investigated via transesterification reaction using two different alcohols and their combination thereof. A reduction in reaction time from 8 h to 20 min has been observed with the use of combined alcohol system compared to only methanol. Due to higher solubility of oil in ethanol, no distinct phase separation of transesterified oil and glycerol is observed with only ethanol. Significant quantities of FAMES of linoleic acids (41.89%) and palmitelaidic acid (7.97%) were found in the transesterified oil with ethanol/methanol system. Also, saturated FAMES of stearic acids (4.62%), arachidic acids (2.54%) along with 6 other FAMES were obtained. Presence of higher proportion of 9, 12 octadecanoic acid methyl esters indicates the suitability of the biodiesel obtained for engine applications. Thus, transesterification of WCO using a combination of alcohol produces FAMES with chemically desirable fuel properties. The approach

described provides a promising cost effective feedstock and process conditions for biodiesel production that suits for Potential engine application.

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