

# Investigation of chemical composition, characterization and determination of biodiesel content for the oil extracted from waste coffee residue of different varieties of coffee beans grown in yirgacheffie, kocherea and yirgalem using homogeneous catalysis and comparing it with fossil fuels

**Tsegay Hiwot**

Department of Chemistry, Dilla University, Dilla, Ethiopia

E-mail address: tsegayhi@gmail.com

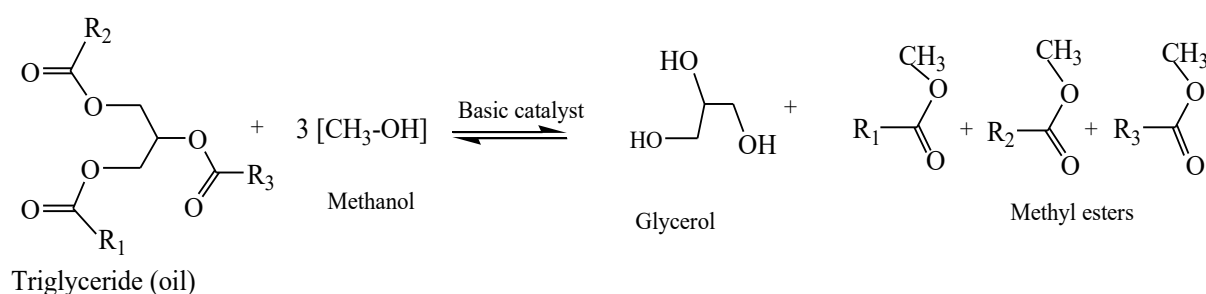
## ABSTRACT

Due to rapid population growth and development in the world there is high energy demand, energy consumption, sharp decline in petro fuels reserves, and greater environmental problems, as a result of using petroleum diesel constrained mankind to investigate newer and renewable feed stocks for liquid transportation fuels from vegetable oils by transesterification reaction. In this study oil of waste coffee residue of yirgacheffie, yirgalem and kocherea (chellelleqtu) weredas were selected as potential raw from indigenous species for biodiesel production. Oil was extracted using n-hexane as a solvent from waste coffee residue of yirga cheffie, yirgalem and kocherea weredas. The oil contents for yirgacheffie, yirgalem and kocherea were 16.67% w/w, 19.7 % w/w and 16.9% w/w respectively. Transesterification were carried out for all oils using methanol in the presence of acidic and basic catalysts to produce biodiesel. The fatty acid methyl esters in the biodiesel prepared from the oil extracted from three waste coffee residues were analyzed by FTIR and GC-MS. Based on GC-MS analysis their chemical compositions were 37.7 wt. % methyl palmitate (C16:0), 41 wt. % methyl linoleate (C18:2), 13.5 wt. % methyl oleate (C18:1) and 8.5 wt. % methyl stearate (C18:0) for yirgacheffie, 35.90 wt.% methyl palmitate (C16:0), 38.28 wt. % methyl linoleate (C18:2), 16.42 wt. % methyl oleate (C18:1) and 9.40 wt.% methyl stearate (C18:0) for kocherea and 26.62 wt. % methyl palmitate (C16:0), 35.18 wt.% methyl linoleate (C18:2), 19.72 wt. % methyl oleate (C18:1) and 18.48 wt.% methyl stearate (C18:0) for yirgalem. In addition to this the variables that affect the amount of methyl ester yield were determined and an optimum of 94.7 %, 95.84 and 94.56 fatty acid methyl ester (FAME) conversion were obtained at a methanol to oil molar ratio of 6:1, 1.0 % mass NaOH, 65 °C reaction temperature and 3 hour reaction time for yirgacheffie, yirgalem and kochera respectively. The energy content of the oil and biodiesel were 38, 36.2, 37 MJ/Kg and 38.68, 38, 41 MJ/ Kg for yirgacheffie, yirgalem and kochera respectively which is determined by bomb calorimeter. Other physicochemical properties of the biodiesel were determined and all these lie within the ASTM and EN biodiesel standards except acidic value. Therefore, coffee seed oil methyl ester could be used as an alternative energy resource in diesel engine.

**Keywords:** Waste coffee oil; yirgacheffie; yirgalem; kocherea; transesterification; biodiesel; fatty acid methyl ester; FTIR and GC-MS

## 1. INTRODUCTION

Biodiesel is a clean, renewable, biodegradable, environmentally benign, energy efficient and diesel substituent fuel used in diesel engine. It is a carbon neutral fuel because there is no overall increase in CO<sub>2</sub> in the atmosphere due recycling by the growing plants used to feed the biodiesel industry [1]. Emissions of SO<sub>2</sub>, SO<sub>3</sub>, CO, un burnt hydrocarbons and particulate matter are lower than that of petroleum diesel [2,3]. It is produced by the transesterification of triglycerides. Transesterification is a three-step reversible reaction of vegetable oils or animal fats with a methanol to form fatty acid methyl esters (FAMES) and glycerol as a final product as shown in Figure 1.



**Figure 1.** Base catalyzed transesterification processes.

Currently, about 84 % of the world biodiesel production is met by rapeseed oil [4]. The remaining portion is from sun flower oil (13 %), palm oil (1 %), soybean and others (2 %) [5]. since more than 98 % of the biodiesel is made from edible oil, there are many claims due to the depletion of edible oil supply worldwide.

Therefore in order to overcome these devastating phenomena, the feed stock for the biodiesel production must be replaced by non-edible oil, frying oil and oil extracted from waste substances. Therefore, for this study oil extracted from the waste coffee seed grown in yirgacheffie, kocherea and yirgalem were used for the production of biodiesel because this have two advantages such as waste management and the oil is non-edible as a result it does not compete with food security.

### 1. 1. Objectives of the study

#### 1. 1. 1. General objective

The general objective of this study is to investigate the chemical composition and characterization for the biodiesel of oil extracted from waste coffee residue of different varieties of coffee beans grown in yirgacheffie, kocherea and yirgalem using homogeneous catalysis and comparing it with fossil fuels.

#### 1. 1. 2. Specific objectives

- Extraction of crude oil from waste coffee residue grown in different environments by Soxhlet apparatus using n-hexane as an extracting solvent.
- Determine the amount of oil from waste coffee residue prepared for the coffee beans grown in different environments.

- Determine the optimum conditions/parameters (such as reaction temperature, alcohol-to-oil molar ratio, type and concentration of catalyst and reaction time) for the production of maximum amount of biodiesel.
- Determine the physicochemical properties of crude oil extract, oil blends, biodiesel and biodiesel blends such as acid value, density, kinematic viscosity, iodine value and higher heating values.
- Compare the physicochemical properties of oil, oil blends, biodiesel and biodiesel blends with the biodiesel standards (ASTM D6751 and EN14214 standards).
- Analyze the chemical composition of the biodiesel using chromatographic and spectroscopic techniques such as gas chromatography coupled with mass spectrometry (GC-MS) and FT-IR spectrometry.

## **2. MATERIALS AND METHODS**

### **2. 1. Materials**

#### **2. 1. 1. Chemicals and reagents**

Methanol (99 %), sodium hydroxide, sulfuric acid (98 %), n-hexane, sodium thiosulfate, phenolphthalein, ethanol (96 %), anhydrous sodium sulphate, and potassium hydroxide.

#### **2. 1. 2. Instrumentations**

Soxhlet apparatus, Rotary evaporator, GC-MS, FT-IR, bomb calorimeter, viscometer, hot plate thermometer, round bottom flask, separatory funnel, mortar and pestle will be used.

### **2. 2. Experimental**

The experimental work was done in the research laboratory of Department of Chemistry, Dilla University, Mekelle University and Adigrat pharmaceutical industry.

#### **2. 3. Waste coffee residue sample preparation**

Fresh coffee bean varieties were collected from yirgacheffie, kocherea and yirgalem. After that the waste coffee residue was prepared and oil is extracted from it for biodiesel production.

### **2. 4. Extraction Methods**

#### **2. 4. 1. Extraction of oil from beans of waste coffee residue by Soxhlet apparatus**

Oven dry waste coffee residues of varieties of coffee beans were grounded in to powder by using pestle and mortar. After that 100 g of the sample was loaded in to thimble in Soxhlet apparatus. Next to that extraction was carried out using 600 ml normal hexane at 68 °C (boiling temperature of hexane) for 24 h in an electrical heater. The mixture of the extracted oil and the hexane was separated by rotary evaporator and the percentage of the oil was calculated by the following formula:

$$\% \text{ Oil} = \text{Mass of Oil} \times 100 / \text{sample}$$

## 2. 5. Analytical methods

### 2. 5. 1. Analysis of biodiesel by GC-MS

The composition of the raw material was determined by gas chromatography equipment equipped with a flame ionization detector and with a DB 23 column. Firstly, the methyl esters were obtained using 1 % wt. of sodium hydroxide and methanol. The reaction was carried out at 45 °C, 55°C and 65 °C with a reaction time of 20 minutes.

After the reaction, the excess methanol was evaporated under a vacuum using a rota-evaporator. Then, the mixtures of ester and glycerol were separated by separator funnel, and the methyl ester portion was purified by washing with water to remove the excess catalyst and the glycerol. After that, the ester was dried with anhydrous sodium sulfate.

Next 0.1 ml of biodiesel was diluted to 10 ml using n-heptane (HPLC-grade, Merck). The sample was analyzed in a HP gas chromatograph model STAR 3600CX (Lexington, MA) equipped with a mass spectrometry and with a HP5 column (30 m x 0.320 mm, J&W Scientific, Folsom, CA).

Injector and detector temperatures was set at 250 °C and 300 °C, respectively. The carrier gas used is helium at 46 ml/min. Air and hydrogen flow rates are 334 and 34 ml/min, respectively. The program of the oven temperature is as follows: starting at 50 °C for 2 min; from 50 °C to 180 °C at 10 °C/min; 180 °C is held for 5 min; from 180 °C to 240 °C at 5 °C/min. Identification of different fatty acid methyl esters (FAMES) were done based on a reference standard.

### 2. 5. 2. FT-IR spectrometry

The FT-IR spectra were recorded using KBr pellets. The samples was prepared as follows: 2 mg of the studied samples was grounded together with 200 mg KBr (Merck) into the fine powder with the particles size below 5mm and compressed to form of clear disk. The FT-IR spectra were recorded using Brücker Tensor-27 spectrometer at ambient temperature in the wave number 4000-500  $\text{cm}^{-1}$ .

## 2. 6. Experimental design

### 2. 6. 1. Experimental Treatments

Two types of catalysts, acidic catalyst ( $\text{H}_2\text{SO}_4$ ) and basic catalysts (NaOH & KOH) was used at different reaction temperatures to study which catalyst is better for optimum biodiesel production from the oils of the different varieties of coffee beans of waste coffee residue. In addition to this blending of biodiesel was conducted with petroleum diesel.

Finally the physicochemical properties of the oil extracted from waste coffee residue, biodiesel and blended biodiesel was determined and compared with a set of parameter according to European Standard, EN 14214 and American standard test and material, ASTM6751 [6,7].

**Table 1.** Experimental treatments.

Methanol to oil molar ratio (T <sub>1</sub> )	Temperature in °C (T <sub>2</sub> )	% w/w of H <sub>2</sub> SO <sub>4</sub> to oil (T <sub>3</sub> )	% w/w of NaOH & KOH to oil (T <sub>4</sub> )	% V/V biodiesel/petroleum diesel ratio (T <sub>6</sub> )
3:1	45	3	1	10:90 = B10
6:1	55	4	2	20:80 = B20
9:1	65	5	3	

where: T = treatment B10 = 10 % Biodiesel B20 = 20 % Biodiesel

## 2. 7. Determination of the physicochemical properties

Density, specific gravity, kinematic viscosity, acid value, saponification value, iodine value, peroxide value and higher heating value of the coffee oil, biodiesel and biodiesel blends were determined.

## 3. RESULTS AND DISCUSSION

### 3. 1. Physicochemical properties

The biodiesel and biodiesel blends had lower specific gravity, density and kinematic viscosity compared to coffee oil (Table 2). This is due to the fact that coffee oil contains three esters combined together while the biodiesel contains a single ester.

Conversely biodiesel and biodiesel blends had higher heating value than the coffee oil. The main reason for the increased higher heating value is due their lower specific gravity and kinematic viscosity.

Besides to this the higher heating values of the biodiesel blends were larger than the biodiesel but lower than the petroleum diesel. This is due further reduction in specific gravity and kinematic viscosity of the blends. The carbon residue of the oil was higher than the biodiesel, biodiesel blends and petroleum diesel.

This is due to the fact that there will be no complete combustion as a result of the higher kinematic viscosity of the oil. Even though the kinematic viscosity of petroleum diesel was lower than the biodiesel and biodiesel blends its carbon residue was higher. This is because of the incomplete combustion of the non-oxygenated hydrocarbons and aromatic compounds in petroleum diesel.

The higher heating value and carbon residue were increasing as the amount of the petroleum diesel increases in the blend. The main reason for the increasing of the higher heating value is the decrease of specific gravity and kinematic viscosity of the blends.

The higher heating values of biodiesel blends lie between the heating values of their constituents.

Generally the physicochemical properties of the biodiesel and biodiesel blends (up to C<sub>20</sub>) lie within the biodiesel standard limits. Therefore these biodiesel and biodiesel blends can be used in diesel engine to substitute petroleum diesel (Table 2).

**Table 2.** Physicochemical properties of yirgacheffie, yirgalem and Kocherea coffee oil, biodiesel, biodiesel blends and diesel fuel.

Property	Yirgacheffie				Kocherea (chellellqtu)				Yirgalem				Petroleum diesel
	YO <sub>100</sub>	YB <sub>100</sub>	YB <sub>20</sub>	YB <sub>10</sub>	KO <sub>100</sub>	KB <sub>100</sub>	KB <sub>20</sub>	KB <sub>10</sub>	YAO <sub>100</sub>	YAB <sub>100</sub>	YAB <sub>20</sub>	YAB <sub>10</sub>	
Specific gravity	0.955	0.886	0.870	0.864	0.953	0.874	0.8692	0.8589	0.942	0.873	0.860	0.851	0.845
Density at 15 °C	955	886	870	864	953	874	8692	8589	942	873	860	851	845
Peroxide value	17	49.8	52	54	24	58	61	62	27	63	65	67	-----
Kinematic viscosity at 40 °C	36.7	5.18	4.9	4.54	37.94	5.45	4.92	4.73	39.48	5.67	5.2	4.64	2.8
Acid value	3	0.79	0.79	0.79	4.3	0.8	0.8	0.8	4.7	0.92	0.92	0.92	-----
Higher heating value	38	38.68	44.8	44.5	37	38	43	44	36.2	41	42.4	43	45
Carbon residue		0.027	0.005	0.007	0.025	0.0042	0.0049	0.0069	0.023	0.0047	0.0048	0.0068	0.049
Ester content	-----	94.7	-----	-----	-----	94.56	-----	-----	-----	95.84	-----	-----	
Iodine value	76	76	76	76	89	89	89	89	92	92	92	92	-----

where, YO<sub>100</sub> = Yirgacheffie 100 % oil, YB<sub>100</sub> = Yirgacheffie 100 % biodiesel  
 YB<sub>20</sub> = Yirgacheffie 20 % biodiesel, YB<sub>10</sub> = Yirgacheffie 10 % biodiesel  
 KO<sub>100</sub> = Kocherea 100 % oil, KB<sub>100</sub> = Kocherea 100 % biodiesel  
 KB<sub>20</sub> = Kocherea 20 % biodiesel, KB<sub>10</sub> = Kocherea 10 % biodiesel  
 YAO<sub>100</sub> = yirgalem 100 % oil, YAB<sub>100</sub> = yirgalem 100 % biodiesel  
 YAB<sub>20</sub> = yirgalem 20 % biodiesel, YAB<sub>10</sub> = yirgalem 10 % biodiesel

### 3. 2. Effect of different variables on transesterification process

Several variables which affect the yield of FAMES were studied. These are types and mass weight of catalyst, methanol to oil molar ratio and temperature. Their effect was described in tables 3, 4 and 5 below.

**Table 3.** Methyl ester content, as function of catalyst type and mass weight of catalyst at methanol/oil molar ratio, 9:1; reaction temperature, 55 °C; reaction time of 3 hours.

Type of catalysts	Mass weight of catalyst, wt. %	Temperature	Methyl ester content, w/w %
H <sub>2</sub> SO <sub>4</sub>	3	55	48
	4	55	49.5
	5	55	51
NaOH	1	55	90
	2	55	94
	3	55	88

**Table 4.** Methanol /oil molar ratio influence on the amount of methyl ester content, at fixed reaction temperature (65 °C), reaction time 3 hours and mass Weight of catalysts.

Methanol to oil molar ratio	Catalyst	% W of catalyst	w/w % of methyl ester content
3:1	H <sub>2</sub> SO <sub>4</sub>	3 wt. %	47
6:1			49.8
9:1			52
3:1	NaOH	1 wt. %	75
6:1			96.7
9:1			94

**Table 5.** Influence of the reaction temperature on the methyl ester content, catalyst type, NaOH; catalyst amount, 1 wt. %; methanol/oil molar ratio, 9:1.

Temperature in °C	Type of catalyst	Mass weight % catalyst	Methyl ester content, w/w %
45	NaOH	1 wt. %	89
55			90
65			93.3

### 3. 3. GC-MS and FT-IR analysis of biodiesel prepared from coffee oil

Based on GC-MS and FT-IR analysis, the FAME of biodiesel prepared from coffee oil of yirgacheffie, yirgalem and kocherea four compounds were identified as described in detail in Table 6 below.

**Table 6.** Chemical composition of FAMES of coffee oil by GC-MS and FT-IR analysis.

No	Name of compound	Molecular formula	Molecular weight	Retention time (min)	Amount % Yirgacheffie	Amount % Yirgalem	Amount % kocherea
1	methyl palmitate	C <sub>16</sub> H <sub>34</sub> O <sub>2</sub>	270	7.34	37.7	26.62	35.90
2	methyl linoleate	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	294	9.28	41	35.18	38.28
3	methyl oleate	C <sub>18</sub> H <sub>36</sub> O <sub>2</sub>	296	9.83	13.5	19.72	16.42
4	methyl stearate	C <sub>18</sub> H <sub>38</sub> O <sub>2</sub>	298	10.5	8.5	18.48	9.4

### 3. 4. Analysis of mass fragmentation of Fatty Acid Methyl Esters coffee biodiesel

Gas chromatography - coupled with mass spectroscopy was used to analyze the chemical composition of the biodiesel prepared from waste coffee seed oil of a yirgacheffie, yirgalem and kocherea. As their mass spectra is shown in **Figs. 2a to 2d**, methyl palmitate, methyl linoleate, methyl oleate and methyl stearate were identified at a retention times of 7.34, 9.28, 9.83 and 10.5 minutes respectively in all of the three coffee grown in different areas with two un identified peaks in yirgacheffie and kocherea. The molecular ion (parent) peaks of methyl palmitate, methyl linoleate, methyl oleate and methyl stearate were observed at 270, 294, 296 and 298 respectively as expected. It is interesting to observe that the saturated FAMES detected in the biodiesel from *waste coffee* (methyl palmitate and methyl stearate) show CH<sub>3</sub>OC(=OH<sup>+</sup>)CH<sub>2</sub> fragment and appears at m/z = 74 as the base peak (100 %) which is the result of McLafferty rearrangement during the MS analysis due to a six member ring structure of an intermediate. Methyl linoleate shows [CH<sub>2</sub>=CHCH=CHCH<sub>2</sub>]<sup>+</sup> fragment which appears at m/z = 67 as the base peak (100 %). Methyl oleate shows [CH<sub>2</sub>=CHCH<sub>2</sub>CH<sub>2</sub>]<sup>+</sup> fragment which appears at m/z = 55 as the base peak (100 %).



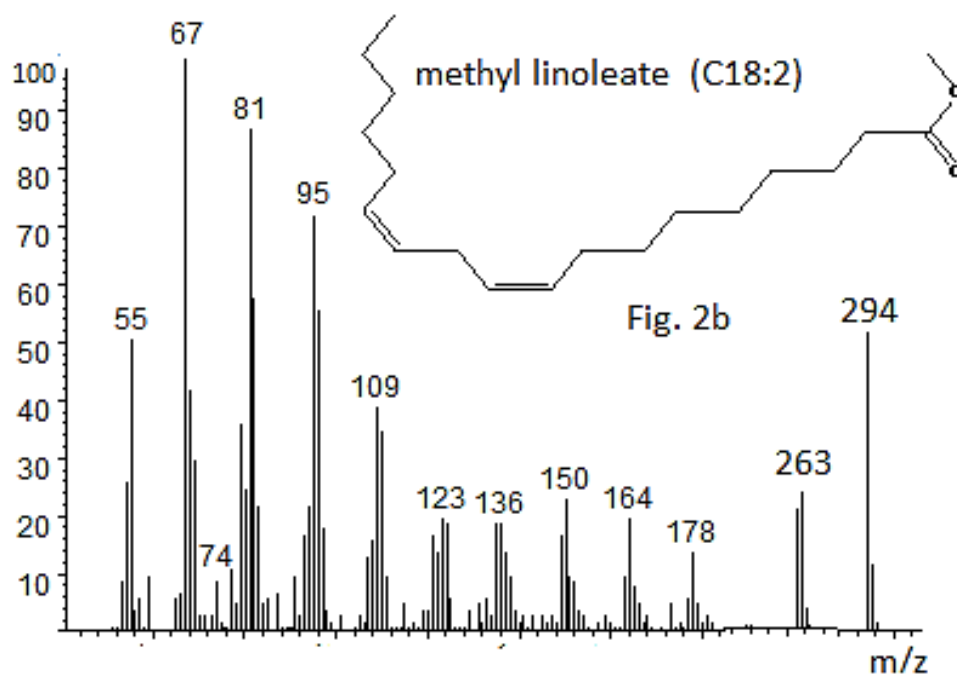
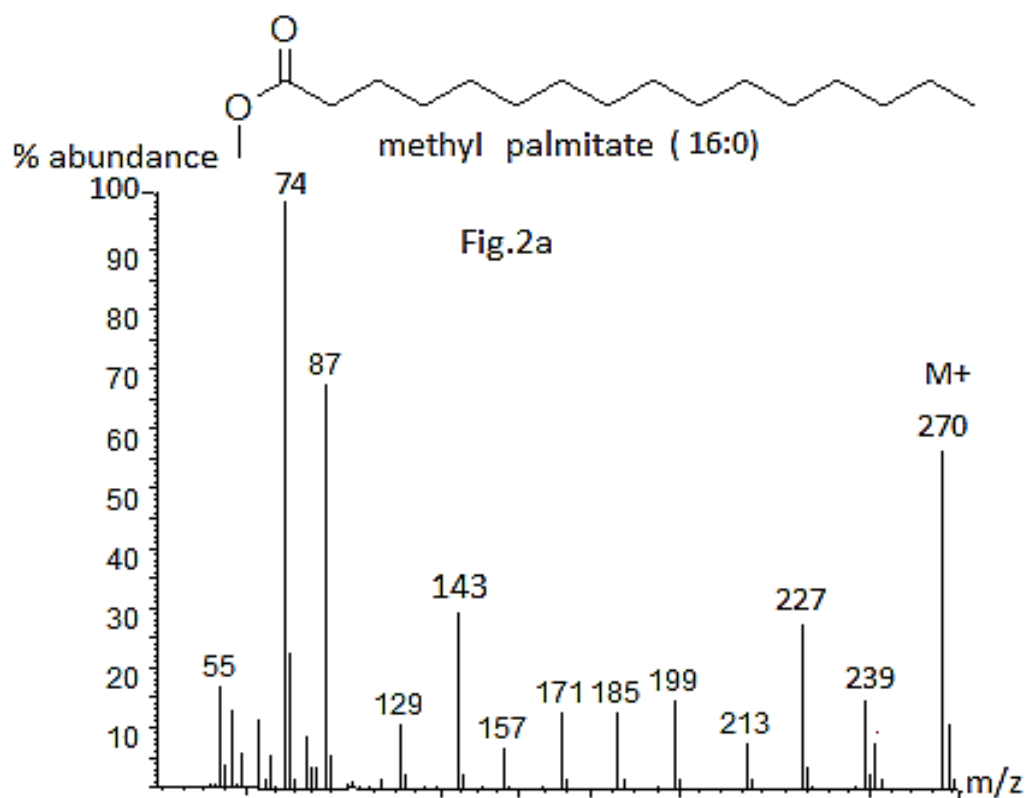


Fig. 2. Mass spectra of methyl palmitate, methyl linoleate, methyl oleate and methyl stearate.

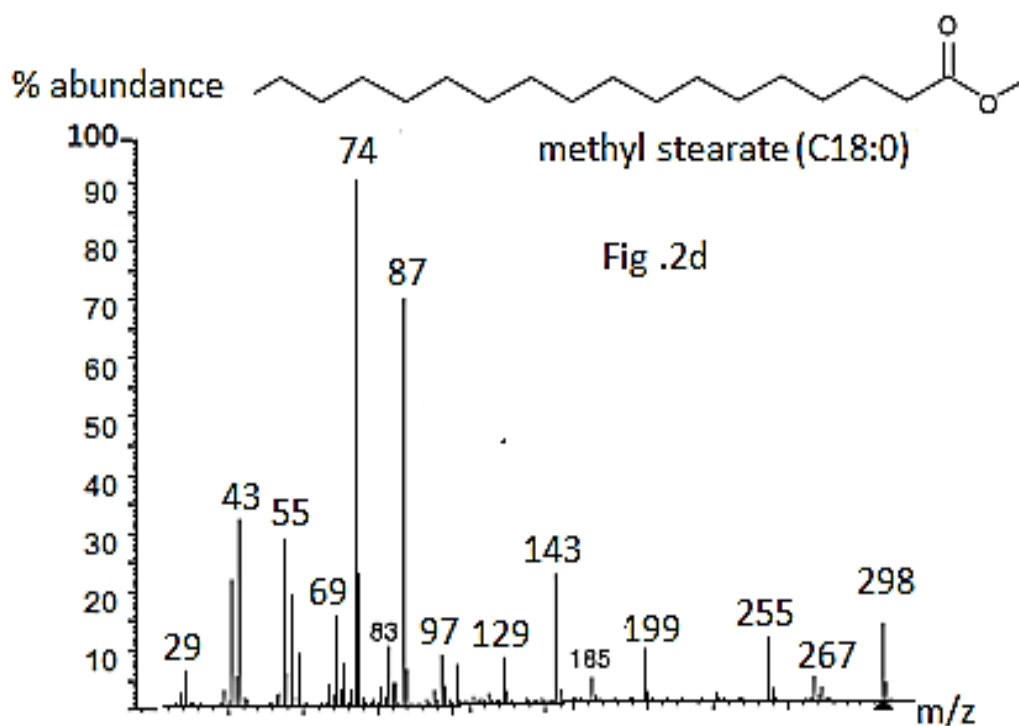
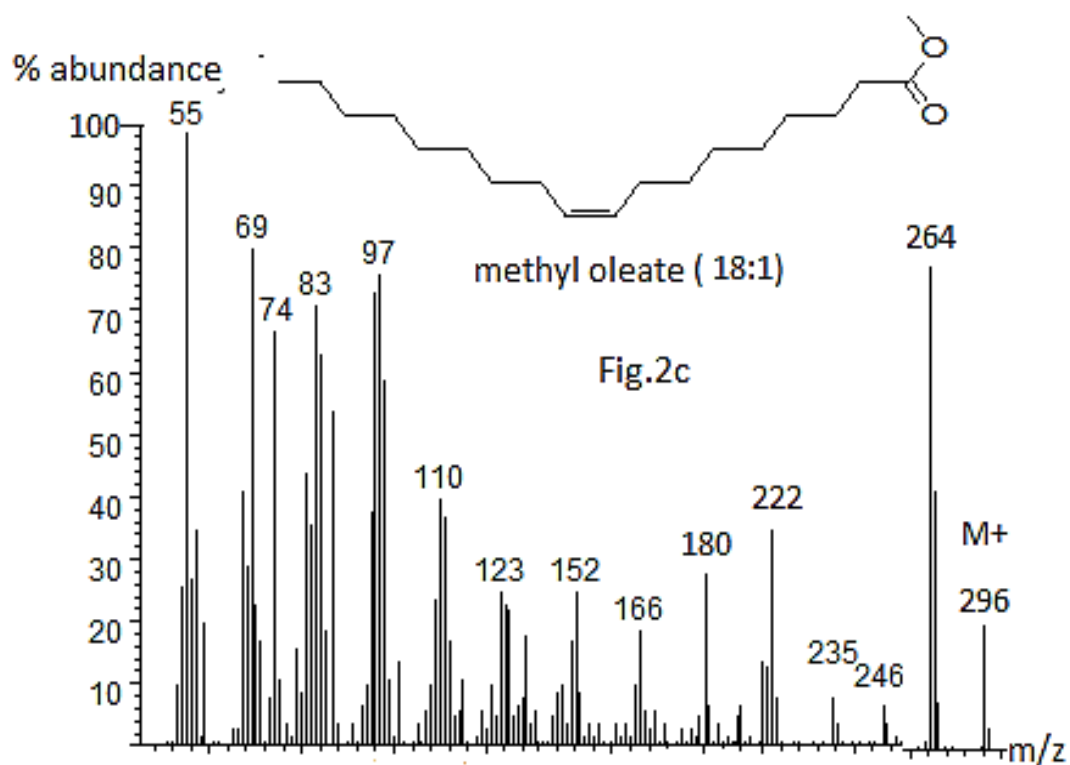


Fig. 2(continue). Mass spectra of methyl palmitate, methyl linoleate, methyl oleate and methyl stearate.

The methyl palmitate base peak ion at  $m/z = 74$  undergoes McLafferty rearrangement losing the methyl ester which is fragmented between the  $\alpha$  and  $\beta$  substituted carbons while the ion at  $m/z = 87$  is fragmented between  $C_4 - C_5$  also losing methyl ester and a hydrogen atom. An ion with  $m/z = 57$  is fragmented between  $C_3$  and  $C_4$  losing a methylene diol and three hydrogen atoms via McLafferty rearrangement. Methyl linoleate's molecular ion occurs at 294  $m/z$ . Both ions at  $m/z = 67$  and 81 represent hydrocarbon fragments with general formula  $[C_nH_{2n-3}]$  losing dialkenes and a hydrogen atom. Methyl oleate's parent peak is observed at  $m/z = 296$ .

The peak at  $m/z = 74$  represents the rearranged McLafferty methyl ester fragment while the peak at  $m/z = 87$  represents fragmented hydrocarbon ions with general formula  $[CH_3OCO(CH_2)_n]$ . Methyl stearate's molecular ion occurs at  $m/z = 298$ . The ion present at  $m/z = 74$  corresponds to the McLafferty rearranged methyl ester fragmented between the  $\alpha$  and  $\beta$  carbons while the ion at  $m/z = 87$  represents loss of methyl ester and a hydrogen atom fragmented between  $C_3$ - $C_4$  respectively. Molecular ion at  $m/z = 67$  and 81 represent hydrocarbon fragments with general formula  $[C_nH_{2n-3}]$  due to loss of alkenes and a hydrogen atom.

#### 4. CONCLUSION

In this study, the four transesterification parameters affecting the yield of biodiesel such as reaction temperature, molar ratio of methanol to oil, type and mass weight of catalyst have been studied. The result of the study indicates that all the process variables have significant effect on the yield of the biodiesel and a maximum of biodiesel yield (94.7 %, 95.84 and 94.56) was obtained from raw coffee oil by using the optimum process parameters such as methanol to oil molar ratio of 6:1, 1 % of NaOH, reaction temperature of 65 °C and reaction time of 3 hours.

Therefore, it can be concluded that NaOH is an effective catalyst for the production of biodiesel from waste coffee oil via homogeneous transesterification. In addition to this the waste coffee seed oil biodiesel was characterized by FT-IR, and GC-MS and four fatty acid methyl esters were identified. These are methyl palmitate methyl linoleate methyl oleate and methyl stearate.

The main advantage of transesterification reaction conducted for biodiesel production in this study was to lower the high kinematic viscosity of the oil. All the physicochemical properties of the biodiesel produced from coffee were determined and meet the ASTM specification.

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