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Gas Chromatography-Mass Spectrometry Studies of Waste Vegetable Mixed and Pure Used Oils and Its Biodiesel Products

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Abstract: Biodiesel production from waste vegetable used oils have a great interest as a substitute for petroleum diesel to reduce dependence on imported petroleum and provide an alternate and sustainable source for fuel with more benign environmental properties. In the present research biodiesel was prepared from three samples waste vegetable [mixture (sunflower 75% + soybean 25%), sunflower and cotton] oils (collected as wastes from Egyptian local restaurants) by transesterification. The reference used oils and the produced biodiesel samples of the studied oils were chemically characterized by gas chromatography mass spectrometry (GC–MS). All fatty acid, methyl esters (FAMEs) and other obtained compounds were identified by retention times and confirmed by comparing their mass fragmentation patterns with the GC-MS instrument library storage mass spectra. The percentage of obtained methyl esters of the studied oils before and after change to biodiesel was reported and discussed. Mixture (sunflower 75% + soybean 25%) waste oil have the best conversion to biodiesel with fatty acid, methyl ester content equal to 91.03% followed by cotton waste oil 89.56% then sunflower waste oil 86.92%. The importance of this work is to get benefits of the local environmental wastes as sources for renewable energy.

Keywords: GC-MS, waste vegetables used oils, biodiesel

1 Introduction

Biodiesel, as an alternative fuel, can be made from natural, renewable sources such as vegetable oil and fats [1]. The main advantages of using biodiesel are its renewable nature, the slightly better exhaust gas emissions and its biodegradability. The transesterification of vegetable oils in batch processes is the most commonly used technology for biodiesel production, in which a short chain alcohol reacts with the oil in a stirred tank to produce the alkyl esters of fatty acids (biodiesel), with a basic homogeneous catalyst being used to accelerate the reaction [2]. The most common biodiesel is the one produced via the transesterification method from oils such as soybean [3-4], sunflower [5-6], palm [7], rapeseed [8], canola [9], cotton seed [10] and Jatropha [11]. The characteristics of this type of biodiesel are similar to those of conventional diesel of fossil origin, rendering biodiesel an excellent candidate to replace diesel fuel [12]. Gas chromatography is more convenient and precise method for qualitative and quantitative analysis of fatty acid methyl esters, and comparative chromatographic analysis of changes in the concentrations of fatty acid methyl esters [13].

There are several articles commonly used to identify fatty acids or their derivatives (fatty acid methyl esters, FAME), including gas chromatography-flame ionization detector (GC-FID), gas chromatography- mass spectrometry (GC-MS) [14], FTIR [15] and silver ion thin-layer chromatography TLC [16-19]. Of these techniques, gas chromatography (GC) along with any one of a number of detectors offers a simple, rapid and relatively inexpensive method for the identification or quantification of FAME in lipid research [20]. There are limits associated with the use of GC-MS spectra may not always contain ions indicative of structural features (e.g., the positions of double bonds in the aliphatic chain cannot always be definitively determined); so in the current study we reported the most intense ions for each mass spectrum of the result fatty acids components. Another limitation of using GC-FID is obtaining adequate standards, as standards are not available for many of the fatty acids found in mammalian tissue, especially for the more complicated polyunsaturated fatty

acids [21-22]. Therefore, there are instances when FAME analysis is best served by a combination of GC-MS chromatogram and confirmed by the most fragments ions, either for confirmatory purposes (to ensure the correct identification of a peak) or as an exploratory guide for further work.

On the other hand, gas chromatography-mass spectrometry studies are necessary to clarify the compounds present in the pure and used frying oils as well as the produced biodiesel and be useful in determination of the quality of biodiesel (European Standard, 2003a; 2003b[23-24]).

The objective of the present study is to use the GC/MS for determination of the total chemical composition of waste vegetable (sunflower 75% + soybean 25%) mixture, sunflower and cotton oils and the produced biodiesel and compared. Also, identify which type of methyl esters is present in the produced biodiesel and it concentration percentage and determine the conversion rate of triglycerides of waste cooking oils to methyl esters.

2 Materials and Methods

The chemical used in this study were of the highest purity available. They included methanol 99%. Sodium hydroxide pellets 99% , sulfuric acid 27%, waste vegetable oil (sunflower 75% + soybean 25%) mixture, sunflower oil and cotton oil heated at 50 ^{o}C for 1 hour) phenolphthalein indictor (ph.ph). The water was always distilled for all glass equipment.

2.1. Solutions

The 0.1% sodium hydroxide solution used for titration to determine free fatty acid content was prepared by dissolving 1 g of NaOH to 1000 mL distilled water. Next, add 100 mL of the 1% solution to 900 mL of distilled water. This will make a 0.1% NaOH solution. Phenolphthalein (ph.ph) was used as indicator.

2.2. Experimental procedure

2.2.1. Transesterification

Methyl ester biodiesel preparation: The amounts of reactants are calculated using the following equation: Amount of methanol in liters = 0.225 x volume of oil in liters. Amount of sodium hydroxide required in Kg = volume of oil /140. Then charged into a reactor of closed reaction vessel and the waste vegetable oil is added. The system is totally closed to prevent the alcohol loss. The reaction mix is kept just above the boiling point of the alcohol (around 70 ^{o}C) to speed up anywhere from room temperature to 55 ^{o}C for safety reasons; reaction time was 1 hour.

2.2.2. Esterification

The esterification is done when the FFA content is higher than 2.5%; require the use of an acid catalyst to mediate the reaction of a fatty acid with alcohol producing fatty acid alkyl ester and water, for this purpose sulfuric acid 27% was used as catalyst as given in the flow sheet (Fig.1)

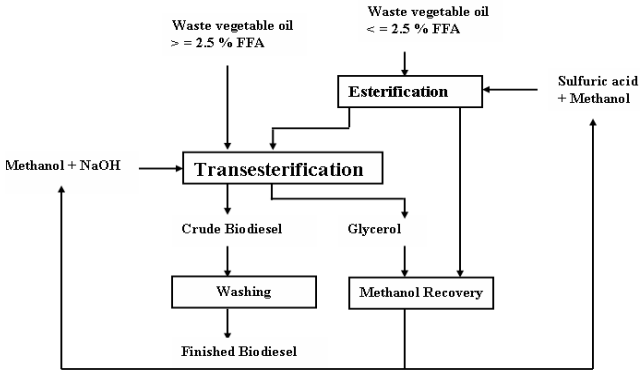

Fig. 1. Flow sheet for biodiesel preparation process.

2.2.3. Gas chromatography–mass spectrometry (GC-MS) analysis

The chemical composition of the studied samples were performed using Shimadzu [GC 17- A] Gas chromatograph) with a direct capillary column TG WAX–MS (30 m x 0.25 mm x 0.25 µm film thickness). The column oven temperature was initially held at 80 °C and then increased by 5°C /min to 200°C withhold time 2 min then increased to 280 with hold time 10 C/min. The GC injector temperature was set up to 270 °C. Helium was used as a carrier gas at a constant flow rate of 1 ml/min. EI mass spectra were collected at 70 eV ionization voltages over the range of m/z 40–550 in full scan mode. The ion source and transfer line temperatures were set at 200 and 250°C respectively. The components were identified by comparison of their retention times and mass spectra with those of NIST 05 mass spectral database.

3 Results and Discussion

Chromatographic analysis have been used in many ways in quantifying and identifying individual components in biodiesel samples, such as the identification of contaminants and fatty acids methyl esters. GC-MS is vital in modern quality control analysis of biodiesel hence, its wide application in the study of biodiesel composition [25]. GC-MS was used to determine the total chemical composition of the synthesized [mixture (sunflower 75% + soybean 25%), sunflower and cotton] oils before and after biodiesel production. Comparing the chemical composition content of each sample and its biodiesel product has been investigated. The total ion chromatogram obtained by GC-MS for the studied samples are shown in Fig. 2-6. Each peak in these chromatograms have been identified from the library match software (NIST 05) and the most fragment

Table 1: The chemical composition of waste cooking oil mixture (75% sunflower + 25 %soybean)

peak	R.t*	Name	Area %	Height%	Molecular Weight	Molecular formula	Most fragment ions with R.I**
1	24.526	9.12,octadecadienoic acid (Z,Z)-, 2 hydroxy- 1-(hydroxyl) ethyl ester	4.52	6.06	354	$C_{21}H_{38}O_4$	262 (52%), 95 (47%), 81 (72 %, 67 (100%) and 55 (88%)
2	25.301	Glycine, N-butoxy carbonyl-, propyl ester	4.02	5.19	217	$C_{10}H_{19}NO_4$	
3	26.962	Cyclopropane,1,1-dichloro-2,2,3,3-tetramethyl	8.03	10.11	166	$C_7H_{12}Cl_2$	
4	27.106	Linoleic acid, trimethylsilyl ester	11.97	14.74	352	$C_{21}H_{40}O_2S$	262 (30%), 131 (96%), 117 (100%), 81 (44%) 67 (62%) and 55 (53%)
5	28.718	2,6,10,14,18,22-tetracosalexane,2,6,10,15,19,23-hexamethyl-(au-E)	5.03	6.89	410	$C_{30}H_50$	
6	30.533	Beta-Tocopherol	18.37	14.85	416	$C_{28}H_{48}O_2$	416 (82%), 191 (19%), 151 (100%) and 55 (15%)
7	31.215	Alpha-Tocopherol-beta-D-man	16.98	16.29	592	$C_{35}H_{60}O_7$	430 (89%) and 165 (100%)
8	32.054	Campesterol	3.60	10.60	400	$C_{28}H_{48}O$	400 (95%), 289 (47%), 315 (5%), 145 (58%), 95 (68%) and 81 (65%)
9	33.697	9,19-cyclolanostan-3-ol acetate(3 beta)	8.18	6.59	470	$C_{32}H_{54}O_2$	175 (22%), 109 (46%), 95 (67), 81 (58%) and 69 (88%)
10	34.429	Stigmast-4-en-3-one	19.3	8.7	412	$C_{29}H_{48}O$	412 (28%), 370 (9%), 229 (37), 124 (100%), 95 (53%) and 81 (39%)

*R.t, retention time (min).

**R.I, relative intensity (%)

ions of the obtained fatty acid methyl ester and some of other important compounds have been report in Table 1-6.

3.1. GC-MS analysis of waste mixture (75% sunflower + 25 % soybean) sample and its biodiesel product.

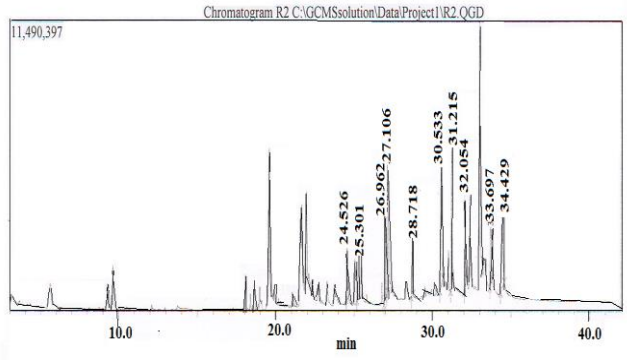

Fig 2 The GC-MS chromatogram of waste cooking oil mixture (75% sunflower + 25 %soybean).

The chemical composition of waste mixture (75% sunflower + 25 %soybean) oil sample and it biodiesel product are listed in Table 1. The GC-MS analysis of waste oil mixture (75% sunflower + 25 %soybean) sample were carried out and led to the identification of 10 main different components as shown as in Fig. 2. The identified components with their percentages, retention times and molecular formulas are listed in Table 1. Stigmast-4-en-3-one (19.3%) represents the main constituent. Beta-Tocopherol (18.37%) was the second major constituent detected followed by Alpha-Tocopherol-beta-D-man (16.98%). The most fragment ions of all components with their relative intensities (R. I. %) are listed in Table 1. Beta-Tocopherol and Campesterol compounds are the most stable compounds due to the stability of their molecular ions peaks m/z 416 (R. I. = 82%) and m/z 400 (R. I. = 95%) respectively.

After the treatment of waste oil mixture (75% sunflower + 25 %soybean) sample to produce the biodiesel and carried out the GC-MS analysis as shown as in Fig. 3. The obtained main components of the waste oil mixture (75% sunflower + 25 %soybean) sample are changed into biodiesel components (yield 98%) on heating at 1 hour at 60 ^oC during methyl esterification process, these new components are: Docosanoic acid, methyl ester (31.68%) represent the main constituent of the produced biodiesel. Tetracosanoic acid, methyl ester (18.91%) was the second major constituent detected followed by 9, 12-octadecadenoic acid, methyl ester (15.73%) followed by Eicosanoic acid, methyl ester (12.07%) as shown as in Table 2.

Table 2: The chemical composition of mixture (75% sunflower + 25 %soybean) obtained biodiesel.

peak	R.t*	Name	Area %	Molecular Weight	Molecular formula	Most fragment ions with R.I**
1	18.330	Cyclopropane octanoic acid, methyl ester	5.22	282	$C_{18}H_{34}O_2$	250 (6%), 208 (6%), 87 (24%), 74 (35%), 69 (54%) and 55 (100%)
2	19.033	Hexadecanoic acid, methyl ester	7.58	270	$C_{17}H_{34}O_2$	270 (10%), 227 (8%), 143 (14%), 87 (59%), 74 (100%) and 57 (21%)
3	19.542	Eicosanoic acid, methyl ester	12.07	326	$C_{21}H_{42}O_2$	326 (16%), 143 (18%), 87 (65%), 74 (100%) and 55 (38%)
4	24.088	Docosanoic acid, methyl ester	31.68	354	$C_{23}H_{46}O_2$	354 (22%), 143 (21%), 87 (68%), 74 (100%) and 55 (39%)
5	21.058	9,12-octadecadenoic acid, methyl ester	15.73	294	$C_{19}H_{34}O_2$	294 (8%), 109 (23%), 95 (50%), 81 (71%), 67 (100%) and 55 (74%)
6	21.160	10-octadecenoic acid, methyl ester	6.93	296	$C_{19}H_{36}O_2$	296 (3%), 264 (16%), 97 (35%), 74 (42%), 69 (53%) and 55 (100%)
7	25.265	Tetracosanoic acid, methyl ester	18.91	382	$C_{25}H_{50}O_2$	382 (30%), 143 (24%), 87 (73%), 74 (100%) and 55 (42%)
8	29.644	Hexacosanioc acid, methyl ester	0.85	410	$C_{27}H_{54}O_2$	410 (38%), 367 (14%), 143 (29%), 87 (77%), 74 (100%) and 55 (41%)
9	29.942	Alpha- Tocopherol	0.49	430	$C_{29}H_{50}O_2$	430(86%), 205(13%), and 165(100%)
10	31.867	Gamma-sitosterol	0.54	414	$C_{29}H_{50}O$	414 (100%), 396 (44%), 213 (51%), 145 (50%), 107 (63%), 95 (61%) and 55 (90%)

*R.t, retention time (min).

**R.I, relative intensity (%)

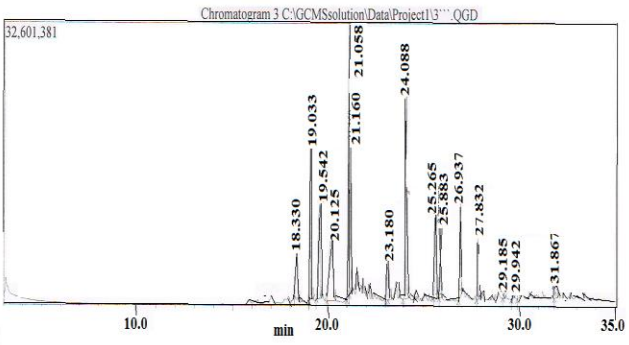

Fig. 3. The GC-MS chromatogram of oil mixture (75% sunflower + 25 %soybean) obtained biodiesel

Authors have been found that the total fatty acid methyl ester represent 91.03%. The Gamma-sitosterol and Alpha-Tocopherol contaminant compounds represent 8.87%.

The mass spectra of the major fatty acids in the oil mixture (75% sunflower + 25 %soybean) biodiesel sample have been obtained using electron ionization (EI) technique at 70 eV. The chemical composition of the oil mixture (75% sunflower + 25 %soybean) biodiesel sample shows three major fatty acid namely: Docosanoic acid, methyl ester, Tetracosanoic acid, methyl ester and 9,12-octadecadenoic acid, methyl ester, respectively, as shown in Table 2. The three fatty acids methyl ester mass spectra are shown in Figs. 4-6.

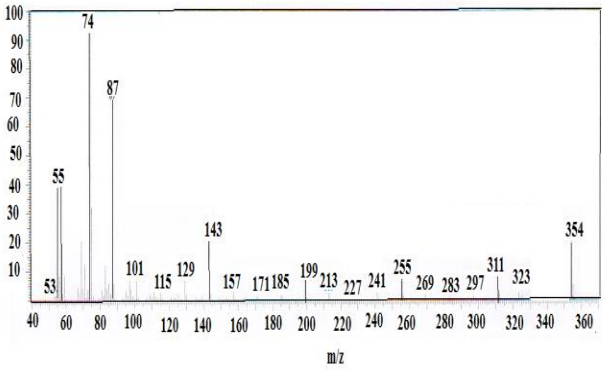

Fig. 4. Mass spectrum of Docosanoic acid, methyl ester.

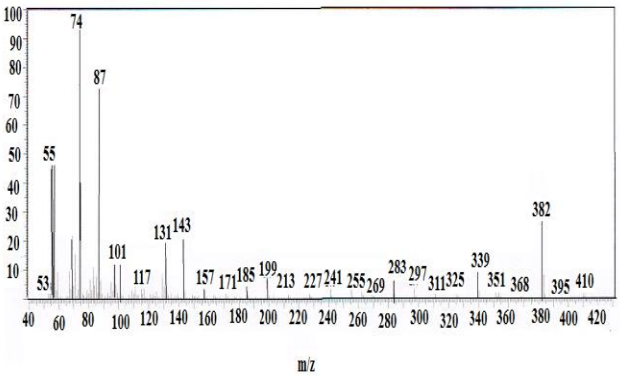

Fig. 5. Mass spectrum of Tetracosanoic acid, methyl ester.

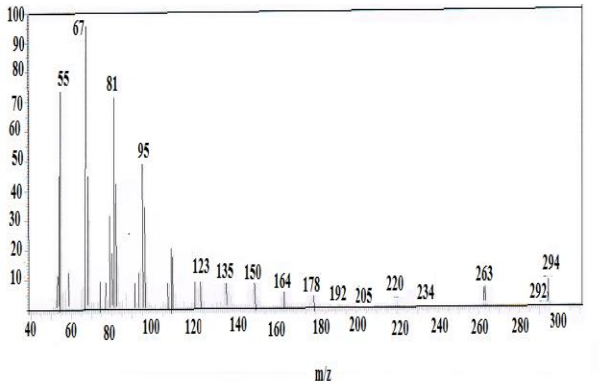

Fig.6. Mass spectrum of 9, 12-octadecadenoic acid, methyl ester.

The observed peak at m/z 354 (R.I. 22%) represent the molecular ion $[M]^{+\bullet}$ of Docosanoic acid, methyl ester and its fragment ions are: m/z 143 (R.I. 21%), m/z 87 (R.I 68%), and m/z 55 (R.I 39%). The molecular ion peak of Tetracosanoic acid, methyl ester were observed at m/z 382 (R.I. 30%) and the fragment ions of this molecular ion are m/z 143 (R.I. 24%), m/z 87 (R.I. 73%) and m/z 55 (R.I. 42%) while the fragment ion at m/z 74 (R.I. 100%) represent the base peak in the mass spectra of the Docosanoic acid, methyl ester and Tetracosanoic acid, methyl ester. Also, the mass spectrum of 9,12-octadecadenoic acid, methyl ester show peak at m/z 294 (R.I. 8%) represent its molecular ion and the most fragment ions are : m/z 109 (R.I. 23%), m/z 95 (R.I. 50%), m/z 81 (R.I. 71%) and m/z 55 (R.I. 74%) while the fragment ion at m/z 67 (R.I. 100%) represent the base peak of 9,12-octadecadenoic acid, methyl ester.

3.2. GC-MS analysis of waste sunflower oil and its biodiesel product.

The main components of the waste sunflower oil which freighting more than one time with washing and purification before going to change to biodiesel have been determined by the GC-MS (Fig. 7) and its chemical composition are listed in Table 3.

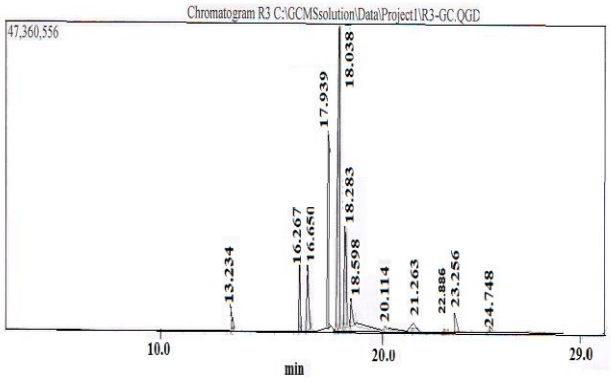

Fig. 7. The GC-MS chromatogram of waste sunflower oil.

The chemical composition of waste sunflower oil carried out using the GC–MS analysis led to the identification of 11 different components. The identified components with their percentages, retention times and molecular formulas are listed in Table 3. Linoleic acid, methyl ester (32%) represent the main constituent. 8-octadecenoic acid, methyl ester (30.14%) was the second major constituent detected followed by Oleic acid (12%) , Stearic acid, methyl ester (8%) and Palmitic acid, methyl ester (4%). The most fragment ions of all components with their relative intensities (%) are listed in Table 3. The fragment ion at m/z 55 (RI=100%) represent the base peak in the mass spectra of 8-octadecenoic acid, methyl ester and 9-octadecenoic acid(Z)-,2,3-dihydroxy propyl ester. The fragment ion at m/z 57 (100%) represent the base peak of Octanoic acid, 2-butyl ester. The fragment ion at m/z 59 (100%) represent the base peak of 2-Heptacosanone. The fragment ion at m/z 67 (100%) represent the base peak of Linoleic acid , methyl ester . The fragment ion at m/z 73 of n-Hexadecanoic acid, while the fragment ion at m/z 74 (100%) represent the base peak in the mass spectra of Palmitic acid, methyl ester , Stearic acid, methyl ester and Eicosanoic acid, methyl ester.

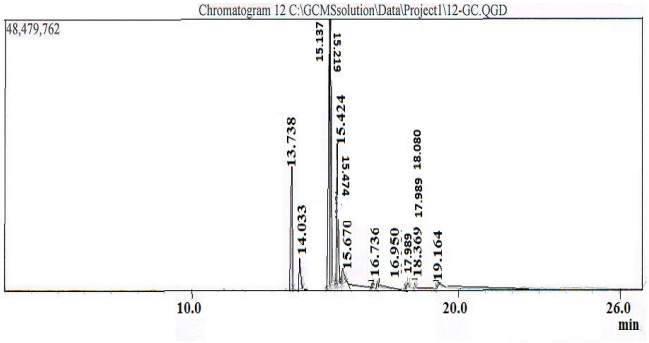

Fig. 8. The GC-MS chromatogram of waste sunflower oil biodiesel.

The obtained components of the waste sunflower oil are changed into biodiesel components on heating at 50 ºC for 1 hour during methyl esterification process. These new components are listed in Table 4. Including linoleic acid, methyl ester (39.89%) represents the main constituent of the product biodiesel sample (Fig 8). Oleic acid, methyl ester (28.96%) was the second major constituent followed by Stearic acid, methyl ester (9.48%) then

Table 3: The chemical composition of waste sunflower oil.

peak	R.t*	Name	Area %	Molecular Weight	Molecular formula	Most fragment ions with R.I**
1	13.234	Octanoic acid ,2-butyl ester	0.29	200	$C_{12}H_{24}O_2$	187 (13%), 145 (25%), 127 (86%), 74 (49%) and 57 (100%)
2	16.267	Palmitic acid, methyl ester	4.03	270	$C_{17}H_{34}O_2$	270 (9%), 143 (16%), 87 (59%) and 74 (100%)
3	16.650	n-Hexadecanoic acid	7	256	$C_{16}H_{32}O_2$	256 (26%), 129 (40%), 73(100%), 60 (79%) and 57 (72%)
4	17.939	Linoleic acid, methyl ester	32	294	$C_{19}H_{34}O_2$	294 (11%), 95 (62%), 81 (93%), 67 (100%) and 55 (57%)
5	18.030	8-octadecenoic acid, methyl ester	30.14	296	$C_{19}H_{36}O_2$	296 (5%), 264 (25%), 222 (16), 97 (53%), 83 (60%), 74 (65%), 69 (74%) and 55(100%)
6	18.283	Stearic acid, methyl ester	8	298	$C_{19}H_{38}O_2$	298 (13%), 87 (62%),74 (100%) and 55 (20%)
7	18.598	Oleic acid	12	282	$C_{18}H_{34}O_2$	282 (2%), 264 (13%), 97 (56%, 83 (62%), 69 (83%) and 55 (100%)
8	20.114	Eicosanoic acid, methyl ester	0.15	326	$C_{21}H_{42}O_2$	326 (14%), 143 (19%), 87 (64%),74(100%) and57 (14%)
9	22.886	9 -octadecenoic acid (Z)-, 2, 3-dihydroxy propyl ester	1.37	356	$C_{21}H_{40}O_4$	264 (20%), 98 (65%), 83 (45%), 69 (62%) and 55 (100%)
10	23.256	2-Pentacosanone	0.27	366	$C_{25}H_{50}O$	366 (6%), 85 (24%), 71 (51%), and 59 (100%)
11	24.748	2-Heptacosanone	0.53	394	$C_{27}H_{54}O$	396 (6%), 85 (24%), 71 (50%), and 59 (100%)

*R.t, retention time (min).
**R.I, relative intensity (%)

Table 4 The chemical composition of sunflower biodiesel.

peak	R.t*	Name	Area %	Molecular Weight	Molecular formula	Most fragment ions with R.I**
1	13.738	Palmitic acid, methyl ester	7.68	270	$C_{17}H_{34}O_2$	270 (10%), 87 (54%) and 74 (100%)
2	14.033	n- Hexadecanoic acid	3.52	256	$C_{16}H_{32}O_2$	256 (28%), 129 (41%), 73 (100%) and 60 (75%)
3	15.117	linoleic acid, methyl ester	39.89	294	$C_{19}H_{34}O_2$	294 (13%), 95 (60%), 81 (91%), 67 (100%) and 55 (53%)
4	15.219	Oleic acid, methyl ester	28.96	296	$C_{19}H_{36}O_2$	296 (5%), 264 (25%), 222 (15%), 97 (52%), 74 (64%), 69 (71%) and 55 (100%)
5	15.424	Stearic acid, methyl ester	9.48	298	$C_{19}H_{38}O_2$	298 (15%), 199 (11%), 143 (21%), 87 (62%), and 74 (100%)
6	15.474	Oleic acid	6.12	282	$C_{18}H_{34}O_2$	282 (3%), 264 (14%), 97 (60%), 83 (67%), 69 (86%) and 55 (100%)
7	15.670	Oleic acid	1.58	282	$C_{18}H_{34}O_2$	
8	16.736	Oleic acid, methyl ester	0.21	296	$C_{19}H_{36}O_2$	
9	16.950	Eicosanoic acid, methyl ester	0.44	326	$C_{21}H_{42}O_2$	
10	17.989	Oleic acid	0.27	282	$C_{18}H_{34}O_2$	
11	18.080	Hexanoic acid, tridecyl ester	0.33	298	$C_{19}H_{38}O_2$	
12	18.369	Docosanoic acid, methyl ester	0.26	354		
13	19.164	Heptatonic acid, docosyl ester	1.26	438	$C_{29}H_{58}O_2$	

*R.t, retention time (min).
**R.I, relative intensity (%)

Palmitic acid, methyl ester (7.68%). From the above GC-MS analysis of sunflower biodiesel sample, authors have been found that the total fatty acid methyl ester content is (86.92%).

The mass spectra of the three major fatty acids (linoleic acid, methyl ester, Oleic acid, methyl ester and Stearic acid, methyl ester) in sunflower and cotton biodiesel samples (Tables 4,6) have been obtained using EI mode at 70 eV as shown in Figs. 9-11. These confirm the expected structures for the produced fatty acids.

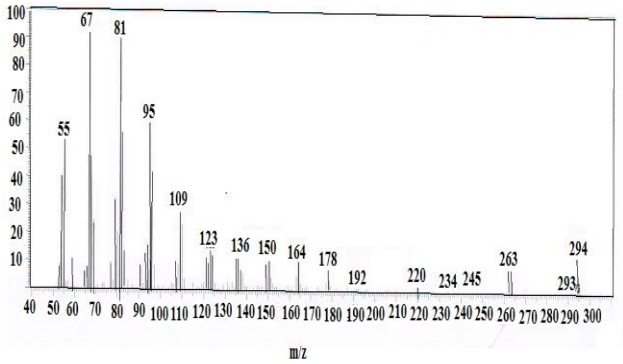

Fig. 9. Linoleic acid, methyl ester mass spectrum.

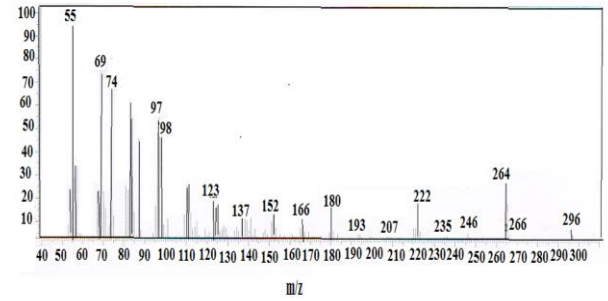

Fig. 10. Oleic acid, methyl ester mass spectrum.

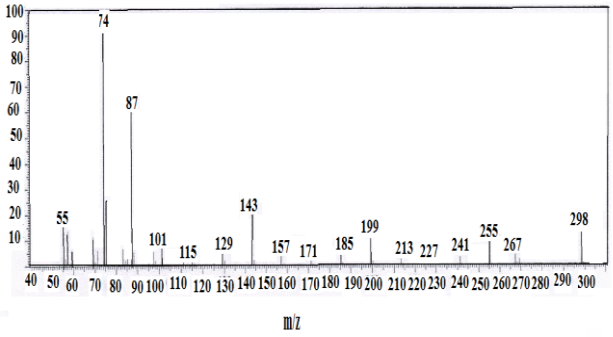

Fig. 11. Stearic acid, methyl ester mass spectrum.

The observed peak at m/z 294 (R.I. 13% represent the molecular ion $[M]^{+\bullet}$ for linoleic acid, methyl ester. The fragmentation process of this molecular ion led to the fragment ions at m/z 95 (R.I 60%), m/z 81 (R.I. 91%) and m/z 55 (R.I. 53%) while the fragment ion at m/z 67 (R.I. 100%) represent the base peak in Linoleic acid, methyl ester mass spectrum as shown in Fig.9. The mass spectrum of Oleic acid, methyl ester show the fragment ion at m/z 296 (R.I. 5% which represent the molecular ion peak and the fragmentation process of this molecular ion led to the formation of the fragment ions at m/z 264 (R.I. 25%), m/z 222 (R.I. 15%), m/z 97 (R.I. 52%), m/z 74 (R.I. 64%) and m/z 69 (R.I. 71%) while the fragment ion at m/z 55 (R.I. 100%) represent the base peak of the Oleic acid, methyl ester mass spectrum as shown as Fig. 10. Finally, the fragment ion at m/z 298 (R.I. 15%) represent the molecular ion of Stearic acid, methyl ester and its fragment ions are m/z 199 (R.I. 11%), m/z 143 (R.I. 21%) and m/z 87 (R.I. 62%), while the fragment ion at m/z 74 (R.I. 100%) represent the base peak as shown as in Fig.11.

3.3. Gas chromatography mass spectrometry analysis of waste cotton oil and its biodiesel product.

The analysis of waste cotton oil heating 1 hour at 50 ºC with washing and purification before going to change to biodiesel have been done using the GC-MS (Fig.12) and the chemical composition are obtained and listed in Table 5. The main components of waste cotton oil are Linoleic acid, methyl ester (28.4%) represent the major components, oleic acid, methyl ester (27.89%) is the second major component followed by oleic acid (16.36%) followed by stearic acid, methyl ester (9.01%).

These components of the used cotton oil are changed into biodiesel components on heating 1 hour at 50 ºC during methyl esterification process as shown as in Fig.13 and Table 6. These new components are: Linoleic acid, methyl ester (40.96%); which represents the major component of the cotton biodiesel sample, Oleic acid, methyl ester (26.56%) is the second major component followed by Palmitic acid, methyl ester (10.72%). Authors have been found that the total fatty acid methyl ester of cotton biodiesel sample represent (89.56%).

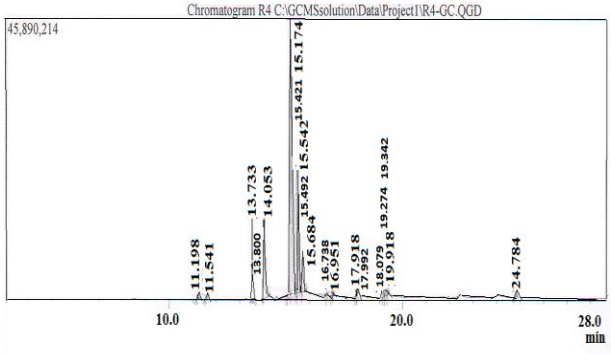

Fig.12. The GC-MS chromatogram of waste cotton oil.

The fatty acid methyl ester contents of the studied samples are listed in Table 7. Author have been found that all product biodiesel samples have been contain a fatty acid methyl ester content more that its waste oils before applying any methyl esterification. Mixture (sunflower 75% + soybean 25%) biodiesel have the most fatty acid

Table 5: The chemical composition of waste cotton oil.

peak	R.t*	Name	Area %	Molecular Weight	Molecular formula	Most fragment ions with R.I**
1	11.198	Xylitol,1-O-octanoyl-	0.38	278	$C_{13}H_{26}O_6$	145 (56%), 127 (91%) and 57 (100%)
2	11.541	p-heptyl benzonitrile	0.15	201	C14H19N	201 (20%) and 117 (100%)
3	13.733	Palmitic acid, methyl ester	4.32	270	$C_{17}H_{34}O_2$	270 (10%), 143 (16%), 87 (57%) and 74 (100%)
4	13.800	1,4dimethyladamantane	0.19	164	$C_{12}H_{20}$	149 (100%) and 93(12%)
5	14.053	Palmitic acid	8.03	256	$C_{16}H_{32}O_2$	256 (29%), 129 (41%), 73 (100%) and 60 (74%)
6	15.174	Linoleic acid, methyl ester	28.4	294	$C_{19}H_{34}O_2$	294 (12%), 109 (30%), 95 (59%), 81 (93%), 67 (100%) and 55 (60%)
7	15.211	Oleic acid, methyl ester	27.89	296	$C_{19}H_{36}O_2$	296 (5%), 264 (26%), 222 (16%), 98 (49%), 87 (45%), 74 (67%), 69(74%) and 55 (100%)
8	15.421	Stearic acid, methyl ester	9.01	298	$C_{19}H_{38}O_2$	298 (13%), 143 (20%), 87 (61%) and 74 (100%)
9	15.492	Oleic acid	12.42	282	$C_{18}H_{34}O_2$	264 (15%), 97 (59%), 83 (68%), 69 (89%) and 55 (100%)
10	15.684	Oleic acid	3.94	282	$C_{18}H_{34}O_2$	
11	16.738	11-eicosenoic acid, methyl ester	0.14	324	$C_{21}H_{40}O_2$	292 (20%), 97 (50%),74 (46%), 69 (72%) and 55 (100%)
12	16.951	Eicosanoic acid, methyl ester	0.31	326	$C_{21}H_{42}O_2$	326 (15%), 87 (65%) and 74 (100%)
13	17.992	1,3,5-trisiaclohexane	0.30	132	$C_3H_{12}Si$	
14	18.079	Hexadecanoic acid, 2-hydoxy-1-(hydroxyl methyl) ethyl ester	1.75	330	$C_{19}H_{38}O_4$	
15	19.166	1cyclohexyldimethylsiyoxybutane	0.43	214	$C_{12}H_{26}OSi$	
16	19.274	9-octadecenoic acid (Z)-2,3-dihroxy propyl ester	1.63	356	$C_{21}H_{40}O_4$	
17	19.342	1,2,3,4-tetrahydo-3-(phenyl acetamido) quinoline	0.27	266	$C_{27}H_{18}N_2O$	
18	24.784	3,5-choloestadien-7-one	0.44	382	$C_{27}H_{42}O$	

*R.t, retention time (min).
**R.I, relative intensity (%)

Table 6: The chemical composition of cotton oil biodiesel.

peak	R.t*	Name	Area %	Height%	Molecular Weight	Molecular formula	Most fragment ions with R.I**
1	11.887	Meristic acid, methyl ester	0.54	0.93	242	$C_{15}H_{30}O_2$	242 (6%), 87 (57%) and 74 (100%)
2	13.518	Palmitoleic acid, methyl ester	0.59	1.02	268	$C_{17}H_{32}O_2$	268 (4%), 236 (16%) ,96 (47%), 74 (64%), 69 (72%) and 55 (100%)
3	13.739	Palmitic acid, methyl ester	10.72	18.16	270	$C_{17}H_{34}O_2$	270 (9%), 143 (14%), 87 (48%) and 74 (100%)
4	14.030	n-Hexadecanoic acid	3.29	3.63	256	$C_{16}H_{32}O_2$	256 (27%), 129 (41%), 73 (100%) and 57 (70%)
5	15.13	Linoleic acid, methyl ester	40.96	27.46	294	$C_{19}H_{34}O_2$	294 (13%), 95 (58%), 81 (90%), 67 (100%), and 55 (53%)
6	15.215	Oleic acid, methyl ester	26.56	27.46	296	$C_{19}H_{36}O_2$	296 (5%), 264 (25%), 87 (43%), 74 (65%), 69 (73%) and 55 (100%)
7	15.421	Stearic acid, methyl ester	8.49	12.08	298	$C_{19}H_{38}O_2$	298 (14%), 255 (11%), 143 (20%), 87 (62%) and 74 (100%)
8	15.473	Oleic acid	5.63	6.01	282	$C_{18}H_{34}O_2$	282(3%), 97 (57%), 83 (65%), 69 (84%) and 55 (100%)
9	15.670	Oleic acid	1.5	1.5	282	$C_{18}H_{34}O_2$	282 (3%), 97 (57%), 83 (65%), 69 (84%) and 55 (100%)
10	16.950	Eicosanoic acid, methyl ester	0.53	0.84	326	$C_{21}H_{42}O_2$	326 (15%), 143 (20%), 87 (65%), 74 (100%) and 55 (20%)
11	18.080	Hexanoic acid, methyl ester	1.17	1.19	298	$C_{19}H_{38}O_2$	131 (23%), 117 (100%), 98 (38%), 71 (19%) and 55 (36%)

*R.t, retention time (min).
**R.I, relative intensity (%)

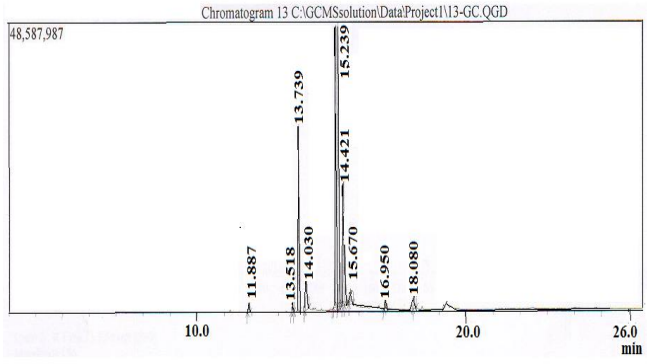

Fig.13. The GC-MS chromatogram of waste cotton oil biodiesel.

Table 7: The fatty acid methyl ester content of the studied oils samples before and after change to biodiesel.

sample	**Fatty acid methyl ester %**
mixture (sunflower 75% + soybean 25%) waste oil	-
mixture (sunflower 75% + soybean 25%) biodiesel	91.03
Sunflower waste oil	74.32
Sunflower biodiesel	86.92
Cotton waste oil	70.07
Cotton biodiesel	89.56

methyl ester (94.03%), cotton biodiesel is the second with

fatty acid methyl ester content 89.56% followed by sunflower biodiesel (86.92%).

The obtained biodiesel from the studied waste oils show that the mixture (sunflower 75% + soybean 25%) waste oil has great potential for production of biodiesel confirmed by its highest percentage content of fatty acid, methyl ester 91.03% as shown in Table 7. followed by cotton and sunflower waste oils.

4 Conclusions

The biodiesels of [mixture (sunflower 75% + soybean 25%), sunflower and cotton] oils were synthesized by transesterification with methanol. The chemical composition of these oils before and after change to biodiesel was obtained using the gas chromatography mass spectrometry and their contents were discussed. Mixture (sunflower 75% + soybean 25%) biodiesel shows 8 types of FAMEs, sunflower oil biodiesel and cotton oil biodiesel shows 7 and 8 types of FAMEs, respectively. They were identified by retention times and comparing its mass spectra with standards in GC-MS instrument library. The [mixture (sunflower 75% + soybean 25% have the highest percentage (91.03%) conversion of oil into biodiesel indicates that this oil has great potential for production of biodiesel.

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