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Characterization of methyl ester compound of biodiesel from industrial liquid waste of crude palm oil processing

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ABSTRACT

The second generation of Bioenergy: a study of CPO liquid waste-based biodiesel production technology has been conducted. The aims of this study were to obtain biodiesel from Industrial liquid waste of CPO processing and to identify the kind of methyl-ester compound of the biodiesel. The production of biodiesel was applied in two steps of reactions; esterification reaction using H_2SO_4 and transesterification using CaO catalyst at 60 °C for 2 h. GC-MS analysis result showed that methyl ester from liquid waste of CPO contains methyl hexadecanoate 12.87%, methyl 9-octadecanoate 19.98%, methyl octadecanoate 5.71%, and methyl 8,11-octadecadienoate 10.22%.

1. Introduction

The need for fuel increases along with the development of industry and population in Indonesia. The greatest fuel consumption is identified in the sector of industry and transportation. The increased utilization of fuel causes fuel insufficiency [1]. In 1970s, the production of unrefined oil in Indonesia reached 18 million barrels per day and it decreases to 700,000 barrels per day today [2]. Limited investment in new oil resource exploration and increased domestic fuel consumption turn Indonesia to be oil importer [3]. Furthermore, the use of fossil-based fuel is not considered environmentally friendly because it boosts the concentration of carbon dioxide (CO_2). This gas triggers greenhouse effect that contributes to the event of global warming [4,5]. For these reasons, the development of alternative energy resources should be carried out to substitute diesel-based fuel. One alternative energy resource which is widely developed is biodiesel [6]. Biodiesel (methyl-ester) is an option proposed to substitute fuel-based fuel because it is vegetable oil-based fuel which is renewable and environmentally friendly [7]. Compared to other fuel, biodiesel is biodegradable and non-toxic; it also has low CO_2 emission and sulfuric gas content [8].

Many varieties of oil have been examined to be processed as biodiesel, for instance, vegetable oil, animal fat, algae oil, and vegetable oil waste [9]. One of potential raw materials to produce biodiesel is crude palm oil (CPO) [10]. Indonesia and Malaysia are the major producers of CPO in the world that make them capable of developing CPO-based biodiesel [11–13]. The abundant oil content of palm tree makes CPO potential to produce biodiesel [14]. The utilization of CPO of agricultural and victuals needs as the raw material of biodiesel is categorized as the first generation of biodiesel [15]. However, the use of the CPO as vegetable-based fuel sets off competition with the need for foodstuff [16]. Besides, the price of CPO increases constantly that makes it uneconomical to be processed as long-term bio-energy.

Liquid waste of palm oil is one of the renewable raw materials of biodiesel. The use of agricultural raw material is abundant and does not clash with the need for foodstuff is categorized as the second generation of biodiesel [17]. Liquid waste of palm oil has 0.5–1% of oil content which can be processed as biodiesel [18]. The great amount of palm oil liquid waste within palm oil processing is considered as environmental pollution; in spite of that fact, it is a quite potential raw material to be processed as vegetable-based fuel which is economical in price and sumptuous in supply.

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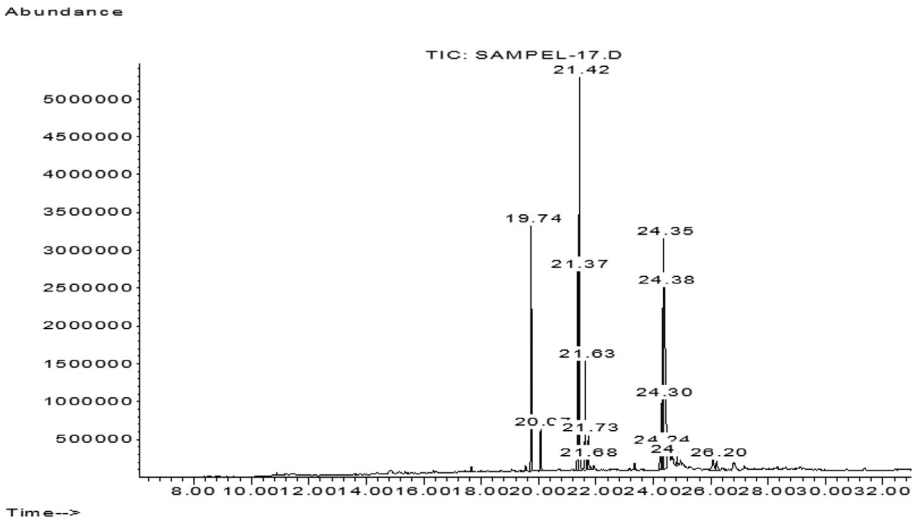

Fig. 1. GC-MS Chromatogram of biodiesel samples.

Direct use of vegetable oil as the fuel of diesel (biodiesel) still exhibits a weakness in term of its higher viscosity than diesel petroleum. This high viscosity of vegetable oil disturbs the process of injection and atomization of fuel [19]. To overcome these problems, the process of converting vegetable oil into methyl-ester through the transesterification process with catalyst should be carried out [20].

Transesterification process can be carried out by using homogenous, heterogeneous, or enzymatic catalyst. Homogenous catalyst is a catalyst with the same phase as its catalyst reagent, while the heterogeneous catalyst is a catalyst with different phase to its reagent [9]. The use of homogenous catalyst such as sodium hydroxide (NaOH) and potassium hydroxide (KOH) is more effective than heterogeneous catalyst. The result of methyl ester conversion which is carried out using liquid alkaline catalyst can reach out 98%, while the result of methyl ester conversion which is carried out using liquid acid catalyst can reach out 99%. The only problem that occurs when producing biodiesel by using up liquid alkaline catalyst is the complexity of separating the biodiesel and the catalysts because liquid acidic and alkaline catalysts in glycerol partially dissolve in biodiesel [21]. In addition to that, liquid catalyst used to produce biodiesel is corrosive and not reusable [9].

Enzymatic catalyst in transesterification is one of the alternative methods since enzyme can broaden the reaction rate than the usual reaction [22]. Transesterification reaction makes use of an enzyme that can work in low temperature and produce high, environmentally friendly methyl ester yield [23]. Enzymatic catalyst is used in esterification and transesterification to produce methyl-ester [24]. Many recent researches use heterogeneous catalyst since it is more economical, easily separated, reusable, and non-corrosive [25,26].

Potassium oxide (CaO) catalyst is an alkaline earth metal oxide catalyst which is quite potential to be developed because it has good activities and produces an optimal yield of biodiesel in soy oil [27]. Therefore, this study attempted to process liquid waste of palm oil through the esterification process using sulfuric acid (H_2SO_4) and transesterfication process using CaO catalyst.

2. Experimental

2.1. Degumming process

150 mL of CPO industrial liquid waste is heated in the temperature of 104 °C for an hour while being distilled. Then, 6 mL of H_3PO_4 85% is added up and distilled for 30 min. The sample is

Table 1
Methyl ester of biodiesel according to the results of GC-MS analysis.

Retention time, Rt (minutes)	Compounds identified	Molecular formula	Composition (%)
19.74	Methyl hexadecanoate	$C_{17}H_{34}O_2$	12.87
20.07; 24.82	Hexadecanoate acid	$C_{16}H_{32}O_2$	3.23
21.37	Methyl 8,11-octadecadienoate	$C_{19}H_{34}O_2$	10.22
21.42	Methyl 9-octadecenoate	$C_{19}H_{36}O_2$	19.98
21.63	Methyl octadecanoate	$C_{19}H_{38}O_2$	5.71
21.68	9,12-octadecadienoate acid	$C_{18}H_{32}O_2$	0.50
21.73; 26.20	9-octadecenoate acid	$C_{18}H_{34}O_2$	3.38
24.24	cyclohexane	C_6H_{12}	1.32
24.30	Propanenitrile	C3H5N	4.33
24.35	3-butyl phenol	C10H14O	6.39
24.38	Phenol	C_6H_6O	0.948

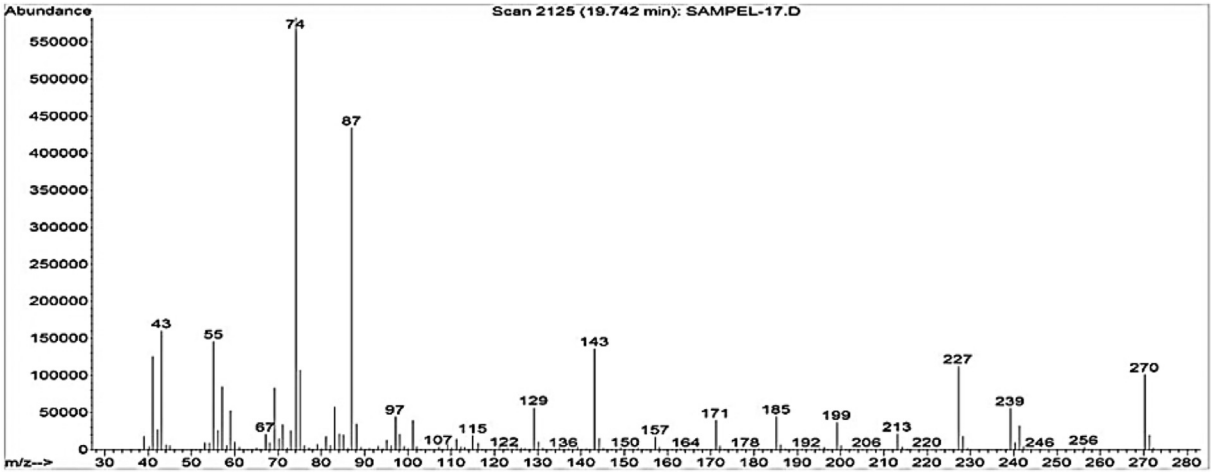

Fig. 2. Mass spectrum of methyl hexadecanoate.

centrifuged for 3 min by the speed of 600 rpm to separate gum from the oil.

2.2. Esterification process

CPO industrial liquid waste (85.15 g) from degumming process is added with 63.36 g of methanol and 2 mL of H_2SO_4 97%. This mixture is heated for 2 h within the temperature of 60 °C and stirred by magnetic stirrer. Oil and methyl-ester which are produced are separated from glycerol and water as by-products of esterification process by using centrifuge.

2.3. Transesterification process

CPO industrial liquid waste of esterification process is weighed (69.30 g) and CaO catalyst is added up with the variations of catalyst content of 1, 2, 3, and 4%; each of them is dissolved in 52.03 g of methanol and heated within the temperature 60 °C for 2 h. Methyl-ester formed is separated from glycerol and residual catalyst by using centrifuge.

2.4. Characterization

The identification of biodiesel compound is performed using Gas Chromatography-Mass Spectroscopy (GC-MS).

3. Results and discussion

Biodiesel is a concoction of long chain fatty acid ester with the number of carbon atom lying in the long chain ranging from 14 to 22 [28]. To identify the building blocks of methyl ester resulted in this research, an analysis using GC-MS is carried out. The result of this analysis can be exhibited in Fig. 1 with the percentages of each component of methyl ester listed in Table 1.

The results of GC-MS analysis on the produced methyl ester indicate that there is a substance of methyl hexadecanoate in methyl ester with the retention time of 19.74 and the composition of 12.87%. The spectrum of fragmentation mass of methyl hexadecanoate is written by m/z 270 of molecular ion of $C_{17}H_{34}O_2^+$ resulted from methyl hexadecanoate substance when it is exposed with 70 eV of energy. Molecular ion of $C_{17}H_{34}O_2^+$ experiences fragmentation by releasing C_3H_7 radical and produces fragments by m/z 227 originating from $C_{14}H_{27}O_2^+$, while the bottom peak lies in m/z 74 originating from $C_3H_6O_2^+$ takes its form since it undergoes McLafferty reorganization. The mass spectrum of methyl hexadecanoate can be seen in Fig. 2 and the fragmentation is displayed in Fig. 3.

The results of GC-MS analysis indicate that there is a substance of methyl octadecanoate with the retention time of 21.63 and the composition of 5.71%. The mass spectrum of methyl octadecanoate is written by m/z 298 originating from the molecular ion of $C_{19}H_{38}O_2^+$ resulted from methyl octadecanoate. Molecular ion of $C_{19}H_{38}O_2^+$ experiences radical fragmentation by releasing C_3H_7 radical and produces fragments by m/z 225 originating from $C_{16}H_{31}O_2^+$. The peak of m/z 129 originating from $C_7H_{13}O_2^+$ resulted from $C_{16}H_{31}O_2^+$ which releases C_5H_{10}. Molecular ion of $C_7H_{13}O_2^+$ experiences McLafferty reorganization by releasing $C_3H_6O_2$ and it produces the peak within m/z 55 originating from C_4H_7, while the peak of m/z 87 comes from $C_4H_7O_2^+$ originating from the fragment of $C_{19}H_{38}O_2^+$ releasing $C_{15}H_{31}$ radical. The bottom peak lies in m/z 74 originating from $C_3H_6O_2^+$ takes its form since it undergoes McLafferty reorganization. The pattern of mass fragmentation of methyl octadecanoate can be seen in Figs. 4 and 5.

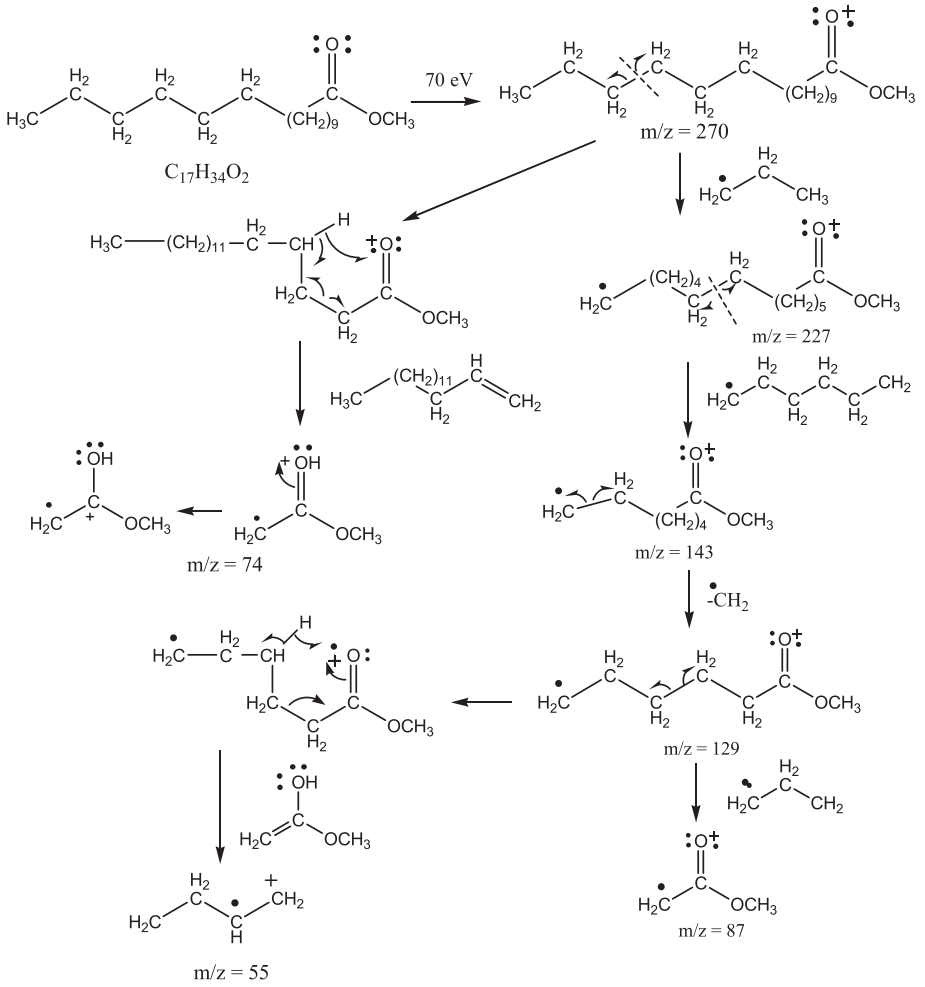

Fig. 3. Fragmentation pattern of methyl hexadecanoate.

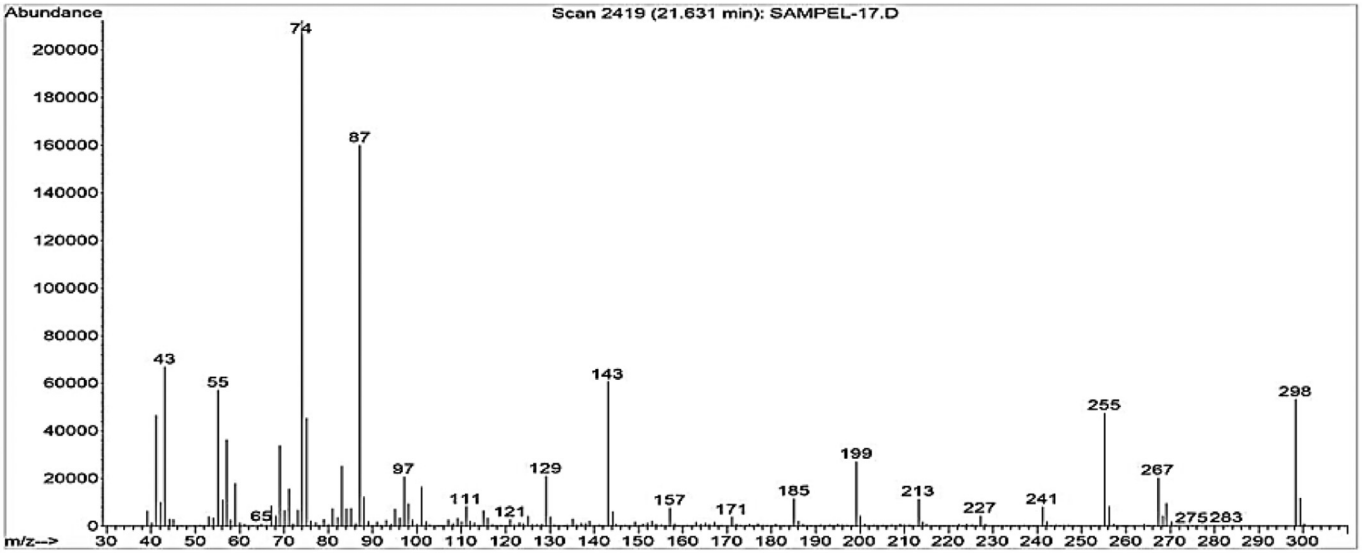

Fig. 4. Mass spectrum of methyl octadecanoate.

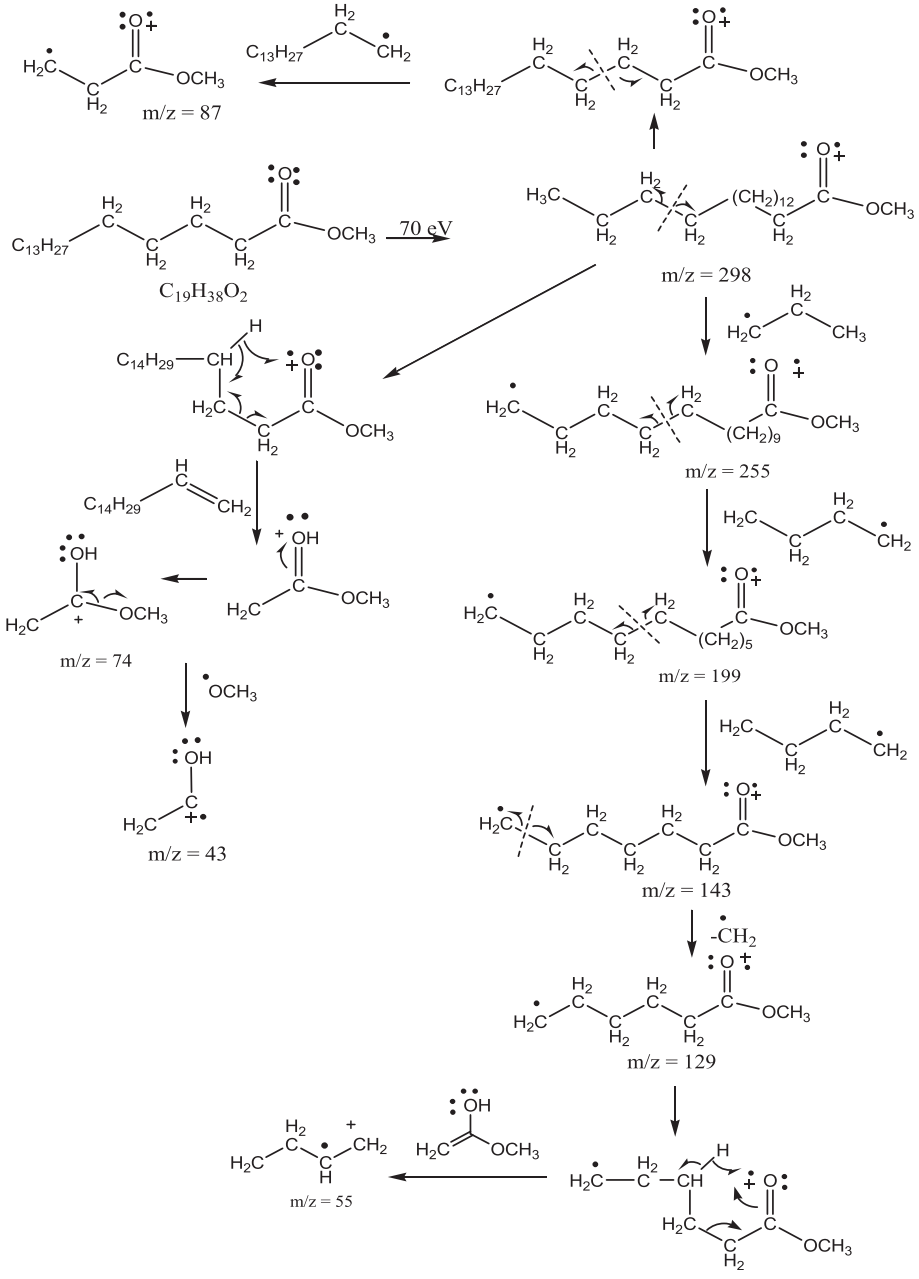

Fig. 5. Pattern of mass fragementation of methyl octadecanoate.

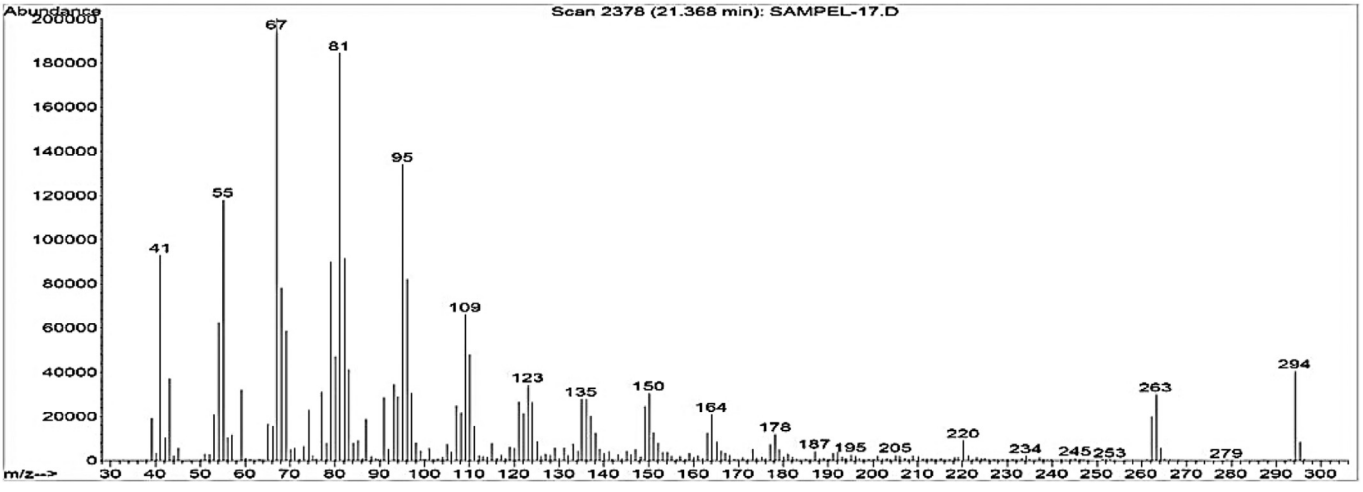

Fig. 6. Mass spectrum of methyl 8, 11-octadecanoate.

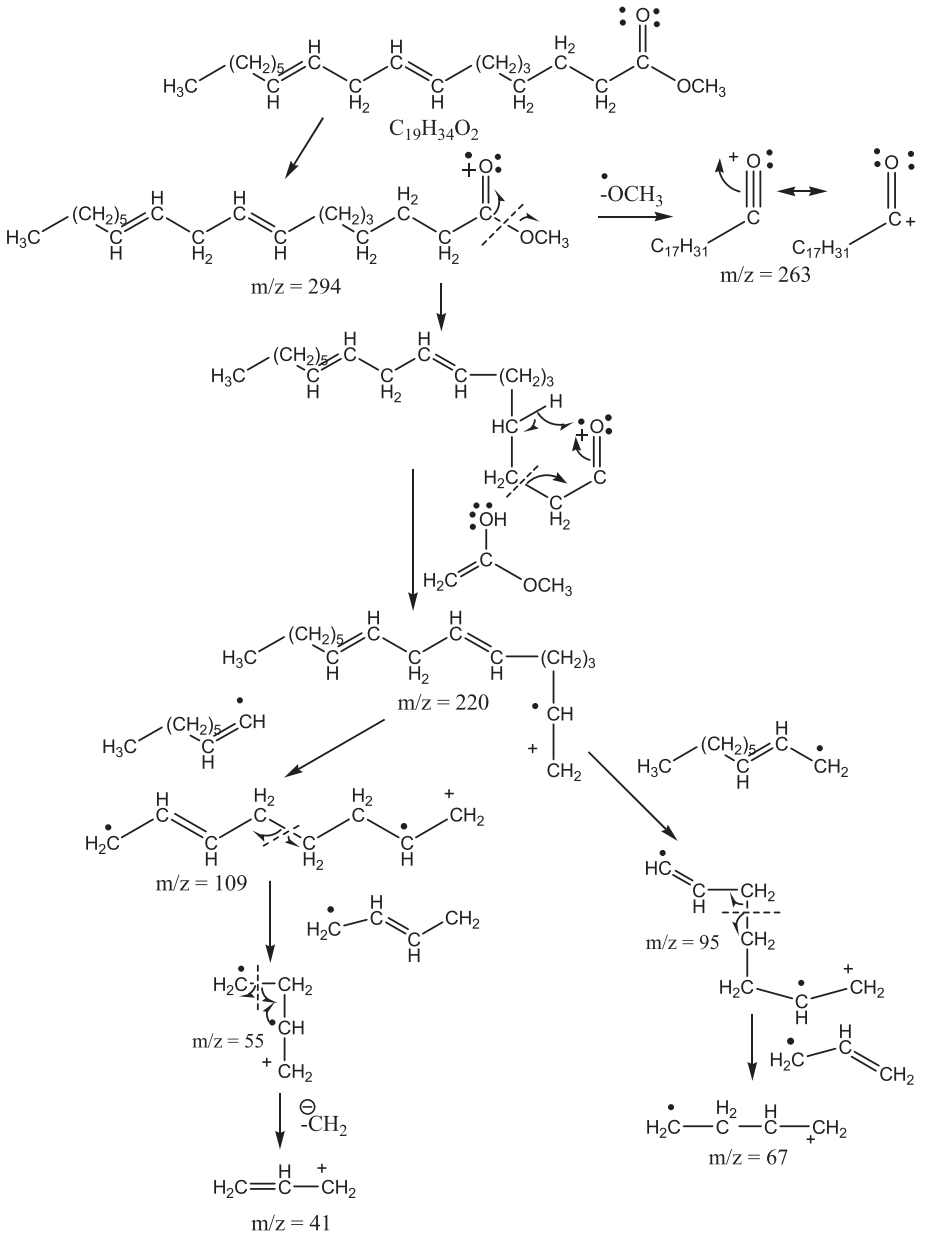

Fig. 7. The pattern of fragmentation of methyl 8,11-octadecadinoate.

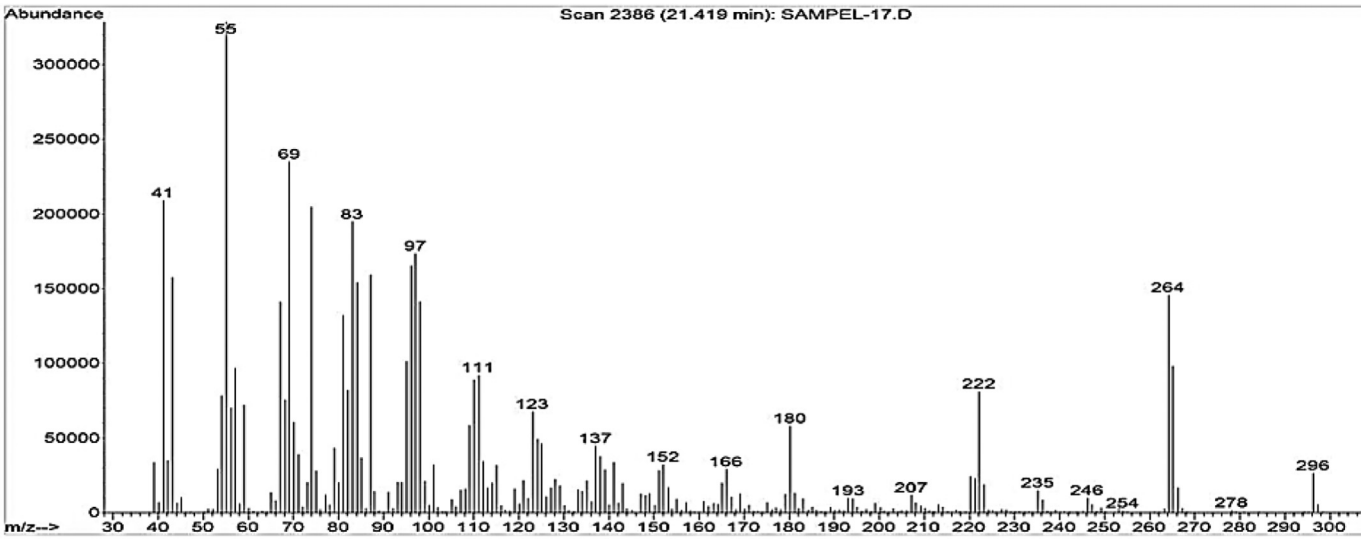

Fig. 8. Mass spectrum of methyl 9-octadecanoate.

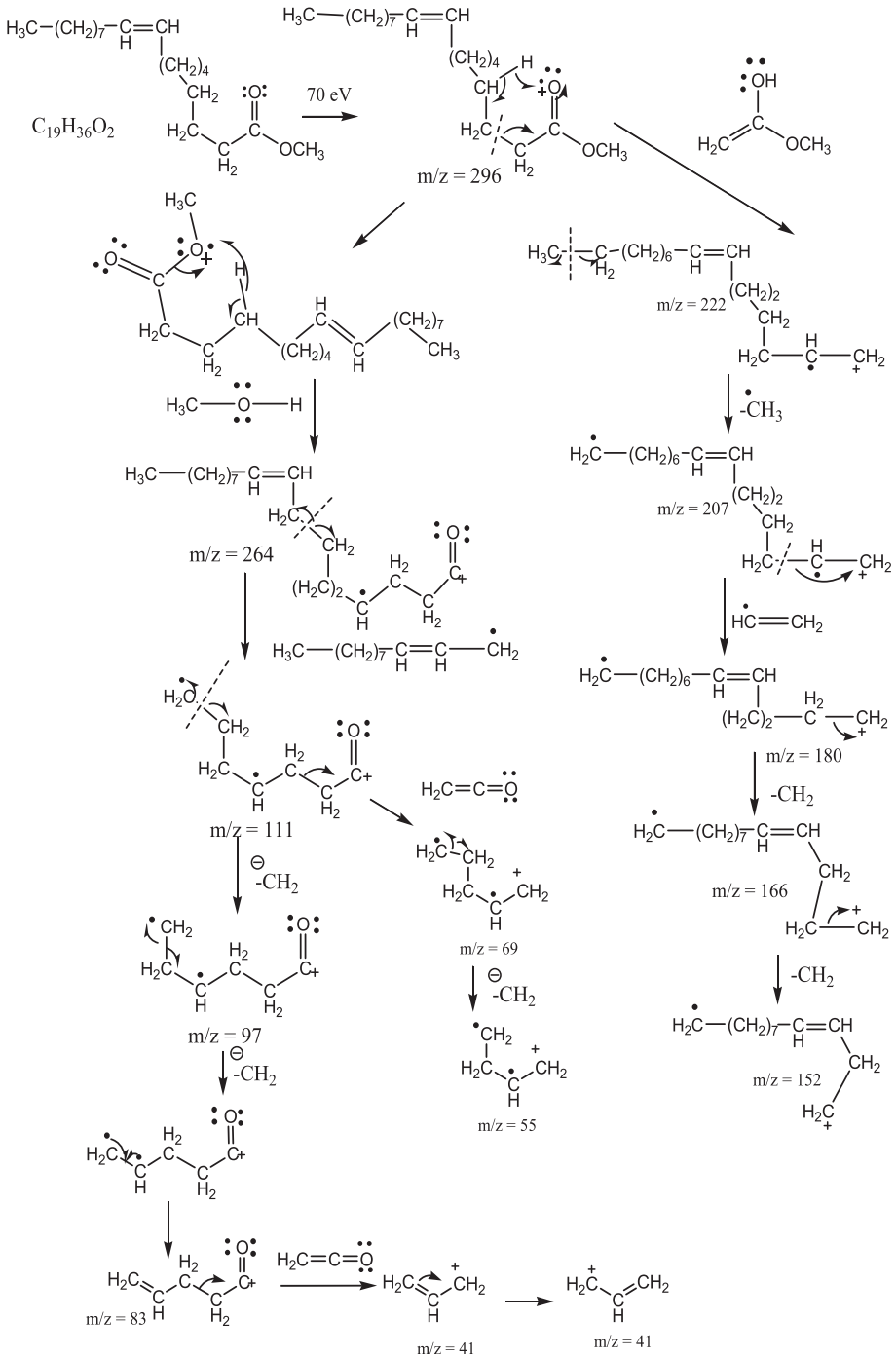

Fig. 9. The pattern of fragmentation of methyl 9-octadecanoate.

The results of GC-MS analysis of methyl 8, 11-octadecadenoate with the retention time of 21.37 and the composition of 10.22% is an isomer compound of methyl linoleat which has the same molecular formula that is $C_{19}H_{34}O_2$. Isomerization reaction is called positional isomer in which the position of the double bond in methyl linoleat lies in the carbon atom number 9 and carbon atom number 12 changes position to number 8 and 11.

The mass spectrum of methyl 8, 11-octadecadenoate is written by m/z 294 originating from the molecular ion of $C_{19}H_{34}O_2^+$ which is formed when it is exposed by 70 eV of electron. Molecular ion of $C_{19}H_{34}O_2^+$ undergoes fragmentation by releasing CH_3O radical and it produces the peak by m/z 263 originating from $C_{18}H_{31}O^+$. The peak lies in m/z 220 originating from $C_{16}H_{28}^+$ formed by McLefferty reorganization of $C_{18}H_{31}O^+$ releasing C_2H_3O. The peak lying in m/z 95 originates from $C_7H_{11}^+$ coming from $C_{18}H_{31}O^+$ releasing C_9H_{19} radical. The mass spectrum of methyl 8,11-octadecanoate contains bottom peak by m/z 67 originating from C_4H_7. The pattern of fragmentation of 8,11-octadecanoate can be seen in Figs. 6 and 7.

The results of GC-MS analysis of methyl 9-octadecadinoate indicate that the retention time required is 21.42 with the composition of 19.98%. The mass spectrum of methyl 9-octadecanoate is written by m/z 296 originating from the molecular ion of $C_{19}H_{36}O_2^+$ which is formed when exposed by 70 eV of energy. Molecular ion of $C_{19}H_{36}O_2^+$ releases $C_3H_6O_2$ radical and produces fragments by m/z 222 originating from $C_{16}H_{30}$ which then releases CH_3 radical which forms the peak of m/z 207 originating from $C_{15}H_{27}^+$. The peak of m/z 180 originating from $C_{13}H_{24}$ which undergoes fragmentation by releasing CH_2 radical produces peak by m/z 166. Molecular ion of $C_{19}H_{36}O_2^+$ can also experience fragmentation by releasing CH_3OH and it produces the peak within m/z 264 originating from $C_{18}H_{32}O^+$. The peak with m/z 111 originating from $C_7H_{11}O^+$ releases CH_2 radical and produces m/z 97 originating from $C_6H_9O^+$; while the bottom peak originates from $C_4H_7^+$ with m/z 55. The pattern of fragmentation of methyl 9-octadecanoate can be seen in Figs. 8 and 9.

4. Conclusion

The results of GC-MS analysis shows that there are several methyl ester substances, i.e. methyl hexadecanoate with the composition of 12.87%, methyl 9-octadecanoate with the composition of 19.98%, methyl octadecanoate with the composition of 5.71% and methyl 8,11-octadecadienoate with the composition of 10.22%.

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