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REVIEW

Methyl Ester Type Produced by Catalytic Transesterification: From Various Oil Feedstock to Biodiesel Products

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ABSTRACT

Biodiesel research has been carried out via transesterification. However, biodiesel products (methyl esters) have not encountered new insights, because feedstocks have been explored and studied. Various optimum conditions on transesterification reaction could produce different methyl ester type with different compound. So, this review describes various oil feedstock that were to find new insights about methyl ester type. The review took the results of study that has been published with experience for 10 years. The results of the study reviewed on the transesterification method, characterization of methyl esters, and its components. The component reviewed and correlated to the literature, structure, and GC-MS analysis. The review can provide challenges for methyl ester research in future research.

KEYWORDS

Biodiesel; methyl ester; transesterification; feedstock; catalytic reaction

Nomenclature

SNI	Standar Nasional Indonesia

1 Introduction

Biodiesel is known as an alternative renewable fuel. In developing countries, biodiesel is a promising alternative fuel thanks to its largely economical manufacturing process, and abundant source of feedstocks [1]. Feedstocks in the form of triglycerides could come from oil [2]. The used feedstock can reduce both pollution and waste. Interest in biodiesels have been influencedby rising global energy demand and growing environmental concern to find green renewable alternative fuels [3].

Oil is divided into two types: e.g., vegetable oil and animal oil [4]. Vegetable oils are commonly used in biodiesel, including palm oil, coconut oil, castor oil, thumba oil, and used cooking oil. Animal oils as feedstock for biodiesel including chicken oil, beef oil, and fish oil. However, these two oil types always have different levels of triglyceride components [5]. This difference has caused the production of biodiesel fuels with under 100% yield; in fact, this happens quite naturally.

One of the most common processes of converting triglycerides into biodiesel is called catalytic transesterification, because it is widely applied in industrial parameters [6]. Prior to the transesterification reaction, many studies applied pretreatment (such as extraction, refining, cavitation, and esterification) to improve the quality of feedstocks [7]. The previous studies have evaluated the importance of pretreatment of biodiesel feedstocks because transesterification requires triglycerides, not other types of compounds often contained in the feedstocks. For this reason, the experiment needs the right technique in terms of initial pretreatment of biodiesel feedstocks, such as the use of catalysts, adsorbents, microwave, and cavitation techniques [8–10].

On the other hand, catalysts played a role in the development of transesterification. Theoretically, the catalyst accelerates the rate of the transesterification reaction to produce biodiesel. The previous studies, the categories of catalyst in transesterification were homogeneous base-catalyst, homogeneous acid-catalyst, heterogeneous base-catalyst, heterogeneous acid-catalyst, and enzyme. Another process was non-catalytic supercritical transesterification [11]. As a long review and development, transesterification catalysts essentially required a catalyst with a high degree of basicity (strong base) [12]. Two types of known catalysts were homogeneous catalysts and heterogeneous catalysts. Homogeneous catalysts have caused product separation problems, and they are not environmentally friendly. An example of a homogeneous catalyst was NaOH [13] and KOH [14]. Furthermore, heterogeneous catalysts have given rise to the problem of suboptimal catalytic activity. Examples of heterogeneous catalysts that have been applied were CaO, MgO, Al_2O_3, K_2O, ZnO, and various other catalyst modifications [15]. So, until now, heterogeneous catalytic transesterification is still being explored because the catalyst has affected the transesterification results of biodiesel products [10]. Another study reported that the transesterification catalyst in a hydrodynamic cavitation reactor was not an important parameter of reaction [16]. However, the developed reactor influenced by the benefit of transesterification in recent years [17]. The technology for biodiesel production required cheap, simple, operator-friendly, and efficient [18].

A problem with biodiesel products produced from catalytic heterogeneous catalytic transesterification is inconsistency in the yield and characterization of the alkyl ester. In this review, the observed biodiesel product is methyl ester. The methyl ester is obtained from the reaction between methanol and triglycerides. It has also been well nown that methanol has a better reaction activity compared to other types of alcohol, such as ethanol and propanol [19]. Methyl ester products have long been characterized in order to obtain information on the quality of methyl esters, such as the characterization of density, viscosity, acid number, and refractive index. Then, the characterization was compared with biodiesel quality standards, such as SNI 7182:2015 (in Indonesia). So, the biodiesel with various methyl esters needs to be reviewed.

2 Transesterification of Various Oil Feedstock

Transesterification can be applied to various oil feedstock. Theoretically, transesterification is a chemical reaction between 1 mole of triglycerides and 3 moles of alcohol which can produce alkyl esters and glycerol. As reactants, methanol and ethanol are good alcohol based on their activity [19], but methanol is better than ethanol. In real experimental conditions, the ratio of triglycerides (oil) and alcohol is not equal to 1:3. The oil: Alcohol ratios commonly used in transesterification research are 1:10, 1:12, 1:15, and 1:16. Some of the optimum transesterification conditions from the reported studies are shown in Table 1.

Table 1: Transesterification condition of various oil feedstock

Catalyst	Feedstock	Methods	Transesterification condition	Ref.
$CaO\text{-}K_2O$	Waste cooking oil	(1) refining, (2) transesterification with ultrasonic	65°C, catalyst 8% w/w, mole ratio of oil:methanol (1:15), 5 min Ultrasonic wave	[20]
KOH	Tobacco oil (Voor-Oogst)	(1) isolation, (2) esterification, (3) transesterification with ultrasonic	65°C, catalyst 1% w/w, oil: 3 mL methanol, 10 g oil, 10 min ultrasonic wave	[21]
$MgO\text{-}K_2O$	Off grade crude palm oil	(1) refining, (2) esterification, (3) transesterification with ultrasonic	65°C, catalyst 15% w/w (MgO: K_2O 10:2 grams), mole ratio of oil:methanol 1:16, 30 min ultrasonic wave	[22]
CaO-MgO	Crude palm oil	(1) refining, (2) transesterification	65°C, catalyst 5% w/w, mole ratio of oil:methanol 1:10, 3 h	[23]
KOH	Papaya seed	(1) isolation, (2) esterification, (3) transesterification	65°C, catalyst 1% w/w, 10 g oil, 6 mL KOH alkoholis (basa dalam methanol), 2 h, 200 rpm	[24]
K_2O/Al_2O_3	Off grade crude palm oil	(1) refining, (2) esterification, (3) transesterification	60°C, catalyst 4% w/w, mole ratio of oil:methanol 1:12, 4 h, 300 rpm	[25]
CaO-MgO	*Jatropha curcas* L.	(1) esterification, (2) transesterification with microwave,	65°C, catalyst 7.5% w/w, mole ratio of oil:methanol 1:18, microwave 10 min, 200 rpm	[26]
$CaO@CoFe_2O_4$ Nanoparticles	Used cooking oil	(1) refining, (2) transesterification	60°C, catalyst 2% w/w, mole ratio of oil:methanol 1:12, 4 h, 400 rpm	[27]
CaO-ZnO	Off grade crude palm oil	(1) refining, (2) esterification, (3) transesterification	65°C, catalyst 4% w/w, mole ratio of oil:methanol 1:15, 3 h, 300 rpm	[28]
CaO-MgO	Chicken oil	(1) extraction, (2) transesterification,	65°C, catalyst 5% w/w, mole ratio of oil:methanol 1:15, 2 h, 300 rpm	[29]

(Continued)

Table 1 (continued)

Catalyst	Feedstock	Methods	Transesterification condition	Ref.
H_2SO_4	Rice Bran oil	(1) extraction, (2) esterification	60°C, catalyst 3% w/w, mole ratio of oil:methanol 1:15, 4 h,	[30]
TiO_2	Thumba oil	(1) tran-sesterification in hydrodynamic cavitation	60°C, catalyst 1.2% w/w, mole ratio of oil:methanol 1:6, 1 h	[16,31] [32]
Amberlyst	Thumba oil	(1) trans-esterification	65°C, catalyst 1.2% w/w, mole ratio of oil:methanol 1:6, 1 h	[33]
KOH	Waste cooking oil	(1) filtration, (2) esterification, (3) transesterification	60°C, catalyst 2% w/V, 50 mL oil, 4.8 g methanol, 2 h	[34]
KOH	Waste cooking oil	(1) adsorption, (2) transesterification	60°C, catalyst 1% w/V, 50 mL oil, 12.5 mL methanol, 1 h	[35]
H-Zeolite	Kapok seed oil	(1) extraction, (2) transesterification	60°C, catalyst 2% w/w, mole ratio of oil:methanol 1:9, 3.3 h	[36]
H-Zeolite	Waste cooking oil	(1) filtration, (2) esterification, (3) transesterification	60°C, catalyst 10% w/w, mole ratio of oil:methanol 1:12, 3 h	[37]
KOH	Waste cooking oil	(1) trans-esterification	60°C, catalyst 1% w/w, 400 mL oil, 100 mL methanol, 1 h	[38]
H-Zeolite	Waste cooking oil	(1) trans-esterification	60°C, catalyst 1% w/w, 400 mL oil, 100 mL methanol, 1 h	[38]
H-Zeolite	Saga seed oil	(1) extraction, (2) transesterification	60°C, catalyst 8% w/w, mole ratio of oil:methanol 1:9, 3.3 h	[39]
NaOH	Waste cooking oil	(1) microfiltration, (2) trans-esterification	65°C, catalyst in the form of sodium methoxide about 1.5% w/w of oil, 1 h	[40]
Cengar clay	Baung fish waste	(1) heating, (2) transesterification	60°C, catalyst 1% w/w, mole ratio of oil:methanol 1:9, 3.5 h	[41]

(Continued)

Table 1 (continued)

Catalyst	Feedstock	Methods	Transesterification condition	Ref.
H-Ledgestone	Waste cooking oil	(1) filtration, (2) transesterification	60°C, catalyst 1% w/w, 50 mL oil, 200 mL methanol, 5 h	[42]
KOH/SiO_2	Crude palm oil	(1) extraction, (2) transesterification	60°C, catalyst 25% w/w, 100 mL oil, methanol, 4 h	[43]
CaO	Waste cooking oil	(1) heating, (2) esterification, (3) transesterification	65°C, catalyst 8% w/w, mole ratio of oil:methanol 1:12, 5 h	[44]
CaO/Zeolite	Waste cooking oil	(1) filtration, (2) transesterification	60°C, catalyst 5% w/w, mole ratio of oil:methanol 1:15, 5 h	[45]
NaOH	Sardin fish oil	(1) heating, (2) esterification, (3) transesterification	70°C, catalyst 1.5% w/w of oil & methanol, 2 h	[46]
H-Zeolite	Crude palm oil	(1) heating, (2) transesterification	60°C, catalyst 2% w/w, mole ratio of oil:methanol 1:6, 1.5 h	[47]
H-Clay	Kapok seed oil	(1) degumming, (2) esterification, (3) trans-esterification	60°C, catalyst 0.45% w/w, mole ratio of oil:methanol 1:9, 1.5 h	[48]
Nb_2O_5-Zeolite	Waste cooking oil	(1) heating, (2) esterification, (3) transesterification	70°C, catalyst 3.75% w/w, mole ratio of oil:methanol 1:12, 2 h	[49]
SO_4^{2-}/ZnO	Soybean oil	transesterification	70°C, catalyst 4% w/w, mole ratio of oil:methanol 1:6, 4 h	[50]
KOH	Beef oil	(1) heating, (2) esterification, (3) transesterification	65°C, Catalyst 1% w/w, mole ratio of oil:methanol 1:12, 2 h	[51]
Gismodine	Waste cooking oil	(1) adsorption, (2) esterification, (3) transesterification	65°C, catalyst:oil:methanol about 1.0:20.0:13.3, 6 h	[52]
H-Zeolite	Baung fish oil	(1) heating, (2) transesterification	60°C, catalyst 10% w/w, mole ratio of oil:methanol 1:5, 3.3 h	[53]
NaOH	Kepayang seed oil	(1) extraction, (2) degumming, (3) transesterification	60°C, catalyst 1% w/w, mole ratio of oil:methanol 1:3, 1.5 h	[54]

(Continued)

Table 1 (continued)

Catalyst	Feedstock	Methods	Transesterification condition	Ref.
H-Zeolite	Kepayang seed oil	(1) extraction, (2) degumming, (3) transesterification	60°C, catalyst 1% w/w, mole ratio of oil:methanol 1:3, 1.5 h	[54]
Ni(2%)/Natural Zeolit	Buta-buta seed oil	(1) extraction, (2) degumming, (3) esterification, (4) transesterification	60°C, catalyst 0.5% w/w, mole ratio of oil:methanol 1:9, 1.5 h	[55]
CaO (Cockle shell)	*Calophyllum inophyllum*	transesterification	60°C, catalyst 3% w/w, mole ratio of oil:methanol 1:8, 3 h	[56]

Based on Table 1, various oil feedstocks have affected transesterification performance. So, before transesterification, the study requires pretreatment. The pretreatment aims to control oil quality so that it does not contain impurities. Although the used oil cannot be 100% pure, examples of the pretreatments were heating, filtration, degumming, extraction, and esterification. In development, esterification in hydrodynamic cavitation reactors [57], esterification in ultrasonic cavitation reactors [58], and microwave pretreatment [9] are profitable techniques. Without pretreatment, the transesterification product will vary greatly, and the obtained alkyl ester is not optimal [59].

Pretreatment is always adjusted to the condition of the feedstocks. Refining is applied to feedstocks such as oil, especially waste oil. Extraction is applied to feedstocks from animal oils and vegetable oils. Esterification has been widely applied to oils to reduce free fatty acid levels to $< 2\%$. Free fatty acids will affect the transesterification, so the alkyl ester product is not optimal [60].

The transesterification conditions played an important process in the production of alkyl esters [2]. Alkyl esters have been defined as biodiesel with applicable product standards, such as EN 14214:2003 (Europe), ASTM D6751:2011 (America), ANP N° 42 (Brazil), IRAM 6515–13 (Argentina), DE 100–04 (Colombia), PNA 16 018 (Paraguay) UNI 1100 (Uruguay), JIS K2390 (Japan), GB/T20828:2007 (China), CNS 15072 (China Taipei), SNI 7182:2015 (Indonesia), IS 15607:2005 (India), MS 2008:2008 (Malaysia), PNS/DOE QS 002:2007 (Philippines), and TCVN 7717:2007 (Vietnam). The transesterification reaction conditions are always influenced by temperature, amount of catalyst, time, and oil: Alcohol ratio [10]. During the transesterification process, stirring has been applied in experiments (note: Some studies do not report details). In addition, the presence of additional devices such as microwave, ultrasonic cavitation, and hydrodynamic cavitation have affected biodiesel synthesis [31]. Also as important, is the used reactor in pretreatment/transesterification, as it affects the results and stability of the process [61]. With this understood, the results will give different characteristics of alkyl esters and yields.

In various oil feedstocks, the categories of feedstocks for biodiesel are three categories: (1) edible oil, (2) non-edible oil, (3) waste oil, (4) animal fat, and (5) microbial oil [17]. As known, edible oils will compete with the food feedstock. non-edible oil was not requiredas a food source, but the low conversion was a problem. The most potential feedstocks were waste oil and microbial oil. For waste oil, the production requires the available sources. Microbial oil, is an excellent source as well [62],

but the difficulty of the source has been a problem in recent years because of both sensitivity and sustainability [63]. Also, it included a different process with other oil feedstocks [64,65].

3 Characterization of Methyl Ester Products

Characterization of biodiesel in the previous study was chosen methyl ester products, because this review controls the input-process-output of the previous study in the same culture. The characterization included density, viscosity, acid number, refractive index and, yield percent. These characterizations can be listed in Table 2.

Table 2: Characterization results of methyl ester products

Catalyst	Feedstock	Characterization				Yield (%)	Ref.
		Density (g/cm^3)	Viscosity (cSt)	Acid number (mg KOH/g)	Refractive index		
-	-	0.85–0.89	2.3–6.0	max 0.4	1.3–1.45	96.50	**SNI**
$CaO\text{-}K_2O$	Waste cooking oil	0.854	5.501	0.55	1.447	92.37	[20]
KOH	Tobacco oil	0.865	4.44	0.56	1.45	84.55	[21]
$MgO\text{-}K_2O$	Off grade crude palm oil	0.876	4.79	0.2735	1.448	88.08	[22]
CaO-MgO	Crude palm oil	0.86	3.23	0.747	1.44819	85.72	[23]
KOH	Papaya seed	0, 85	4.76	0.70	1, 44	75, 82	[24]
K_2O/Al_2O_3	Off grade crude palm oil	0.86	3.61	0.49	1.45	85.58	[25]
CaO-MgO	*Jatropha curcas* L.	0.888	4.23	0.58	1.465	92.39	[26]
$CaO@CoFe_2O_4$	Used cooking oil	No testing	4.68	No testing	No testing	80.62	[27]
CaO-ZnO	Off grade crude palm oil	0.876	3.60	0.39	1.448	84.74	[28]
CaO-MgO	Chicken oil	0.88	5.84	0.69	1.45018	81.32	[29]
H_2SO_4	Rice bran oil	0.850	4.73	0.76	1.45871	72.37	[30]
TiO_2	Thumba oil	0.872	4.04	0.02	No testing	75	[31]
KOH	Waste cooking oil	0.875	4.51	0.19	No testing	No report	[34]
KOH	Waste cooking oil	0.857	No testing	0.29	No testing	No report	[35]

(Continued)

Table 2 (continued)

Catalyst	Feedstock	Characterization				Yield (%)	Ref.
		Density (g/cm^3)	Viscosity (cSt)	Acid number (mg KOH/g)	Refractive index		
H-Zeolite	Kapok seed oil	0.859	5.60	0.56	No testing	79.35	[36]
H-Zeolite	Waste cooking oil	0.870	11.42	No testing	No testing	No report	[37]
KOH	Waste cooking oil	0.850	3.09	No testing	No testing	No report	[38]
H-Zeolite	Waste cooking oil	0.780	0.35	No testing	No testing	No report	[38]
H-Zeolite	Saga seed oil	0.853	5.15	0.49	No testing	86.44	[39]
NaOH	Waste cooking oil	0.908	3.13	0.29	No testing	No report	[40]
Cengar clat	Baung fish waste	0.882	5.18	0.63	No testing	78.01	[41]
H-ledgestone	Waste cooking oil	0.785	0.465	0.04	No testing	74.71	[42]
KOH/SiO_2	Crude palm oil	0.864	5.56	No testing	No testing	60	[43]
CaO	Waste cooking oil	0.875	4.71	No testing	No testing	30.93	[44]
CaO/Zeolite	Waste cooking oil	0.83	No testing	No testing	No testing	98.4	[45]
NaOH	Sardin fish oil	0.888	4.11	No testing	No testing	45.34	[46]
H-Zeolite	Crude palm oil	0.880	4.59	0.65	No testing	84.78	[47]
H-Clay	Kapok seed oil	0.869	2.67	0.45	No testing	92.18	[48]
Nb_2O_5-Zeolite	Waste Cooking oil	0.872	3.498	No testing	No testing	76.76	[49]
SO_4^{2-}/ZnO	Soybean oil	0.887	5.61	0.15	No testing	80.19	[50]
KOH	Beef oil	0.867	4.97	No testing	No testing	78.96	[51]
Gismodine	Waste cooking oil	No testing	No testing	No testing	No testing	85	[52]
H-Zeolite	Baung fish oil	0.890	5.48	0.701	No testing	87.02	[53]
NaOH	Kepayang seed oil	0.860	3.42	0.50	No testing	17.4	[54]

(Continued)

Table 2 (continued)

Catalyst	Feedstock	Characterization				Yield (%)	Ref.
		Density (g/cm^3)	Viscosity (cSt)	Acid number (mg KOH/g)	Refractive index		
H-Zeolite	Kepayang seed oil	0.879	5.87	0.67	No testing	31	[54]
Ni(2%)/Natural zeolite	Buta-buta seed oil	0.885	4.29	0.49	No testing	85.8	[55]
CaO (Cockle shell)	*Calophyllum inophyllum*	0.810	4.25	0.63	No testing	87.4	[56]

Based on Table 2, the transesterification conditions state the differences in the characterization results. The difference still meets SNI 7182:2015 standard. In general, the density and viscosity characteristics have complied with SNI, but not all of the acid number and refractive index have complied with SNI. Then, the yields of methyl ester were all below standard (96.5%). Furthermore, the used catalysts, such as KOH and CaO, proved that the yield percent of biodiesel was different from different types of feedstocks. This means that the catalytic activity of a catalyst is still inconsistent, due to the differences in the components of the biodiesel feedstock. On the other hand, the mixing of catalysts into a reactor needs to be considered because the catalyst is required to be perfectly distributed. The used catalyst in different feedstock also produces different characteristics of biodiesel. In addition, the reactor serves an important role that affects chemical processes, like that of the microwave [26], the ultrasonic cavitation [22], and the hydrodynamic cavitation [31]. So, the transesterification process can be stated that the ongoing process has missing observations. This review will try to evaluate the missing observations in terms of the produced methyl ester. Methyl esters were reanalyzed in depth from the results of the GC-MS test. Methyl ester types will give information about characteristics of the catalyst via inverse direct.

4 Methyl Ester Analysis of Trans-Esterified Various Oil Feedstock

Methyl Esters have been known as biodiesel products from transesterification. Methyl esters have been commonly tested by Gas Chromatography-Mass Spectrophotometry (GC-MS). GC results were in the form of a chromatogram, and MS results were in the form of a mass spectrum according to the retention time of the GC. Various components of methyl esters from trans-esterified various oil feedstock are shown in Table 3.

Based on Table 3, various oil feedstocks have shown various component results of the trans-esterified methyl ester. There are always two main components in various oil feedstock whose levels are more than 20% in various oil feedstock. It shows certain peculiarities. However, in many feedstocks, methyl palmitate ($C_{17}H_{34}O_2$) and methyl oleate ($C_{19}H_{36}O_2$) are always found. Although the retention time value is different, the mass spectrum can show methyl ester specifically.

Table 3: Methyl ester type by GC-MS results

Catalyst	Feedstock	Methyl ester type (Area, %)	Retention time (min)	Ref.
$CaO\text{-}K_2O$	Waste cooking oil	methyl myristate (6.47%), methyl palmitoleate (4.34%), methyl palmitate (**24.62%**), methyl oleate (**49.44%**), methyl stearate (10.72%), methyl arachidate (4.51%)	16.459 18.512 18.930 21.028 21.157 23.887	[20]
KOH	Tobacco Oil (Voor-Oogst)	methyl palmitate (18.72%), methyl linoleate (**30.76%**), methyl oleate (**27.26%**), methyl stearate (9.35%)	18.090 19.860 20.044 20.146	[21]
$MgO\text{-}K_2O$	Off grade crude palm oil	methyl myristate (1.96%), methyl palmitate (**40.42%**), methyl oleate (**44.32%**), methyl stearate (7.46%)	Not known 9.96 Not known 11.161	[22]
CaO-MgO	Crude palm oil	methyl myristate (1.20%), methyl palmitate (**40.64%**), methyl linoleate (9.33%), methyl 7-octadecenoate (**42.99%**), methyl stearate (4.43%)	5.420 9.940 15.073 15.36 15.937	[23]
KOH	Papaya seed	methyl oleate (**78.87%**), methyl palmitate (14.58%), methyl stearate (4.57%)	38.66 42.554 43.753	[24]
K_2O/Al_2O_3	Off grade crude palm oil	methyl palmitate (**49.64%**), methyl linoleate (5.52%), methyl oleate (**40.90%**), methyl stearate (2.14%)	28.199 34.733 34.923 35.693	[25]
CaO-MgO	*Jatropha curcas* L.	methyl palmitoleate (2.40%), methyl palmitate (**21.20%**), methyl oleate (**62.40%**), methyl stearate (14.00%)	18.502 19.759 20.908 21.058	[26]

(Continued)

Table 3 (continued)

Catalyst	Feedstock	Methyl ester type (Area, %)	Retention time (min)	Ref.
$CaO@CoFe_2O_4$ Nanoparticles	Used cooking oil	methyl Laurate (0.24%), methyl Myristate (1.31%), methyl palmitoleate (0.48%), methyl palmitate (**37.42%**), methyl margarate (0.13%), methyl Oleate (**52.42%**), methyl Stearate (6.20%), methyl Oxiraneoctanoate (0.23%), methyl Eicosenoate (0.43%), methyl Eicosanoate (0.71%), methyl behenate (0.13%), Methyl lignocerate (0.13%)	6.883 8.387 9.635 9.866 10.396 11.012 11.080 11.935 12.020 12.149 13.200 14.183	[27]
CaO-ZnO	Off grade crude palm oil	methyl myristate (2.72%), methyl palmitate (**54.87%**), methyl linoleic (5.78), methyl oleate (**26.83%**), methyl stearate (2.55%)	22.104 28.279 34.743 34.949 35.690	[28]
CaO-MgO	Chicken oil	methyl palmitoleic (3.64%), methyl palmitate (**37.05%**), methyl linoleate (4.75%), methyl oleate (**40.90%**), methyl stearate (2.28%)	27.833 28.683 35.087 35.263 36.007	[29]
H_2SO_4	Rice bran oil	methyl myristate (0.38%), methyl palmitate (**40.67%**), methyl oleate (**53.68%**), methyl stearate (5.02%), methyl arachidate (0.14%)	15.745 18.094 19.930 20.053 21.852	[30]
KOH	Waste cooking oil	methyl caprylate (1.74%) methyl caprate (4.74%) methyl laurate (45.63%) methyl myristate (21.07%) methyl palmitate (13.67%) methyl oleate (8.66%) methyl stearate (4.17%) others (0.25%)	7.391 11.341 14.521 17.129 19.407 21.235 21.447 23.008	[34]

(Continued)

Table 3 (continued)

Catalyst	Feedstock	Methyl ester type (Area, %)	Retention time (min)	Ref.
KOH	Waste cooking oil	methyl myristate (1.36%) methyl 9-hexadecanoat (0.96%) methyl palmitate (**20.79%**) methyl 9, 12-octadecadienoate (18.87%) methyl elaidate (**49.45%**) methyl stearate (7.68%) others	15.864 18.527 18.841 21.116 21.214 21.579 -	[35]
H-Zeolite	Kapok seed oil	methyl palmitate (**31.4%**) methyl linoleate (**30.67%**) methyl oleate (**24.07%**) methyl stearate (3.68%)	42.118 45.771 45.854 46.301	[36]
H-Zeolite	Waste cooking oil	methyl myristate (1.57%) methyl palmitate (**44.93%**) methyl linoleate (9.28%) methyl oleate (**39.18%**) methyl stearate (5.04%)	37.724 42.252 45.808 45.924 46.345	[37]
KOH	Waste cooking oil	methyl myristate (1.27%) methyl palmitoleate (4.58%) methyl palmitate (**29.9%**) methyl elaidate (**55.8%**) methyl 9-octadecenoate (6.17%) others	12.432 14.355 14.750 16.783 16.967 -	[38]
H-Zeolite	Waste cooking oil	methyl caprylate (1.1%) dimethyl nonanoate (1.12%) methyl palmitoleate (1.59%) methyl palmitate (**10.85%**) methyl 9.12-octadecadienoate (4.53%) methyl 9-octanoate (**6.14%**) others	4.584 10.329 14.309 14.531 16.340 16.431 -	[38]
H-Zeolite	Saga seed oil	methyl palmitate (**39.61%**) methyl linoleate (10.30%) methyl oleate (**37.92%**) methyl stearate (11.19%)	39.341 42.581 42.815 43.288	[39]

(Continued)

Table 3 (continued)

Catalyst	Feedstock	Methyl ester type (Area, %)	Retention time (min)	Ref.
NaOH	Waste cooking oil	methyl caprylate (8.83%) methyl caprate (6.21%) methyl laurate (9.21%) methyl 12-methyltridecanoate (14.74%) methyl pentadecanoate (11.87%) methyl hexadecatrinoate (1.54%) methyl palmitoleate (**28.13%**) methyl trans-13-octadecenoate (1.64%) methyl palmitate (**15.00%**)	7.894 10.217 12.237 15.560 17.617 18.569 18.745 18.864 18.964	[40]
Cengar clay	Baung fish waste	methyl elaidate (2.33%) methyl myristate (**16.96%**) methyl linoleate (8.22%) methyl oleate (**41.26%**) methyl stearate (4.54%)	20.928 21.195 22.892 23.004 23.226	[41]
H-ledgestone	Waste cooking oil	methyl palmitate (**71.84%**) methyl oleate (**28.16%**)	16.406 18.124	[42]
KOH/SiO_2	Crude palm oil	methyl stearate (**47.45%**) methyl palmitate (**29.87%**) methyl linoleate (16.92%) methyl arachidate (2.01%) methyl myristate (0.93%) methyl oleate (0.83%)	Not known	[43]
CaO	Waste cooking oil	methyl oleate (**42.77%**) methyl palmitate (**36.85%**) methyl linoleate (11.54%)	22.439 18.035 22.206	[44]
CaO/Zeolite	Waste cooking oil	methyl palmitate (**74.66%**) methyl oleate (**25.34%**)	16.407 18.124	[45]
NaOH	Sardin fish oil	methyl palmitate (**20.31%**) methyl oleate (**13.93%**) methyl eicosanoate (10.80%)	23.800 - -	[46]
H-Zeolite	Crude palm oil	trimethyl pinene (**9.92%**) methyl laurate (**54.94%**) methyl myristate (7.22%) methyl palmitate (6.76%) methyl, 6-octadecenoate (1.17%)	11.510 30.681 35.307 37.852 42.361	[47]

(Continued)

Table 3 (continued)

Catalyst	Feedstock	Methyl ester type (Area, %)	Retention time (min)	Ref.
H-Clay	Kapok seed oil	methyl oleate (**34.27%**) methyl palmitate (13.42%) methyl linoleate (**45.67%**) methyl isostearate (3.80%)	Not known	[48]
Nb_2O_5-Zeolite	Waste cooking oil	methyl caprylate (3.76) methyl caprate (3.14%) methyl laurate (**23.09%**) methyl myristate (9.81%) methyl palmitate (21.43%) methyl oleate (**34.67%**)	3.370 4.394 5.884 7.778 10.225 13.229	[49]
SO_4^{2-}/ZnO	Soybean oil	methyl palmitate (4.19%) methyl eicosanoate (9.52%) methyl 9, 12-octadecadienoate (**28.1%**) methyl elaidate (**18.95%**) methyl stearate (2.13%) others	16.437 21.236 22.938 23.014 23.275	[50]
KOH	Beef oil	methyl palmitate (**21.71%**) methyl margarate (3.92%) methyl linoleate (2.11%) methyl oleate (12.52%) methyl stearate (**30.04%**) others	18.050 20.482 22.170 22.377 23.115	[51]
Gismodine	Waste cooking oil	methyl 11-octadecenoate (**40.2%**) methyl palmitate (**37.61%**) methyl nonadecanoate (10.24%)	42.043 38.504 41.858	[52]
H-Zeolite	Baung fish oil	methyl elaidate (2%) methyl palmitate (**18.76%**) methyl linoleate (9.5%) methyl oleate (**51.03%**) methyl stearate (4.46%)	20.942 21.217 22.913 23.032 23.247	[53]
NaOH	Kepayang seed oil	methyl palmitate (3.72%) methyl linoleate (**12.49%**) methyl oleate (**18.94%**) methyl stearate (1.94%)	Not known	[54]

(Continued)

Table 3 (continued)

Catalyst	Feedstock	Methyl ester type (Area, %)	Retention time (min)	Ref.
H-Zeolite	Kepayang seed oil	methyl palmitate (3.42%) methyl linoleate (**11.98%**) methyl oleate (**16.9%**) methyl stearate (2%)	Not known	[54]
Ni(2%)/natural zeolite	Buta-buta seed oil	methyl palmitate (2.11%) methyl linolelaidate (**72.64%**) methyl oleate (**19.1%**) methyl stearate (2.2%) methyl octadic-11-enoate (0.66%)	34.129 84.599 132.293 86.283 84.874	[55]
CaO (Cockle Shell)	*Calophyllum inophyllum*	methyl oleate (**33.63%**) methyl linoleate (**29.53%**) methyl stearate (18.1%) methyl arachidate (0.45%) methyl gadoleate (1.45%)	20.503 21.351 20.430 25.211 26.111	[56]

On the other hand, the retention time possessed by the spectrum of a methyl ester shows a significant difference. It also shows the various database has a high rate of similarity (∼95%–99%). Besides that, the presence of impurities in the methyl ester was caused by the complexity of heterogeneous catalytic transesterification, affected the results of GC-MS analysis. Also, the resulted methyl esters showed the complexity of structure, so it affected the similarity level of the identified methyl esters based on the database. The process of GC-MS analysis requires control to get good information data.

For example, a mass spectrum of methyl ester from used cooking oil with a retention time of 10.176 min is shown in Fig. 1. The peak of the mass spectrum of methyl palmitate has fragments with m/z 43, 74, 101, 143, 185, 227, 270, 297, 327, 355, and 401.

Based on Fig. 1, the results were referred to the NIST17.LIB library with a 99% similarity percentage. The compound was methyl palmitate, about 30.90%, with a retention time of 10.176 min. Furthermore, the fragmentation pattern is shown in Fig. 2. The fragmentation for the molecular ion of methyl palmitate was at m/z 270, m/z 143, and m/z 227. Meanwhile, m/z 43 and m/z 74 were obtained from the fragmentation pattern through McLafferty rearrangement. One of the fatty acids of used cooking oil is palmitic acid, and one of the methyl esters is methyl palmitate.

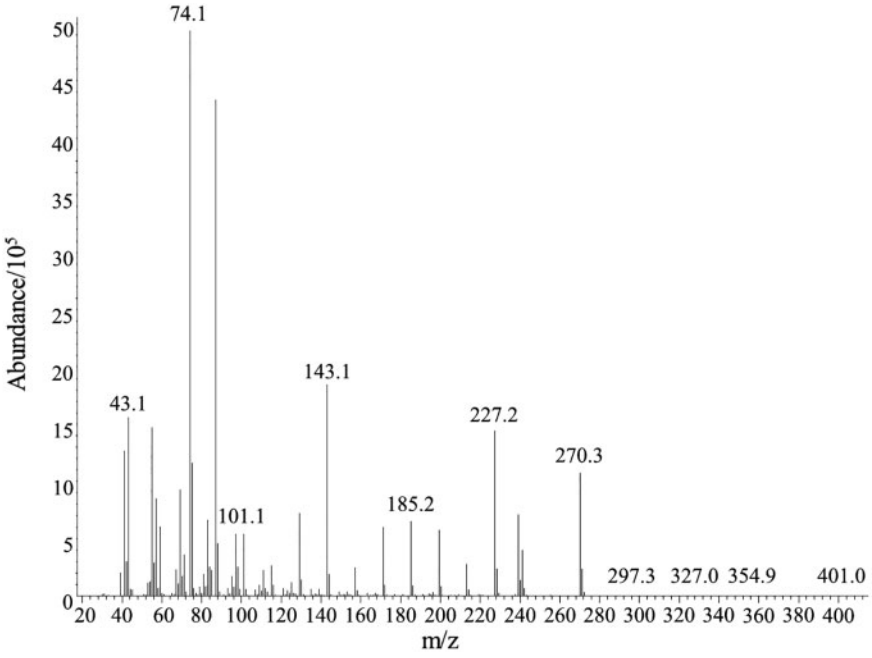

Figure 1: Mass spectrum of methyl palmitate of used cooking oil

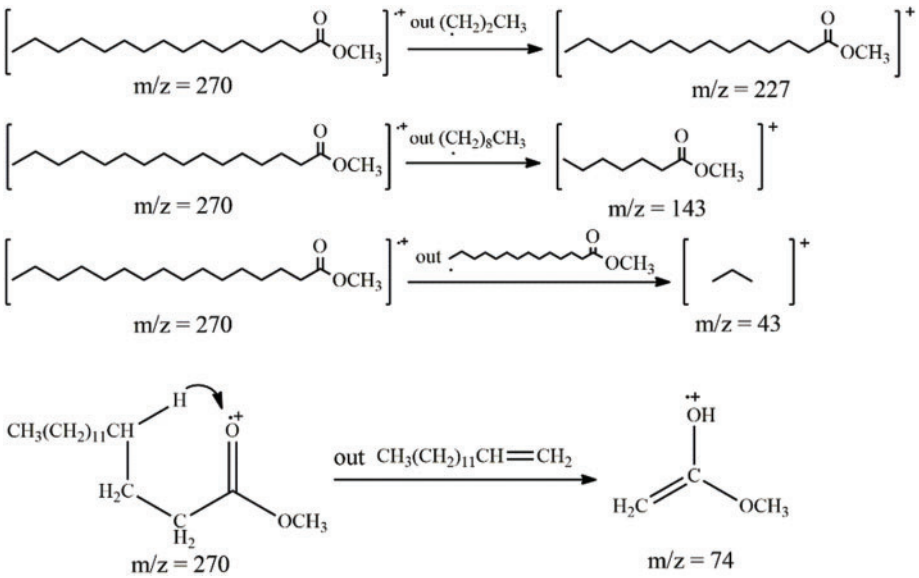

Figure 2: Fragmentation pattern of methyl palmitate of used cooking oil

Furthermore, the mass spectrum of the methyl ester of off grade crude palm oil with a retention time (t_R) of 9.990 min is shown in Fig. 3.

The mass spectrum in Fig. 2 was compared with standard peaks which are relatively the same as the mass spectrum listed in the W10N14.L library. The compound in Fig. 2 has a 98% similarity with library W10N14.L reference number 434884. Furthermore, the fragmentation pattern is shown

in Fig. 4. Fragmentation for molecular ion of methyl palmitate was at m/z 270, m/z 143, and m/z 227. Meanwhile, m/z 43 and m/z 74 are obtained from the fragmentation pattern through the Mc Lafferty rearrangement. Based on the fragmentation pattern that appears at m/z 43, 74, 143, 227, and 270 in the mass spectrum, it proves that the compound formed is methyl palmitate.

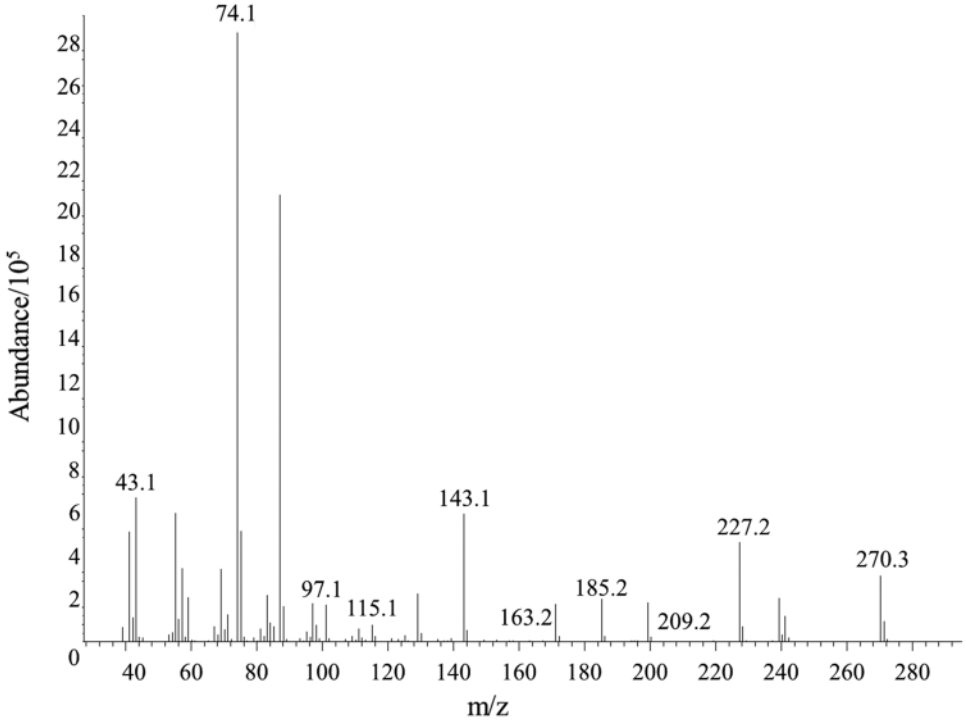

Figure 3: Mass spectrum of methyl palmitate of off grade crude palm oil

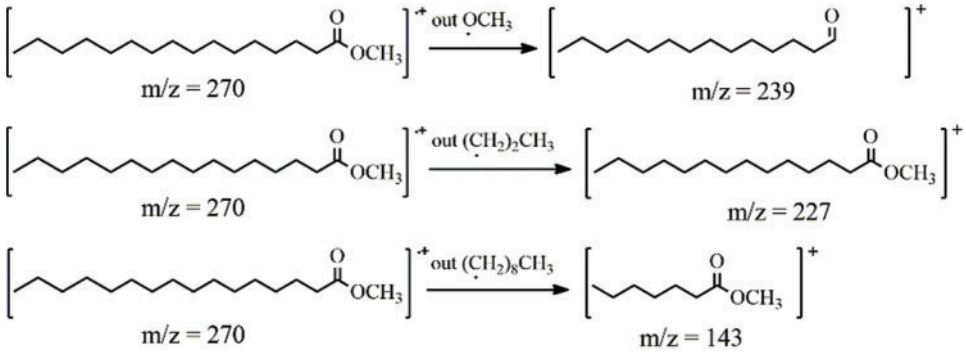

Figure 4: (Continued)

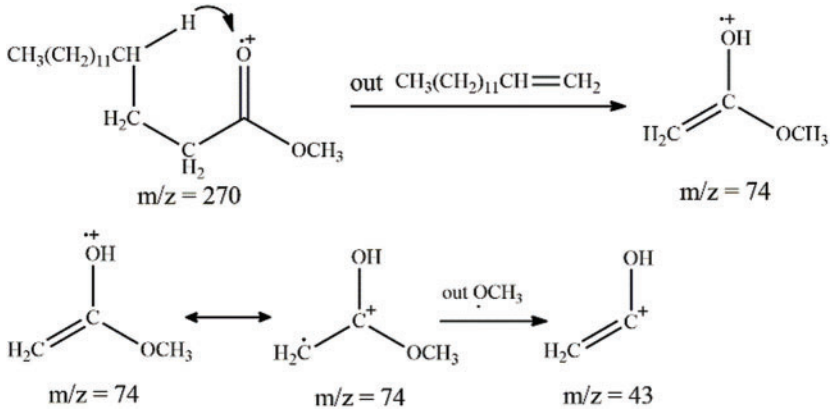

Figure 4: Fragmentation pattern of methyl palmitate of Off grade crude palm oil

5 Conclusions

Transesterification research in optimization efforts is considered unwise if it focuses on modifying the transesterification reactor only. The methyl esters turned out to have peculiarities and characteristics that were always varied and not always the same. The notion is the existence of defect product of methyl ester, like in an immiscible mixture of palm oil: Ethanol [66]. It has been proved that in research by GC-MS analysis. As a notion, the defected product occurred because of a defect in the catalyst material. From the results of GC-MS, the retention time and mass spectrum values obtained from various oil feedstock are always different, so the fragmentation analysis and library data are also different. However, the components that can be found in high levels are methyl palmitate and methyl oleate in the transesterification of triglycerides. For evaluation, the feedstock of transesterification needs to have feedstock component/compound standards. The challenge of further studies is how to prevent transesterification from producing excessive by-products.

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