ISSN: 2621-4709 E-ISSN: 2621-2528
Journal of Applied Agricultural Science and Technology
Vol. 9 No. 3 (2025): 319-331

Transesterification of Palm Olein to Fatty Acid Methyl Esters (POle-ME) Using Base Catalysts

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Abstract. *Palm olein esters are potentially convertible into epoxy oil, which can serve as a plasticizer. Palm olein can be reacted with alcohol in the presence of a base catalyst in a process named transesterification. This study aimed to investigate the application of palm olein to produce fatty acid methyl esters (POLe-ME) using sodium hydroxide and potassium hydroxide as catalysts, which are then evaluated for their potential as plasticizers. The research process involved selecting raw materials based on the iodine and acid numbers. Subsequently, transesterification was conducted using 1% base catalysts. The characterization of POle-ME included evaluating its acid number, iodine number, viscosity, fatty acid composition, and functional groups. The findings indicate that using a molar ratio of oil to methanol of 1:6 and potassium hydroxide as a catalyst achieved the highest yield at 94.99%. The produced POle-ME exhibited a peak at 1436 cm^{-1}, indicating the presence of a methyl ester functional group. The fatty acid composition of POle-ME consisted predominantly of oleic unsaturated fatty acid (C18:1) at 49.13%. Additionally, POle-ME exhibited an iodine number of 60.42, an acid number of 1.395, and a viscosity of 7.16 mPa·s, indicating its potential as a raw material for epoxy oil (plasticizer) production.*

Keywords: *base catalyst; transesterification; methyl ester; palm olein.*

Type of the Paper: Regular Article.

1. Introduction

Indonesia is the world's leading palm olein producer, contributing more than half of the world's total palm olein production. In 2022, Indonesia exported crude palm oil (CPO) at 2% and crude palm kernel oil (CPKO) at 4%, with an increase in the export of downstream products, including refinery and other products, at 73% and 21%, respectively [1]. One of the downstream products derived from palm olein that has the potential as an export commodity is epoxy oil, commonly used as a plasticizer [2–4]. Up to this point in time, the main raw material used to produce epoxy oil as a plasticizer is derived from soybean oil, taking the form of epoxidized soybean oil (ESBO), of which Indonesia is not a producer. However, Indonesia does produce palm olein, another source from which epoxy oil can be derived. In addition to ESBO, phthalic acid and its esters, which are derivatives of petroleum, are widely used in the industry as plasticizers [5]. However, phthalate use in the industry has negative impacts. Since phthalates are not

https://doi.org/10.55043/jaast.v9i3.344
Received September 15, 2024; Received in revised form May 22, 2025; Accepted July 3, 2025; Published August 24, 2025

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chemically bonded to the polymer structure, they can leach from the polymer matrix and be released into the environment during production and manufacturing, leading to their detection as pollutants in the atmosphere, water, soil, and sediments [6,7].

Palm olein, the source of epoxy oil, is produced through refining processes—such as bleaching and deodorization—and fractionation. It remains in liquid phase and is commonly used as cooking oil [8]. It consists of 40% saturated fatty acids (primarily palmitic acid), about 45% monounsaturated fatty acids (primarily oleic acid), and about 10% polyunsaturated fatty acids (primarily linoleic acid). Oleic acid application as a plasticizer in PVC particularly attracts interest in research [9,10] as it has several advantages, such as being biodegradable, renewable, non-toxic, environmentally friendly, and stable against light and heat [11]. Oleic acid content of 55% in palm olein gives it the potential to be developed into a plasticizer through chemical modification via esterification, transesterification, and epoxidation [12].

Reaction with alcohol changes palm olein into ester compounds [13], as palm olein contains a carboxyl group. As this reaction is slow, the presence of a catalyst, whether it be in the acid, base, or carbon form, is critical to its acceleration [14,15]. The use of acid catalysts to esterify fatty acids can be challenging, especially in the purification process, resulting in side reactions like saponification, the formation of emulsions, and a corrosive process. On the other hand, transesterification with base catalysts offers multiple advantages, including ease of purification and lower acidity, which minimizes side reactions and maximizes yields [16].

Numerous studies have reported the transesterification of palm olein using base catalysts such as potassium hydroxide (KOH) for biodiesel production [17]. A few comparative studies have also explored the use of sodium hydroxide (NaOH) and KOH in the transesterification of recycled vegetable oils for biodiesel applications [18]. However, these studies have primarily focused on biofuel, while the implications of catalyst choice for the properties of methyl esters intended for further conversion into epoxidized palm olein, which is used as a plasticizer, remain underexplored.

Since the physicochemical properties of methyl esters—including yield, viscosity, iodine number, and residual free fatty acid content—influence the efficiency of subsequent epoxidation and plasticizer performance, it is important to evaluate how different base catalysts affect the initial transesterification outcome. To the best of our knowledge, no prior studies have directly compared the use of NaOH and KOH in the transesterification of palm olein for the specific purpose of producing fatty acid methyl esters (POle-ME) as precursors for epoxidized plasticizers.

This study aimed to fill that gap by modifying palm olein using both NaOH and KOH catalysts and evaluating the resulting methyl esters in terms of their suitability for further conversion into plasticizers. NaOH and KOH were selected for comparison due to their widespread availability, cost-effectiveness, and proven catalytic efficiency in base-catalyzed transesterification reactions [19]. KOH tends to exhibit better solubility in alcohols, which can enhance reaction kinetics, while NaOH is generally more economical and produces fewer soap by-products under optimized conditions [20]. Comparing these two catalysts offers practical insights for optimizing the transesterification process for plasticizer precursor production, particularly in terms of yield, reaction efficiency, and downstream processing suitability.

The findings are expected to contribute to the development of palm-based plasticizer alternatives, supporting national import substitution efforts and offering a more sustainable, non-phthalate plasticizer option to minimize environmental and health risks.

2. Materials and Methods

2.1. Materials and Equipment

This study used palm olein (food grade, from a local market), methanol (CH_3OH) (analytical grade, 99.9% purity, from Merck), KOH (analytical grade, ≥ 85.0% purity, from Merck), and NaOH (analytical grade, 99.0% purity, from Merck).

The equipment used included three-necked Erlenmeyer flasks (Iwaki Glass, Indonesia), reflux condensers (Iwaki Glass, Indonesia), separating funnels (Iwaki Glass, Indonesia), a thermometer (Iwaki Glass, Indonesia), hot plates with magnetic stirrers (Thermo Fisher Scientific, United States), an analytical balance (Ohaus, United States), an NDJ-9S rotary viscometer (Cgoldenwall, China), a PerkinElmer Frontier C96600 FTIR spectrometer (PerkinElmer, United States), and a GC-MS spectrometer (Shimadzu, Japan).

2.2. Sample Preparation

The iodine number determines the raw material selection, in this case palm olein. It reflects the oil's double bonds; the higher the iodine number, the more double bonds there are. Palm olein, which was used as a raw material for POle-ME, has a high iodine number and a low acid number. Iodine number determination was conducted on three palm olein products from different brands (A, B, and C).

2.3. Palm Olein Transesterification

The palm olein transesterification process in this study followed Daryono and Mustiadi's method [21]. Palm olein (about 100 g) was put into a three-neck Erlenmeyer flask and then heated and stirred. Catalyst solutions were prepared by dissolving 1% catalysts (KOH and NaOH) in methanol at molar ratios of 1:3 and 1:6. Each catalyst solution was added to the oil when the temperature reached 63°C. Stirring was set at 600 rpm. After 135 minutes, the stirring was brought to an end and the product was put in a separating funnel. This separation process lasted for 24 hours until two layers were formed. The top layer, which was POle-ME, was taken and then distilled at 70°C to separate the methanol. The POle-ME product with the highest yield was selected for further processing, with molar ratios of methanol to oil of 1:8 and 1:10.

2.4. POle-ME Characterization

The acid number was determined by titration with potassium hydroxide (KOH) following AOAC Official Method 940.28. The iodine number was measured using the Wijs method in accordance with AOAC Official Method 920.158. Fatty acid composition was analyzed by gas chromatography (GC) after methylation of the fatty acids into fatty acid methyl esters (FAMEs), based on AOAC Official Method 996.06. All measurements were conducted in triplicate at the Food and Nutrition Laboratory, Universitas Gadjah Mada, and the results are reported as mean values. Viscosity measurements were conducted using a rotary viscometer, and functional group analysis was performed using Fourier Transform Infrared (FTIR) spectroscopy at the Instrumentation and Polymer Laboratory, Politeknik ATK Yogyakarta.

2.5. Statistical Analysis

Statistical analysis was performed using SPSS software through ANOVA (analysis of variance) to evaluate the effect of each factor, followed by Duncan’s Multiple Range Test (DMRT) for post hoc comparison. A confidence level of 95% ($\alpha = 0.05$) was applied.

3. Results and Discussion

3.1. Iodine and Acid Numbers of Palm Olein

The iodine number is used to measure an oil or fat's saturation level, with higher values indicating higher levels of unsaturation. A high iodine number indicates the presence of more double bonds in the compound [22]. In producing quality epoxy oil plasticizers, POle-ME raw materials that have high levels of unsaturation or high iodine numbers are needed. Table 1 shows the iodine numbers of several palm olein products.

Table 1. Iodine and acid numbers of palm olein products

Characteristics	Palm Olein A	Palm Olein B	Palm Olein C
Iodine number	59.785 ± 0.615^{a}	58.215 ± 0.165^{b}	60.030 ± 0.460^{a}
Acid number	1.280 ± 0.010^{b}	1.485 ± 0.015^{a}	1.455 ± 0.015^{a}

Source: Data processing results; different statistical notations (a, b) indicate significant differences.

Table 1 shows that palm olein A and palm olein C had relatively similar iodine numbers, whereas palm olein B had a lower iodine number than palm olein A and palm olein C. Based on the acid number, palm olein A was chosen as the raw material for POle-ME in this study. The acid numbers of the palm olein products are shown in Table 1. The acid number is an indicator of the amount of free fatty acids present in a fat or oil. A high acid number indicates a high amount of free fatty acids [23]. Free fatty acids in oil can react with base catalysts in the transesterification process, resulting in soap formation. As a result, the catalyst is lost during the POle-ME formation process, which in turn reduces the amount of yield [24]. Palm olein B had the highest acid number, and palm olein A had a lower acid number than palm olein C. Since palm olein should have a high iodine number and a low acid number to be used as a raw material for POle-ME, palm olein A was chosen as the raw material for POle-ME in this study.

3.2. Fatty Acid Composition of Palm Olein

Analysis revealed that palm olein A contained nine types of fatty acids, as illustrated in Fig. 1. The figure shows that there were several prominent peaks that corresponded to different fatty acid methyl esters. The major fatty acids detected were palmitic acid (C16:0) at a retention time of 7.992 min and oleic acid (C18:1) at 11.794 min, indicating that these were the dominant components in palm olein A. Linoleic acid (C18:2), an essential polyunsaturated fatty acid, appeared at 12.770 min, contributing to the nutritional value of palm olein. In addition to these major components, smaller peaks were observed for lauric acid (C12:0) at 4.285 min, myristic acid (C14:0) at 5.380 min, palmitoleic acid (C16:1) at 8.338 min, stearic acid (C18:0) at 11.024 min, linolenic acid (C18:3) at 14.338 min, and arachidic acid (C20:0) at 16.019 min. Details of the composition of palm olein A are provided in Table 2, with similar results with the chromatogram shown in Fig. 1. The three most abundant fatty acids in palm olein A were oleic acid at 47.28%, palmitic acid at 35.01%, and linoleic acid at 12.10%. This is consistent with previous research [25], which reported palmitic acid, oleic acid, and linoleic acid concentrations in the ranges of 39.30–47.50%, 36.00–44.00%, and 9.00–12.00%, respectively. Similar findings were seen in other research indicating that palm olein from Indonesia mostly comprises oleic acid, linoleic acid, and palmitic acid [26,27].

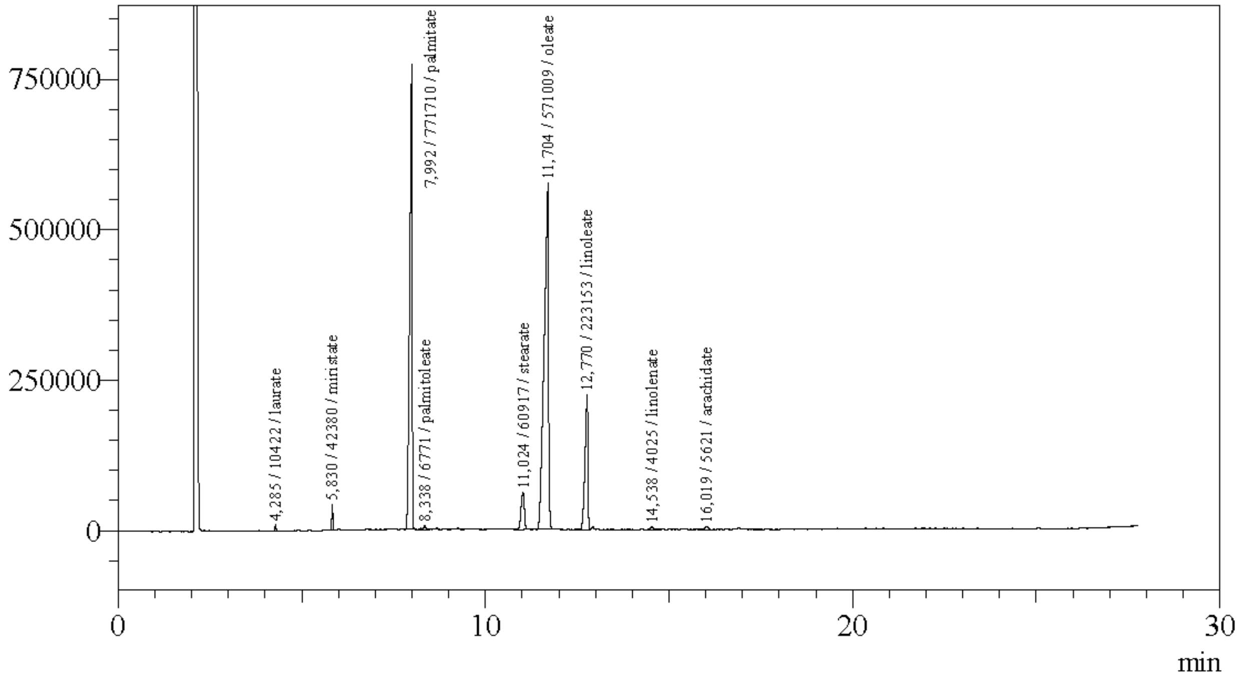

Fig. 1. Chromatogram of fatty acids in palm olein A

Because of its high unsaturated fatty acid content (Table 2), which indicates the presence of double bonds in the hydrocarbon chains of the unsaturated fatty acids, palm olein A was considered as a good raw material for making POle-ME. These double bonds will facilitate the formation of oxirane rings in the future production of epoxy oil. This result is consistent with previous research, which reported that double bonds in unsaturated fatty acids can be effectively converted into epoxide groups, resulting in products suitable for industrial applications, such as plasticizers and epoxy resins [28].

Table 2. The composition of fatty acids of palm olein A

Fatty Acids			Composition (%)
Group	Name	Symbol	
Saturated fatty acids	Lauric Acid	C12:0	0.21 ± 0.03
	Myristic Acid	C14:0	0.83 ± 0.04
	Palmitic Acid	C16:0	35.01 ± 0.46
	Arachidic Acid	C20:0	0.33 ± 0.04
	Stearic Acid	C18:0	3.83 ± 0.05
Monounsaturated fatty acids	Palmitoleic Acid	C16:1	0.25 ± 0.03
	Oleic Acid (Omega 9)	C18:1	47.28 ± 0.55
Polyunsaturated fatty acids	Linoleic Acid (Omega 6)	C18:2	12.10 ± 0.03
	Linolenic Acid (Omega 3)	C18:3	0.17 ± 0.01

3.3. Transesterification Yield

Transesterification of palm olein A was carried out using two types of catalysts—KOH and NaOH—with ratios of yields as shown in Table 3. According to the data presented in that table, transesterification using a KOH catalyst with a molar ratio of methanol to oil of 1:6 produced the highest POle-ME yield, reaching 94.99%. As the KOH catalyst produced a higher yield than its NaOH counterpart, further experiments with ratios of 1:8 and 1:10 were carried out using the KOH catalyst. According to Table 3, a molar ratio of 1:6 was set as the process condition for the future production of POle-ME (raw material for epoxy oil production). The molar ratio of methanol to oil of 1:6 was also used in previous studies [29–32].

Table 3. Transesterification yields using KOH and NaOH catalysts

Molar ratios of methanol to oil	Yield (%)	
	KOH	NaOH
1:3	90.41	80.33
1:6	94.99	94.91
1:8	92.16	-
1:10	93.16	-

The finding showing that the use of the KOH catalyst, with a molar ratio of methanol to oil of 1:6, in transesterification produced a higher yield than the use of the NaOH catalyst is in line with previous research [33]. The KOH catalyst is known to produce less glycerol (residual transesterification) than the NaOH catalyst, as NaOH causes the saponification reaction to run faster and form a gel on the bottom layer.

3.4. POle-ME Characteristics

Palm olein A was transesterified with methanol with a molar ratio of 1:6 in the presence of a KOH catalyst, resulting in POle-ME with properties consistent with those noted in Table 4. The POle-ME produced had an iodine number of 60.42, similar (slightly greater) to the palm olein A feedstock value of 59.785 (Table 1). This indicates that the transesterification process did not significantly affect the unsaturation or the number of double bonds in the hydrocarbon chain.

Table 4. POle-ME characteristics of palm olein A

Characteristics	Value
Iodine number	60.42 ± 0.16
Acid number	1.395 ± 0.015
Viscosity (mPa·s)	7.16 ± 0.29

Table 4 presents the acid number of the synthesized POle-ME, 1.395, which was slightly higher than that of the palm olein A feedstock (1.280) (Table 1). This increase in the acid number is expected to be due to the oil's hydrolysis reaction. Water and the heat of the transesterification process (60°C) accelerate this reaction, and the longer it lasts, the more free fatty acid content is formed [22,34].

Table 4 further shows the viscosity value of the synthesized POle-ME, 7.16 ± 0.29 mPa·s, which was lower than that of the pre-transesterification palm olein A feedstock (57.3 ± 0.346 mPa·s), in line with previous findings [35]. Acid and alcohol molecules react to form ester molecules, which tend to have shorter and straighter carbon chains than the original acid and alcohol. As a result, oils containing esters tend to flow more easily and have lower viscosity. Fig. 2 and Table 5 show that the fatty acid composition of POle-ME mostly consists of methyl oleate (oleic acid) at 49.13%. At 20°C, methyl oleate has a viscosity of 6.83 mPa·s [36], which is almost the same as the viscosity of POle-ME produced in this study. POle-ME, which has a low viscosity (dilute), is expected to produce epoxy oil (plasticizer) with a low viscosity as well, allowing for good performance when used in synthetic leather compounding in the future.

As shown in Fig. 2, which presents the GC chromatogram of fatty acids in POle-ME, the produced POle-ME contained eight types of fatty acids. Several prominent peaks can be observed, representing various fatty acid methyl esters formed after the transesterification of palm olein. The most intense peak corresponded to palmitic acid (C16:0) at a retention time of 7.984 min, indicating that palmitic acid remained the dominant saturated fatty acid component in POle-ME. The other major components were oleic acid (C18:1) and linoleic acid (C18:2), appearing at retention times of 11.059 min and 12.722 min, respectively. These unsaturated fatty acids are important for maintaining the desired fluidity and reactivity of the ester product. Additionally, smaller peaks indicate the presence of lauric acid (C12:0) at 4.279 min, myristic acid (C14:0) at 5.281 min, palmitoleic acid (C16:1) at 6.322 min, stearic acid (C18:0) at 11.011 min, and arachidic acid (C20:0) at 15.978 min.

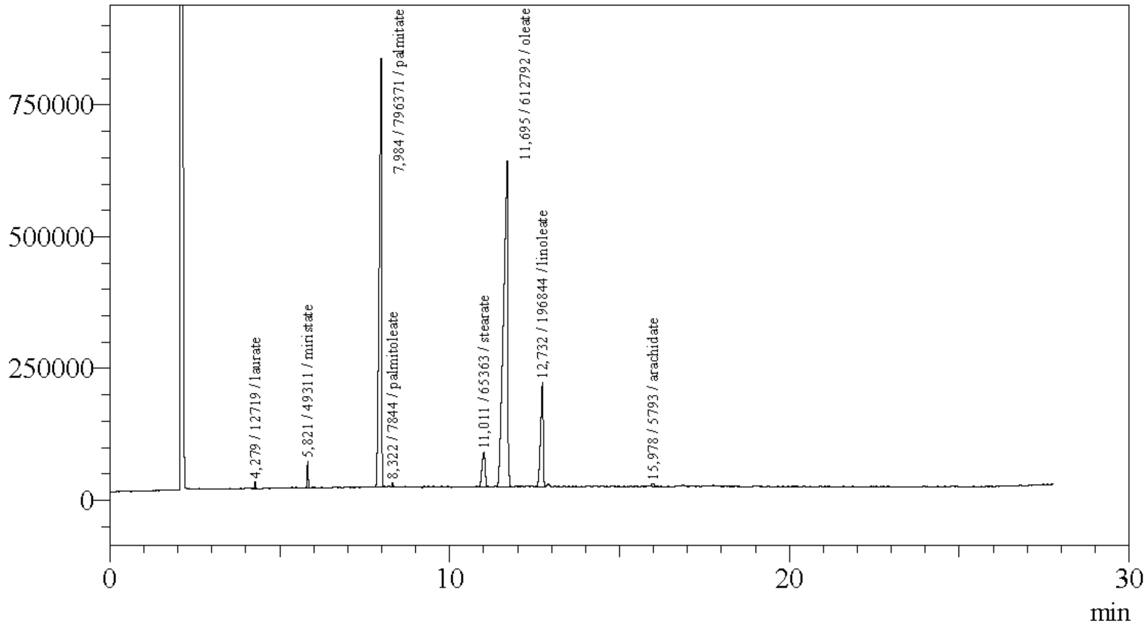

Fig. 2. Chromatogram of fatty acids in POle-ME

Details of the composition of POle-ME are provided in Table 5, similar to the chromatogram depicted in Fig. 2. The three most abundant fatty acids contained in POle-ME were oleic acid (49.13%), palmitic acid (35.82%), and linoleic acid (9.58%). Before transesterification, the oleic acid content of POle-ME was slightly higher than that of palm olein A (47.28%), while the linoleic acid content was lower than that of palm olein A (12.10%) (Table 1). These findings are consistent with previous studies reporting that palm olein methyl esters typically contain high levels of oleic and palmitic acids, with moderate amounts of linoleic acid [37].

Table 5. Composition of fatty acids in Pole-ME

Fatty Acids			Composition (%)
Group	Name	Symbol	
Saturated fatty acids	Lauric Acid	C12:0	0.25 ± 0.04
	Myristic Acid	C14:0	1.01 ± 0.08
	Palmitic Acid	C16:0	35.82 ± 0.18
	Arachidic Acid	C20:0	0.29 ± 0.05
	Stearic Acid	C18:0	3.76 ± 0.18
Monounsaturated fatty acids	Palmitoleic Acid	C16:1	0.16 ± 0.04
	Oleic Acid (Omega 9)	C18:1	49.13 ± 0.34
Polyunsaturated fatty acids	Linoleic Acid (Omega 6)	C18:2	9.58 ± 0.08
	Linolenic Acid (Omega 3)	C18:3	Not detected

3.5. Functional Groups of Palm Olein A and POle-ME

The FTIR spectra's characteristic peaks were classified into four regions. The functional groups in the first region, with peaks ranging from 4000 cm^{-1} to 2500 cm^{-1}, represent O–H, C–H, and N–H single bonds. The peaks from 2500 cm^{-1} to 2000 cm^{-1} represent the second region, showing triple bonds, while the peaks from 2000 cm^{-1} to 1500 cm^{-1} represent the third region, showing C=O, C=N, and C=C double bonds. The functional groups in the fourth region, with peaks from 1500 cm^{-1} to 400 cm^{-1}, represent single bonds [38]. Fig. 3 shows that the IR spectra of palm olein A and POle-ME do not contain peaks in the second region. The identified functional groups in palm olein A and POle-ME are tabulated in Table 6.

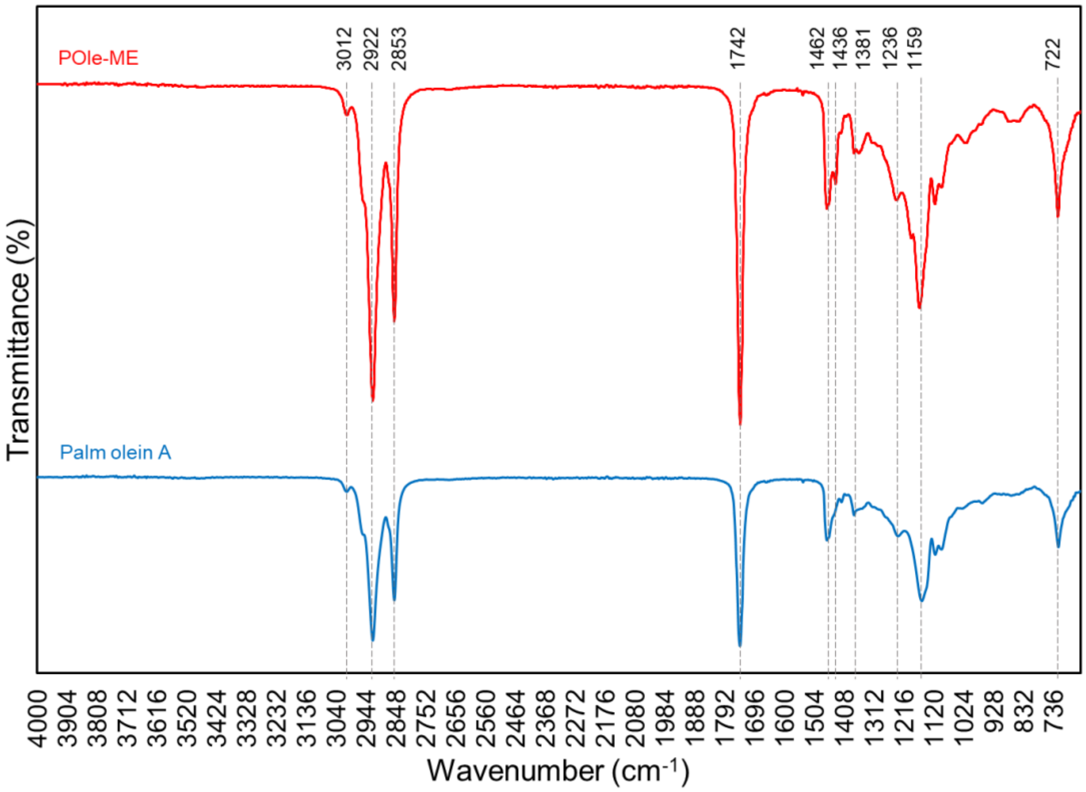

Fig. 3. FTIR spectra of palm olein A and POle-ME

Table 6. Functional group identification parameters of palm olein A and POle-ME

Wavenumbers	Functional groups	References
3012	C–H axial deformation	[35]
2922	Asymmetric stretching of alkane =C–H	[34]
2853	Asymmetric stretching of methylene =C–H	[34]
1742	C=O ester bond stretching	[36]
1462	CH_2 cutout	[35]
1436	CH_3 asymmetric deformation	[35]
1381	Symmetric bending of H–C–H	[35]
1236	Asymmetric stretching of C–O–C	[35]
1159	Stretching of C–O	[34]
722	$(CH_2)_n$ rocking and CH vibration	[35]

Fig. 3 and Table 6 show that the FTIR spectra of palm olein A and POle-ME are similar at most of the peaks (3012 cm^{-1}, 2922 cm^{-1}, 2853 cm^{-1}, 1742 cm^{-1}, 1462 cm^{-1}, 1381 cm^{-1}, 1236 cm^{-1}, 1159 cm^{-1}, and 722 cm^{-1}). This suggests that palm olein A and POle-ME were made up of similar functional groups. The band at 3012 cm^{-1} was caused by the axial deformation of C–H in the olefinic double bond. The bands at 2922 cm^{-1} and 2853 cm^{-1} were caused by the asymmetric stretching vibrations of aliphatic C–H in the CH_2 and terminal CH_3 groups. The bands between 1400 and 1200 cm^{-1} were mostly made up of bending vibrations of aliphatic CH_2 and CH_3 groups. H–C–H bending at 1381 cm^{-1} and CH_2 scission at 1462 cm^{-1} were examples of these. The band at 1236 cm^{-1} represents C–O–C asymmetric stretching vibrations, and the band at 1159 cm^{-1} expresses C–O stretching vibrations. Some cis-disubstituted olefins have vibrations that are rocking $(CH_2)_n$ and vibrations that are out of plane (CH wag). This is shown by the band at 722 cm^{-1}. The strong single peak at 1742 cm^{-1} represents C=O stretching vibrations.

It is important to acknowledge that the distinctive band at 1436 cm^{-1}, which expresses the asymmetric deformation of the CH_3 group, was detected only in POle-ME but not in palm olein A. This 1436 cm^{-1} peak can be used to validate the presence of methyl esters, as stated in a previous study [39].

4. Conclusion

This study demonstrated the successful transesterification of palm olein using both NaOH and KOH as base catalysts. The highest yield of methyl esters (94.99%) was achieved using KOH at a molar ratio of 1:6, indicating superior catalytic efficiency compared to NaOH. The resulting POle-ME showed a functional group of methyl esters at 1436 cm^{-1}. POle-ME's fatty acid composition mostly consisted oleic unsaturated fatty acid (C18:1) (49.13%). Additionally, POle-ME exhibited characteristics such as an iodine number of 60.42, an acid number of 1.395, and a viscosity of 7.16 mPa·s. The physicochemical properties of POle-ME suggest its potential as a plasticizer. However, further studies on its compatibility with polymer matrices and its performance in real applications are needed.

Abbreviations

CPO	Crude Palm Oil
CPKO	Crude Palm Kernel Oil
EP-POLe-ME	Epoxidized Palm Olein-Methyl Ester
ESBO	Epoxidized Soybean Oil
KOH	Potassium Hydroxide
NaOH	Sodium Hydroxide
POle-ME	Palm Olein-Methyl Ester
PVC	Polyvinyl Chloride

Data availability statement

Data will be made available on request.

CRediT authorship contribution statement

Ratri Retno Utami: Data curation, Conceptualization, Investigation, Formal analysis, Methodology, Project administration, Resources, Supervision, Validation, Writing – review and editing. **Andri Saputra:** Data curation, Investigation, Methodology, Resources, Validation, Visualization, Writing – original draft. **Pani Satwikanitya:** Data curation, Investigation, Methodology, Project administration. **Muh. Wahyu Sya'bani:** Conceptualization, Data curation, Investigation, Methodology, Supervision, Validation, Writing – review and editing. **Warmiati:** Data curation, Formal analysis, Investigation. **Luthfi Auliya Indahwati:** Data curation. **Danuraja Ilmannafia:** Data curation.

Declaration of Competing Interest

The authors assert that they own no identifiable conflicting financial interests or personal ties that may have seemingly influenced the work presented in this study.

Acknowledgement

The writers express the gratitude to BPDPKS. for funding this research based on SK Direktur Utama BPDPKS No. KEP-295/DPKS/2023.

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