

# Synthesis of palm oil based polymeric ester through cationic addition polymerisation method

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## Abstract

In this study, the synthesis of palm oil-based polymeric ester for application as a polymeric surfactant was carried out by a cationic addition polymerisation method through two steps. The initial step is a synthesis of fatty acid methyl esters oleate (FAMEO) through esterification reaction between oleic acid and methanol. The optimum conditions of the esterification reaction were carried out at a temperature of 70–80°C for 4 hours with the addition of 1wt% sulfuric acid as a catalyst. The molar ratio between oleic acid and methanol was 1:3. FAMEO was analysed using GCMS to determine the methyl ester content. The second step is the polymerisation of FAMEO. The polymerisation reaction of FAMEO was carried out at 120, 140, and 160°C with 1wt%, 3wt% and 5wt% of boron trifluoride dihydrate as a catalyst and an initiator of polymerisation reaction for 4 to 24 hours of reaction. The reaction conversion of the product was 66%. The polymeric ester was analysed H-NMR. Meanwhile, the molecular weight of that product was 1714 g/mol which analysed using GPC and the PDI was 1.12346 or equal to 1.12. It means that the polymerisation technique was controlled or living polymerisation, which indicates that the distribution type of this product was narrow monodisperse.

**Keywords:** Cationic addition polymerisation, methyl ester, palm oil based, polymeric ester

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## INTRODUCTION

Most oil field in Indonesia is classified as a mature oil field, that marked by a decline in oil production and an increase in water production. The technology that has been developed to increase oil production is a draining technique which is performed by injecting water into the bowels of the earth or oil field. However, the average rate of drainage at the primary and secondary stage with water injection in the old field is still low, only about 35%. Dewatering techniques applied by injecting water at several wells can lead to a continuous increase in water production resulting in a water breakthrough. Some technologies continue to be developed to replace the dewatering enhanced oil recovery (EOR) technique. One of the EOR methods currently under development is polymer injection [1].

Polymers that often used in EOR applications include hydrolysed polyacrylamide (HPAM), sulfonated polyacrylamide, and biopolymers such as polysaccharides and their derivatives such as xanthan gum, chitosan, cellulose, sodium carboxymethyl cellulose (Na-CMC), and hydroxyl ethyl cellulose (HEC). The mostly used surfactants in research petroleum-based polymeric surfactants, whereas palm oil-based polymeric surfactants are still rarely used. In the previous research, palm oil-based anionic polymeric surfactant was synthesised from oleic and polyethylene glycol through esterification and sulfonation reaction [2]. Meanwhile, Keshak [3] conducted a synthesis and characterisation of a new polymeric surfactant for chemical enhanced oil recovery. Palm oil is one of the highly potential vegetable oils for the substitution of products derived from petroleum such as surfactants [4].

Moreover, oleic acid from palm oil has potential as a precursor of polymeric surfactants if it is reacted with the appropriate initiator.

Related to the potential and opportunities of extensive palm oil utilisation, the research activity of palm oil-based polymeric ester is considered very important in terms of diversification of palm oil products, especially in supporting the development of industries in Indonesia. Recent year, research about synthesis of methyl ester sulphonate surfactant from palm oil methyl ester was conducted by Tulathammakit et al. [5]. Whereas Prakoso et al. [6] reported the application of green surfactant from oil palm empty fruit bunches' lignin for EOR.

This research is focusing on polymeric ester through cationic addition polymerisation with boron trifluoride dihydrate as an initiator. The purpose of this research is to obtain a polymeric surfactant product, following the example of the previous research [7] on the synthesis of palm oil and polyethylene glycol-based polymeric surfactants and its aqueous stability study for application in EOR. The synthesis was carried out by esterification and sulfonation reaction. This polymeric ester has potential to be applied in the petroleum industry for EOR. In addition, the analysis of the synthesised polymeric ester was conducted by using Nuclear Magnetic Resonance (NMR) and Gel Permeation Chromatography (GPC).

## METHODS

### Materials and tools

The materials used in this study were oleic acid, BF<sub>3</sub>·2H<sub>2</sub>O (Sigma Aldrich), methanol (Merck), polyethylene glycol (Brataco), ethanol (Merck), potassium hydroxide (Merck), phenolphthalein (Merck), hydrochloric acid (Merck), carbon tetrachloride (Merck), iodine chloride (Merck), acetic acid (Merck), sodium thiosulfate (Merck), potassium iodide (Merck), potassium iodate (Merck), starch (Merck),

methyl red (Merck), sodium tetraborate (Merck), and oxalic acid (Merck). Whereas the equipment used including hotplate, dean-stark apparatus, three-neck flask, beaker glass, condenser, thermometer, stative, clamp, volumetric gauge, magnetic stirrer, separating funnel, and pH indicator.

### Esterification of oleic acid

Synthesis of fatty acid methyl ester oleate (FAMEO) was carried out by esterification reaction. Oleic acid and methanol with moles ratio of 1:3 moles were reacted in a three-neck flask at the temperature of 70–80°C for 4 hours with 1wt% sulfuric acid as catalyst. The product of FAMEO was characterised using titration methods such as AV, EV, IV, and SV analysis. Meanwhile, the FAMEO composition was analysed using GCMS.

### Polymerisation of FAMEO

The polymerisation reaction of FAMEO was carried out at 120, 140 and 160°C with 1wt%, 3wt% and 5wt% of  $\text{BF}_3 \cdot 2\text{H}_2\text{O}$  as a catalyst for 4 to 24 hours of reaction. The polymerisation reaction of FAMEO was carried out by reacting FAMEO itself with an initiator through cationic addition polymerisation, the steps were the initiation of  $\text{BF}_3 \cdot 2\text{H}_2\text{O}$ , propagation of radical FAMEO and termination of polymeric ester. The final product of polymeric ester was analysed using the titration method, NMR, and GPC.

## RESULTS AND DISCUSSION

### Synthesis of FAMEO

Synthesis of FAMEO was carried out by Fisher esterification. The esterification reaction is done by reacting methanol and oleic acid at 70–80°C for 4 hours with the help of sulfuric acid in the atmosphere. The ratio between oleic acid and methanol is 1:0.35 moles. The extra methanol aimed to shift the chemical equilibrium towards the product, in this case, FAME. Meanwhile, the used of dean-stark apparatus is to reduce by-products reaction, in this case, is water then the conversion of FAMEO can be high. Gas Chromatography-Mass Spectroscopy (GCMS) analysis results of FAMEO shown in Figure 1.

GCMS Analysis of FAMEO

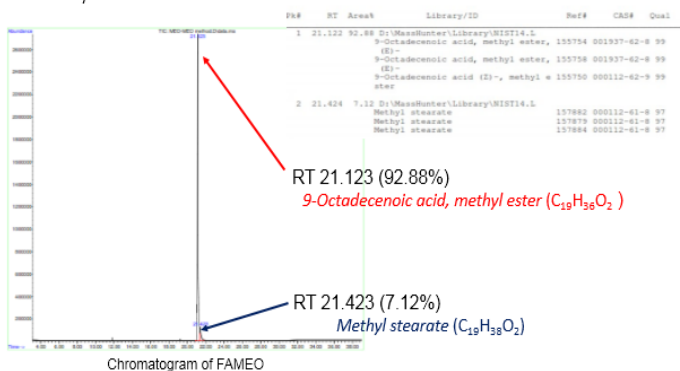


Figure 1. Chromatogram of FAMEO

From GC-MS results of FAMEO in Figure 1, there are two peaks with a retention time (RT) 21.123 with area% was 92.88% indicated as 9-Octadecenoic acid, methyl ester, and RT 21.423 with area% was 7.21% indicated as methyl stearate. Meanwhile, the characterization of FAMEO product from esterification reaction between oleic acid and methanol shown in Table 1.

Table 1. Characterisation of FAMEO.

Entry	Parameter (mg KOH/g)	Oleic Acid	FAMEO
1.	Acid Value (AV)	180.04	26.77
2.	Ester Value (EV)	0	161.28
3.	Iodine Value (IV)	85.59	77.63

Table 1 shows the characteristics of FAMEO, which was analysed using the titration method. It can be seen that acid value (AV) of esterification product decreased from 180.04 mg KOH/g of oleic acid to 26.77 mg KOH/g of FAMEO. It can be interpreted that oleic acid has been converted to FAMEO through esterification reaction. Therefore, the ester value was increased from 0 mg KOH/g of oleic acid onto 161.28 mg KOH/g of FAMEO. Moreover, the conversion of the esterification reaction was 85%, below is the formula:

$$\text{Conversion}(\%) = \frac{AV_i - AV_0}{AV_i} \times 100 = \frac{180.04 - 26.77}{180.04} \times 100 = 85\%$$

### Polymerisation of FAMEO

The polymerisation reaction of FAMEO to form polymeric ester is a reaction between FAMEO and complex catalyst, in this case, boron trifluoride dihydrate. The reaction that occurred between FAMEO itself produced polymeric ester. The polymeric ester is produced by cationic polymerisation which occurs cause the addition reaction of the double bond of the carbon chain (C=C). Mechanism reaction of polymerisation of FAMEO to form a polymeric ester with boron trifluoride monohydrate as a catalyst is shown in Figure 2. It was carried out through 3 steps namely initiation of boron trifluoride, propagation of radical FAMEO, and termination of polymeric ester. Its mechanism is explained as follows:

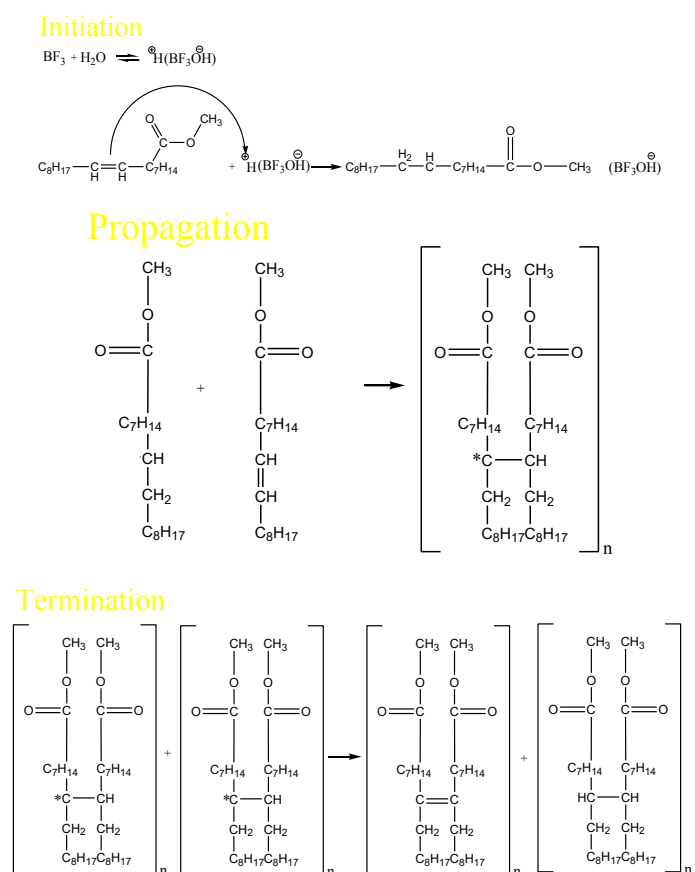


Figure 2. Mechanism Reaction of Polymeric Ester.

The mechanism in Figure 2 shows 3 steps of polymeric ester. Firstly, the initiation step refers to the forming of a radical methyl ester oleate because of protonation reaction of boron. This step is also known as cationic addition polymerisation. Next, the second step is the propagation of radical methyl ester. In this step, radical methyl ester is reacted with methyl ester to form dimer methyl ester. This process is also called ester dimerisation. Finally, the last step was propagation. In this step, the dimer methyl ester is reacted with itself to form a polymeric ester. The number of polymerisation chain of polymeric ester is controlled by condition reaction. Although this approach can predict it, the other result can be shown in iodine value and GPC analysis.

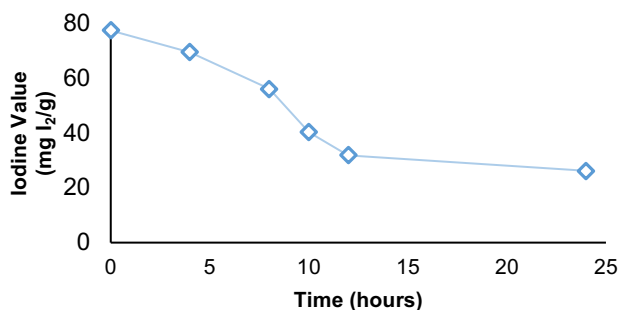
### Iodine value of polymeric ester

The iodine value of polymeric ester was carried out by the titration method. It can indicate the unsaturation fats on the product and also the average number of double bonds of the carbon chain. The results are shown in Figure 3 and Table 2.

**Table 2.** Iodine Value of Polymeric Ester on variation process condition.

BF <sub>3</sub> .2H <sub>2</sub> O	T (°C)	Time (hours)					
		0	4	8	10	12	24
1%	120	77.63	76.85	75.45	73.25	70.57	68.25
	140	77.63	76.52	75.25	72.56	68.23	65.75
	160	77.63	76.50	75.12	72.42	68.08	65.69
3%	120	77.63	70.12	63.25	60.55	49.24	35.22
	140	77.63	69.65	56.24	40.46	31.93	<b>26.29</b>
	160	77.63	69.22	52.25	40.44	31.72	26.30
5%	120	77.63	69.52	58.25	49.12	50.25	48.56
	140	77.63	69.45	57.55	49.55	50.99	49.00
	160	77.63	69.45	58.12	49.43	50.15	49.00

Meanwhile, Table 2 shows the iodine value of polymeric ester on the variation process condition at 120, 140, and 160°C with various concentration of BF<sub>3</sub>.2H<sub>2</sub>O catalyst. It was 1wt%, 3wt%, and 5wt%. The results show that the addition reaction time made the iodine value go down simultaneously from the initial time to 24 hours. Consequently, the lower iodine value was 26.29 mg I<sub>2</sub>/g. It happened at temperature 140°C at 24 hours of reaction with percentage of catalyst was 3wt%. If the iodine value decreases, it means the number of carbon chains of the double bond also decreases [8].



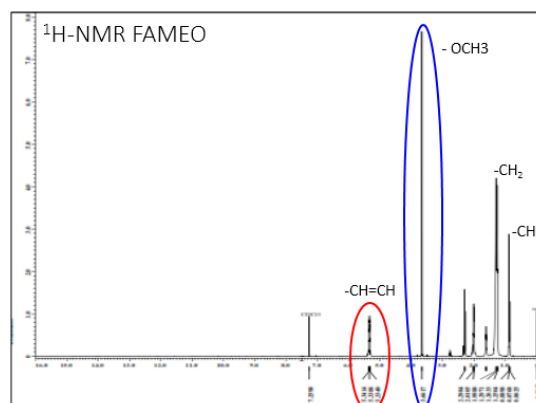
**Figure 3.** Influence of reaction time toward iodine value at 140°C using 3wt% BF<sub>3</sub>.2H<sub>2</sub>O.

Figure 3 shows the influence of reaction time to the polymeric ester product at 140°C using 3wt% BF<sub>3</sub>.2H<sub>2</sub>O. That was the optimum condition of polymeric ester in this study. It can be seen that iodine value steadily fell by an increase of reaction time. The initial iodine value of raw material was 77.63 mg I<sub>2</sub>/g then the final iodine value of the product after 24 hours of the reaction was 26.29 mg I<sub>2</sub>/g using 3wt% of catalyst. Polymeric reaction conversion calculation method based on changes in the iodine value (IV), then the reaction conversion based on 66% which has been explained as follows:

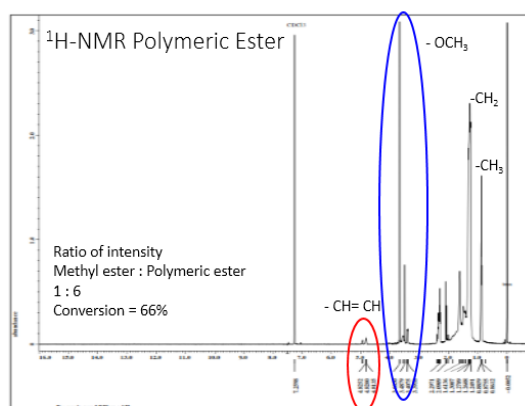
$$\text{Conversion}(\%) = \frac{IV_i - IV_0}{IV_i} \times 100 = \frac{77.63 - 26.29}{77.63} \times 100 = 66\%$$

### NMR Identification of polymeric ester and molecular weight of polymeric ester

Identification of polymeric ester was carried out using NMR. The high resolution of NMR used to provide information about the structure of materials. NMR result of FAMEO and polymeric ester with optimum condition shown in Figures 4 and 5.



**Figure 4.** <sup>1</sup>H-NMR Spectrum of FAMEO.



**Figure 5.** <sup>1</sup>H-NMR Spectrum of polymeric ester.

Figures 4 and 5 show that double bond carbon (-CH=CH-) chain occurs at chemical shift (δ) 4.8200 and 4.9406 ppm. It has a low peak intensity when compared to the methoxy group (-OCH<sub>3</sub>) which occurs at δ 3.6630 ppm. With comparing both of two spectrums, it is shown that the intensity of double bond carbon (-CH=CH-) chain in polymeric ester was less than the intensity of double bond carbon (-CH=CH-) chain in FAMEO. It indicated that polymerisation of the ester has occurred. According to that results, the conversion reaction of a polymeric ester of FAMEO was 66%.

### Gel permeation chromatography analysis of polymeric ester

Gel Permeation Chromatography (GPC) analysis used to measure the molecular weight of polymeric ester. Moreover, it also can indicate the type of polymerisation technique. The parameter and condition of the sample were determined in 0.04 gram of polymeric ester solved in tetrahydrofuran. Then, it was analysed in 1mL/min flow rate at temperature 30°C. The results are shown in Table 3.

**Table 3.** Molecular Weight of Polymeric ester using GPC Analysis.

Entry	Result		
	Mw	Mn	PDI (Mw/Mn)
1	1676	1504	1.11441
2	1738	1545	1.12506
3	1729	1529	1.13091
<b>Averages</b>	<b>1714</b>	<b>1526</b>	<b>1.12346</b>

Table 3 shows that the molecular weight of polymeric ester was 1714 gram/mol. Moreover, the ratio of Mw to Mn is the polydispersity index (PDI), which is a measure of the width of the molar mass distribution. The PDI of polymeric ester was 1.12346 or equal to 1.12. It means that the polymerisation technique on this study is classified in

controlled or living polymerisation. Cationic addition polymerisation also a part of living polymerisation. Its polymerisation occurred because a cationic initiator transfers charge to a monomer which then becomes reactive. In this case, the monomer was methyl ester oleate. Then, it formed into radical methyl ester oleate (see Figure 2). PDI value of 1.12 also means that the distribution type of this product is narrow monodisperse. It is a characteristic of living polymerisation.

## CONCLUSION

The optimum conditions of the esterification reaction were carried out at a temperature of 70–80°C for 4 hours with the addition of 1wt% sulfuric acid as a catalyst. The molar ratio between oleic acid and methanol was 1:3. Fatty Acid Methyl Ester Oleate (FAMEO) was analysed using GCMS to determine the methyl ester content. The second step is polymerisation of FAMEO. The polymerisation reaction of FAMEO was carried out at 120, 140 and 160°C with 1wt%, 3wt% and 5wt% of boron trifluoride dihydrate as a catalyst for 4 to 24 hours of reaction. Polymeric ester was carried out by reacting FAMEO itself. The reaction conversion of the product was 66%. The polymeric ester was analysed using H-NMR. Meanwhile, the molecular weight of that product was 1714 g/mol which analysed using GPC. And the PDI was 1.12346 or equal to 1.12. It means that the polymerisation technique was categorised as a controlled or living polymerisation. Then, it also means that the distribution type of this product was narrow monodisperse.

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