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# Synthesis of Polyethylene Glycol Esters from Oleic, Stearic, and Palmitic Acids as a Pour Point Depressant (PPD)

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**ABSTRACT.** Polyethylene glycol (PEG) ester is a non ionic surfactant compound that could use a pour point depressant (PPD) for crude oil. Synthesis of PEG-ester with reflux and mono wave-50 methods through esterification fatty acid such as oleic acid, stearic acid, and palmitic acid with adding p-toluene sulfonic acid (*p-TSA*) as a catalyst. The product of esterification could be a mixture of monoester and diester. Synthesized PEG ester by reflux method resulted in higher yield than by mono wave-50 method. IR spectra analysis of PEG400-oleate, PEG400-stearate, and PEG400-palmitate show the presence of an absorption band at a wavenumber of around 1100 $cm^{-1}$ that indicates the stretching vibration of the C-O ester. (LC-MS/MS) analysis that shows the molecular weight of PEG400-oleate was 845.6154 g/mol and, PEG400-stearate was 785.5952 g/mol. Mean, while PEG400-palmitate produced three ester compounds with different molecular weights: 741.5669 g/mol, 685.5057 g/mol, and 734.5208 g/mol. The pour point measurement results show that the PEG-fatty acid product in the range of 0.1% to 1% has not been able to reduce the pour point of the crude oil sample.

**Keywords:** Esterification, FTIR, LC-MS/MS, Surfactant

## INTRODUCTION

The depleting national and global oil reserves have prompted the oil industry to explore heavier crude oil fractions. However, the deposition of paraffin wax (wax deposition) from crude oil that occurs in the transportation and distribution pipelines of crude oil is a challenge in the petroleum industry. Precipitation of paraffin wax causes crude oil to flow more difficult so higher pressure is required to transport crude oil (Ganeeva et al 2016). Paraffin wax is a saturated long-chain hydrocarbon compound consisting of at least 15 or more carbon atoms per molecule. (Ganeeva et al 2016; Yang et al 2013). At low temperatures, paraffin wax in crude oil tends to separate from crude oil and crystallize as interlocking networks which then form smooth sheets (Chen et al 2010). Blockage of the flow pipe by wax deposits can damage the oil production engine. In addition, wax deposits can be a problem for fuel consumers in colder climates due to blockages in the fuel lines and filters in the engine. The addition of chemical additives such as pour point suppressants or often called Pour point depressant (PPD) can inhibit the formation of paraffin wax crystals (Zhou et al 2015). It can also reduce the plug point of cold filter or CFPP diesel fuel, which has been shown to be an effective and cost-efficient way to increase oil flow. (Han et al 2009). The lowest temperature at which the oil will flow freely under certain test conditions is called the pour point (Al-Sabagh et al 2013).

Non ionic surfactant as PPD have become one of the hot topics nowadays. Surface-active compounds, often known as surfactant, are molecules that have a non-polar hydrophobic component connected to a polar hydrophilic part, usually consisting of 8-18 carbon atoms. (Tadros 2005; Kronberg et al 2014). The carbon chain in the tail could be linear, branched, or cyclic. At reservoir temperatures, these compounds work well and create emulsions that are possible to break down in refineries (Kelland 2009; Kao et al 2019). PEG ester is a non-ionic surfactant in the form of ethoxylated fatty acids. The carbon chain of the fatty acid is a non-polar group, whereas some monomers of polyethylene glycol as a polar group. Several researchers have synthesized PEG-esters including: El-Shamy et al. (2014) reacted oleic acid and PEG in the presence of a *p*-TSA catalyst to produce $C_{18}E_{68}$ and $C_{18}E_{136}$ compounds. The addition of these compounds in fuel oil can reduce the pour point by 6 °C and 12 °C. Khidr et al. (2015) made a series of ethoxylated non-ionic surfactant, $C_{14}E_5$, $C_{16}E_5$, and $C_{16}E_7$ resulting in a decrease in the pour point of fuel oil at 2000 ppm additive concentrations of 9 °C, 12 °C, and 15 °C.

Fatty acids react with PEG to form esters by a condensation reactions. Condensation reaction is the mixing of two molecules to form one molecule, usually followed by the release of a minor molecule such as water ($H_2O$). Besides that, a reaction between fatty acids and PEG is reversible, involves the esterification of fatty acids and the hydrolysis of esters. The product of esterification of fatty acids is usually a mixture of monoester and diester, as shown in **figure 1** (Abdullah et al 2017). This is since the two ─OH groups of polyethylene glycol have the same activity, resulting in esterification at both ends. The relative content of monoester and diester in the mixed product depends on the composition of the reactants. In this case, which is the mole ratio of the fatty acids and PEG. The higher number of moles of fatty acids compared to PEG prefer results in a higher number of dieters in the mixed product. Vice versa, use the excess of PEG usually results from the higher monoester products (Abo-Shosha et al 2009; Hamid et al 2004). The objectives of this work is to synthesize PEG ester through esterification reaction of fatty acids (oleic acid, stearic acid and palmitic acid) with PEG-400 and addition of *p*-TSA as acid catalyst. The method used is reflux and monowave. The reaction by reflux method took place the temperature of 100°C-150°C for 24 hours, while the reaction by monowave the temperature of 200°C for 45 minutes. The product was characterized using FTIR and LC-MS/MS instruments and and applied to crude oil samples by measuring the pour point.

## EXPERIMENTAL SECTION

### Materials

The materials used include PEG-400 (p.a, Merck KGaA), oleic acid (technical), stearic acid (p.a, Merck KGaA), palmitic acid (p.a, Sigma-Aldrich), p-Toluenesulfonic acid (p.a, Merck KGaA), xylene AR (p.a, Loba Chemie), aquadest, saturated NaCl, anhydrous $Na_2SO_4$ (p.a, Merck KGaA), ethyl acetate (technical), chloroform (p.a, Merck KGaA), methanol.

### Instrumentation

The vibration of the ester group was analyzed using Fourier-Transform Infrared Spectroscopy (Perkin Elmer Spectrum Two & Shimadzu). The molecular weight of PEG ester was analyzed using Liquid Chromatography-Mass Spectrometry/Mass Spectrometry (ACQUITY UPLC®H-Class System-Xevo G2-S QTof).

### Synthesis of PEG ester

Polyethylene glycol ester was synthesized by reflux and using a monowave-50 synthesis reactor. The initial compounds used were fatty acids (oleic/stearic/palmitic), PEG-400, p-TSA (2.5% b/v), and xylene as solvent. Reaction occurs in 2:1 equivalent mole between fatty acid and PEG-400. The reflux method performed at a temperature of 100 °C-150 °C for 24 hours. A dean-stark apparatus added to collect and take out the water resulting from the reaction system. After the reaction was complete, the product cooled at room temperature. Synthesized with mono wave-50 was performed by mixing the amount of the initial compound into the reactor tube and a temperature of 200°C for 45 minutes. After the synthesis was completed, the reactor temperature was immediately lowest to 60 °C.

Next, each of the products was extracted by adding ethyl acetate (3x), then extracted again with saturated NaCl (2x), finally with distilled water (7x). The product in the form of solid at room temperature must be recrystallized with warm water while being heated at a temperature of 60°C first. Each extraction, the aqueous phase was removed until only the organic phase remained. Then, the organic phase was added with solid anhydrous $Na_2SO_4$, then stirred and filtered. The filtering results evaporated using a rotary evaporator at a temperature of 40 °C-60 °C and a rotation speed of 60 rpm. Evaporation performed until the solvent was no longer in the synthesized compound (nothing evaporated). Finally, the result of evaporation was collected.

### Characterization of PEG ester

FTIR and LC-MS/MS was used to characterize the PEG ester. The PEG-oleate was analyzed using the ATR method, whereas the PEG-stearate and PEG-palmitate were analyzed using the KBr plate method. The test for the PEG-oleate was scolded at 4000-400 $cm^{-1}$, while for PEG-stearate and PEG-palmitate was scolded at 4500-500 $cm^{-1}$. The test of LC-MS/MS performed on the UPLC system and a column C18 (1,8 μm 2,1x100 mm) HSS with a column temperature of 50°C (room temperature 25°C). A mobile phase used was water added 5 mM ammonium formate as mobile phase A and acetonitrile added with 0.05% formic acid as mobile phase B. **Table 1** shows the flow rate of a mobile phase, which was 0.2 mL/minute and lasted 23 minutes. The injection volume for each sample was 5 μL (filtered through a 0,2 μm syringe filter first). The mass spectrometry system used was electrospray ionization (ESI). The source temperature was set to 100°C. The desolvation temperature was 350°C, with the flow rate of desolvation gas being 793 L/hour. The gas cone flow rate is set to 0 L/hour. The collision energy used was 4 volts and 25-60 volts (ramp). In the positive ion mode, mass spectra in the m/z range of 50 to 1200 have been recorded.

### Measurement of Pour Point values

The pour point value was used to assess the effect of adding polyethylene glycol ester to crude oil samples. Each polyethylene glycol ester (additive) was combined with a crude oil sample at a concentration of 0.1 to 1% of the total crude oil sample. First, the solidified crude oil sample is heated to 50°C. A total of 4 mL of a mixture of crude oil and additive samples was placed in a test tube, which was then

**Table 1.** LC-MS/MS analysis gradient conditions for PEG ester

| Time (minute) | Flow Rate (mL/minute) | %A* | %B** |
|---|---|---|---|
| 0 | 0.2 | 95 | 5 |
| 2 | 0.2 | 75 | 25 |
| 3 | 0.2 | 75 | 25 |
| 14 | 0.2 | 0 | 100 |
| 15 | 0.2 | 0 | 100 |
| 19 | 0.2 | 95 | 5 |
| 23 | 0.2 | 95 | 5 |

* mobile phase A (water added 5 mM ammonium formate).

** mobile phase B (acetonitrile added with 0.05% formic acid).

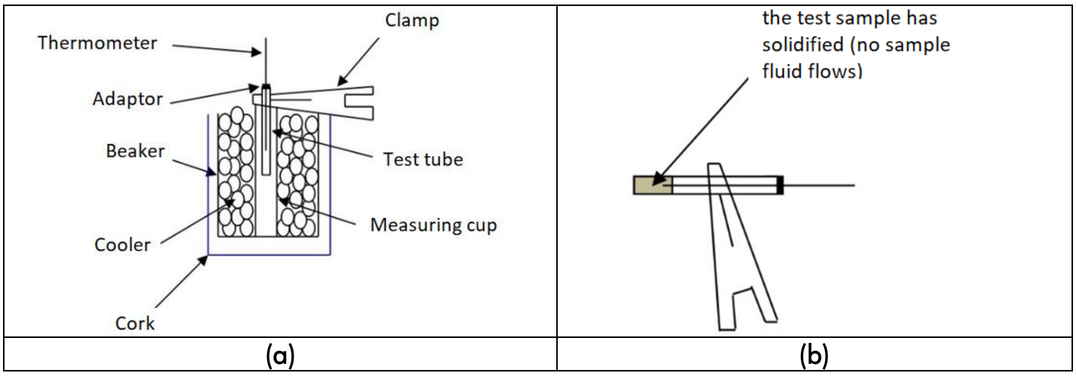

**Figure 1**. Design of a series of tools for pour point measurement (a), position of the test tube for each observation (b)

inserted with a thermometer. The tube containing the test sample was heated to 47°C before being placed in an ice bath to cool. The test sample was seen by removing the test tube and tilting it 90°C. The pour point value is obtained from the observed temperature value when the test sample has solidified plus 3°C. The series of tools for pour point measurement is shown in **Figure 1**.

To establish the value of relative density, the physical parameters of crude oil samples were examined with a picnometer (specific gravity). At a temperature of 50 °C, measurements were taken by weighing the empty mass of the picnometer and the mass of the picnometer holding a sample of crude oil. Entering the observed mass value into the relative density calculation yields the relative density value.

## RESULTS AND DISCUSSION

Polyethylene glycol ester was synthesized through the esterification reaction of fatty acids and PEG-400 with added *p*-TSA as a catalyst. The mole ratio of fatty acids to PEG-400 used was 2:1 . It was predicted that each PEG molecule could be reacted with excess fatty acid to produce more PEG ester. Water is the by-product of the esterification reaction, which is reversible. The reaction of fatty acids and PEG with added *p*-TSA involves the esterification of fatty acids and hydrolysis of PEG esters as shown in **Figure 2**. (Abdullah et al 2017).

The esterification begins with protonation of PEG using a strong acid, in this case it is *p*-TSA as shown in **Figure 3**. The oxygen on the hydroxyl group (-OH) of the electron-rich (nucleophilic) PEG attacks the hydrogen on the hydroxyl group of the electron-less (electrophilic) p-TSA. The O-H bond electrons in *p*-TSA are given completely to the oxygen atom in the -OH group of p-TSA and the free hydrogen atom (taken by PEG). This causes the formation of ions $(PEG\text{-}H)^+$ and $CH_3C_6H_4S0_3^-$.

Based on **Figure 4**, it can be seen that the 1-2-3 pathway is the oleic acid esterification step, while the 3-2-1 pathway is the PEG-oleic hydrolysis step. Ion $(PEG\text{-}H)^+$ which has been formed protonates oleic acid. This step is called oxygen-hydroxyl protonation (line 1-2). The hydroxyl oxygen atom (-OH) of oleic acid which acts as a nucleophile attacks the hydrogen atom in the electron-deficient $(PEG\text{-}H)^+$. This causes the formation of a neutral PEG molecule and the release of $H_2O$ which was previously attached to oleic acid in the form of $C\text{-}O{+}H_2$. It should be noted that $H_2O$ is a good leaving group. The removal of the $H_2O$ group results in the formation of acylium ions from oleic acid (R-C+=O, R is alkyl of oleic acid) which is a transition state in oleic acid esterification and PEG ester hydrolysis. The final step of oleic acid esterification is the reaction between one acylium ion molecule of oleic acid with two PEG molecules (trimolecular esterification). The hydroxyl oxygen atom of one of the PEG molecules attacks the positive carbon atom of the acylium ion (R-C+=O). This causes the O-H bond in PEG to be weak so that the hydroxyl oxygen atom of the other PEG can easily bond with the hydrogen. This step produces PEG ester molecules and ions $(PEG\text{-}H)^+$.

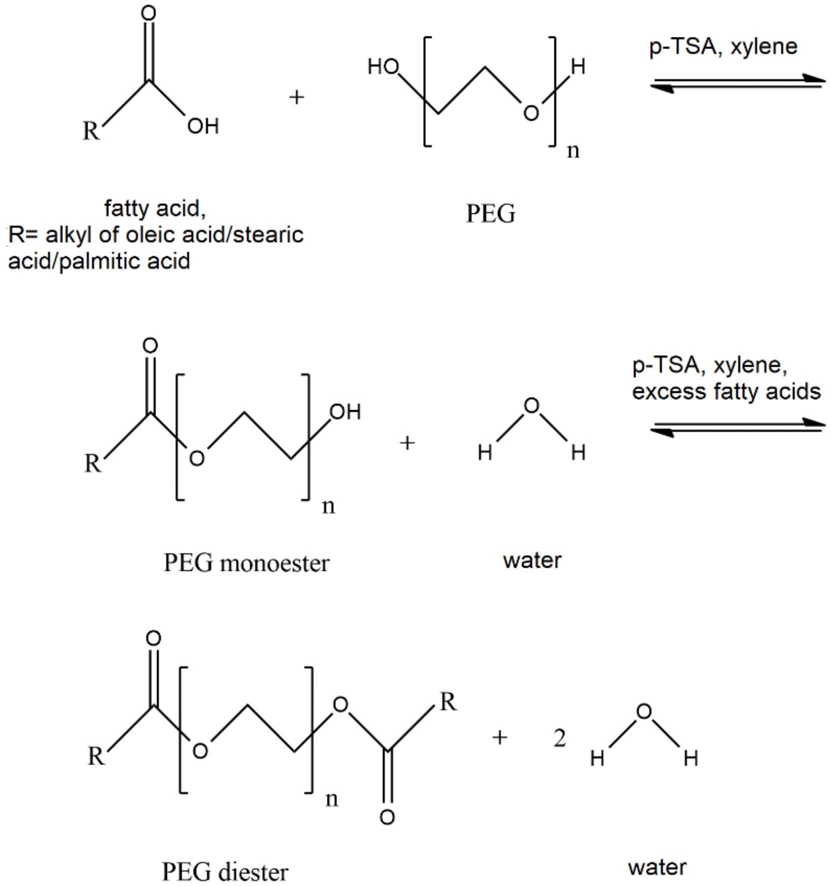

**Figure 2.** Esterification of fatty acids and PEG-400 with addition *p*-TSA as a catalyst.

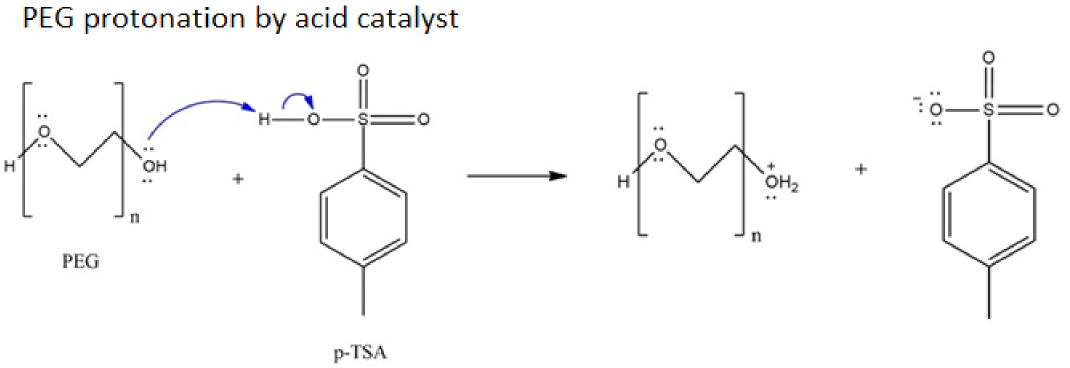

**Figure 3.** PEG protonation mechanism by p-TSA

Trimolecular hydrolysis occurs between one acylium ion molecule and two water molecules. The acylium ion is formed by protonation of alkyl oxygen from the PEG ester molecule that has been produced in the carboxylic acid esterification step. This is the step controlling the rate of ester hydrolysis (line 3-2). The alkyl oxygen atom near the carbonyl group (C=O) attacks the hydrogen on the O-H group of the p-TSA molecule. Furthermore, path 2-1 is trimolecular hydrolysis. The oxygen atom of one of the $H_2O$ molecules attacks the positive carbon atom of the acylium ion (R-C+=O). This causes the O-H bond in $H_2O$ to be weak so that the oxygen atom of the other $H_2O$ easily bonds with the hydrogen. This step produces a neutral molecule of oleic acid and $H_3O^+$ ions (Shi and Hua 2015).

There have been two methods used to synthesize polyethylene glycol ester: reflux and monowave. **Table 2** shows Synthesis PEG-ester using the reflux technique, the percentage yield is higher (up to 90% higher) than when using the monowave-50 methods. It resulted in that a monowave, the water produced was trapped in the reaction system so that it could hydrolyze the ester that was already produced (PEG ester amount significantly decreased). Furthermore, Dean-Stark was putting on a reflux apparatus in the reflux method that accommodates the water released during the synthesis.

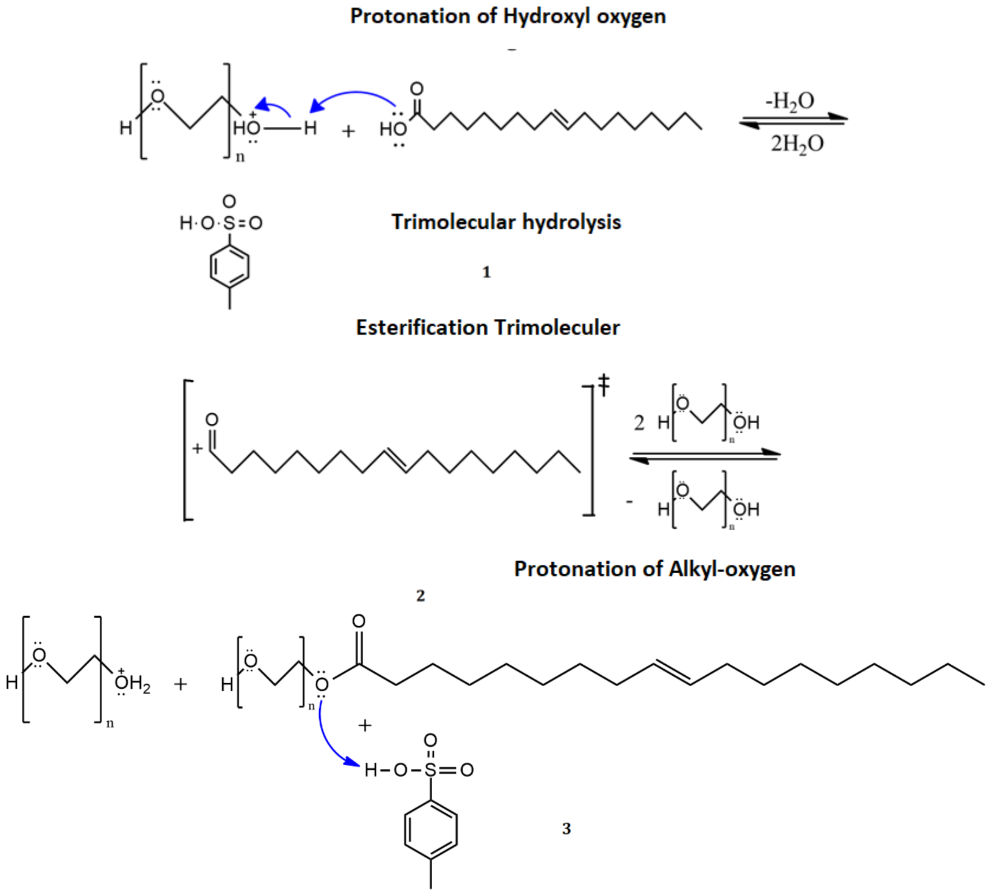

**Figure 4.** The reaction mechanism of oleic acid esterification (lane 1-2-3) and PEG-oleic hydrolysis (lane 3-2-1).

**Table 2.** The precentage yield of the PEG ester

| Method | Synthesis | Yield (%) |
|---|---|---|
| Reflux | PEG400-Stearate | 92.18 |
| | PEG400-Palmitate | 96.10 |
| Monowave | PEG400-Oleate | 65.94 |
| | PEG400-Stearate | 14.75 |
| | PEG400-Palmitate | 67.36 |

**FTIR Analysis**

The FTIR spectroscopic data is being used to determine the initial identification of ester products. While wavenumber values for each bond refer to literature (Silverstein et al 2015). **Figure 5** shows absorption bands at wavenumbers 3478 $cm^{-1}$ and 3444 $cm^{-1}$ indicate O—H stretching vibrations, then absorption at wavenumbers 2927 $cm^{-1}$, 2854 $cm^{-1}$, 2927 $cm^{-1}$, 2854 $cm^{-1}$ indicate stretching vibrations aliphatic C—H. Absorption at wavenumbers 1740 $cm^{-1}$, 1707 $cm^{-1}$ indicate stretching vibrations of C=O. For oleic acid, O—H bending vibrations of -COOH and C—O stretching vibrations of —COOH was identified by the appearance of an absorption band at a wave number of 1288 $cm^{-1}$. The presence of an absorption band at wave number 1102 $cm^{-1}$ was detected as a characteristic of the ester structure. This indicates the C—O stretching vibration of —COOC. Supported from reference (Banerjee et al 2017) that a wide absorption band at a wave number of around 1100-1060 $cm^{-1}$ is the vibration of the C-O-C ether bond, which increases in the presence of PEG400. The following is a comparison of the spectrum of PEG-oleic with oleic acid.

Similar analysis results are also shown in the FTIR spectra for PEG-stearate (**figure 6**) and PEG-palmitate (**Figure 7**). However, PEG-oleate has O—H stretching vibration with a higher transmittance percentage than PEG-stearate and PEG-palmitate. It means that the synthesis of PEG-ester using oleic acid produces more PEG diester products than the PEG monoester. A Comparison of the spectrum of PEG-palmitate with palmitic acid is shown in **Figure 7.** A Comparison of the spectrum of PEG-stearate with stearic acid is shown in **Figure 6**.

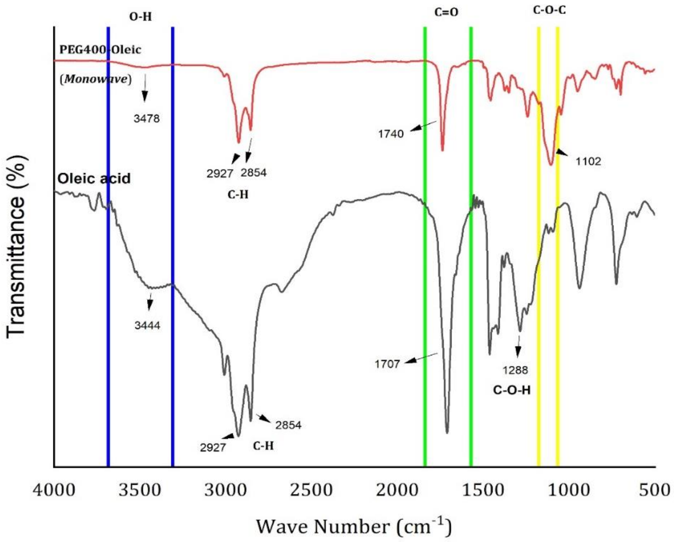

Figure 5. IR spectra of PEG-oleic and oleic acid

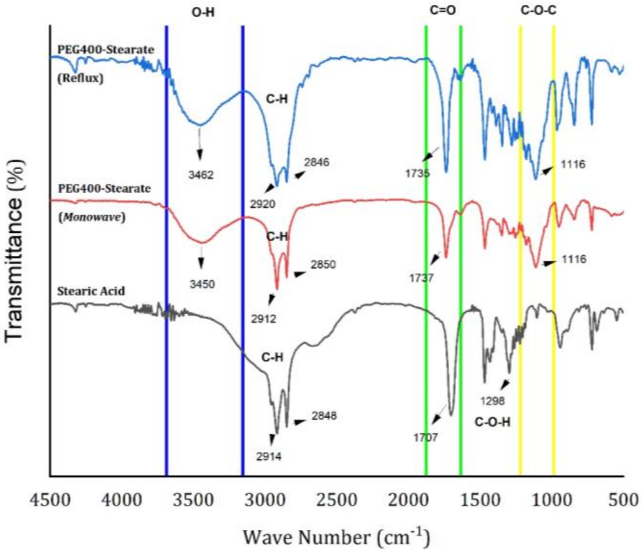

Figure 6. IR spectra of PEG-stearate and stearic acid

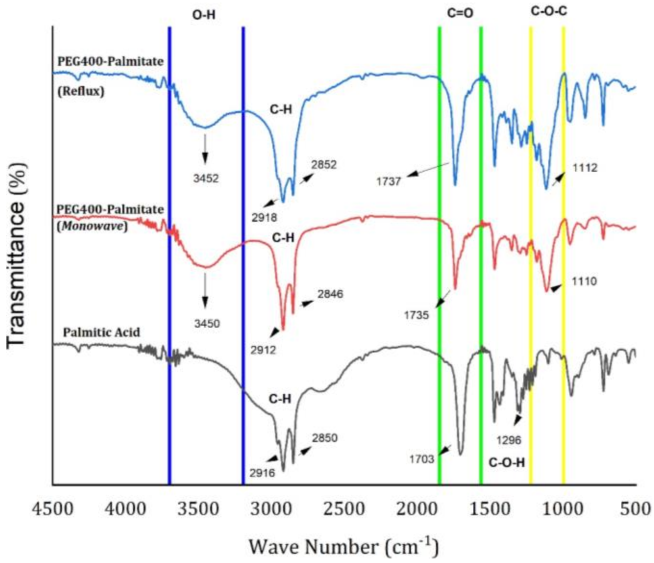

Figure 7. IR spectra of PEG-palmitic and palmitic acid

### LC-MS/MS Analysis

The molecular weight of the ester product was determined using LC-MS/MS validation. The m/z values were obtained in the positive ion mode. The chromatogram shows the compound components contained in the synthesis product that has been extracted and evaporated. The mass spectra of PEG-oleate, PEG-stearate, and PEG-palmitate was in the form of distribution of m/z values with different abundances (as seen from the peak height). PEG-oleate mass spectra appeared at a retention time of 16.81 minutes with a molecular weight of 846.6154 g/mol is shown in **Figure 8**. While the PEG-stearate mass spectra appeared at a retention time of 18.13 minutes with a molecular weight of product was 785.5952 g/mol is shown in **Figure 9**.

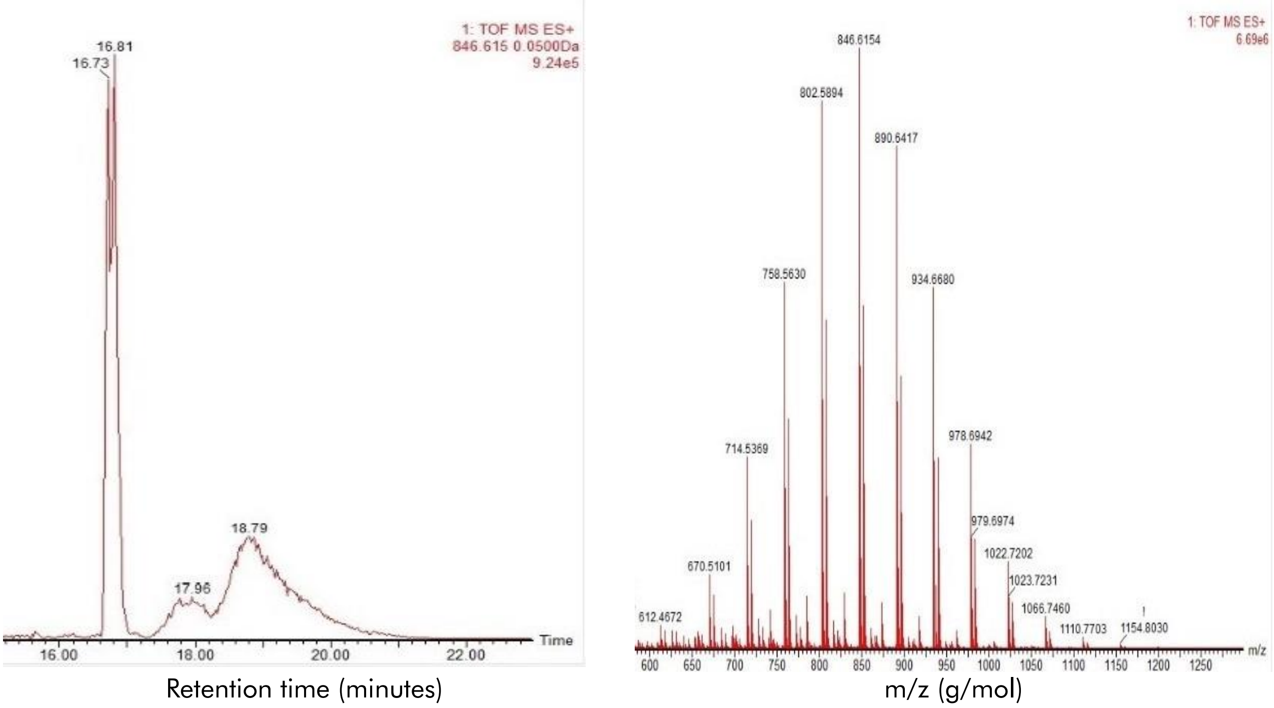

**Figure 8.** Chromatogram of PEG-oleate and Mass spectra of PEG-oleate

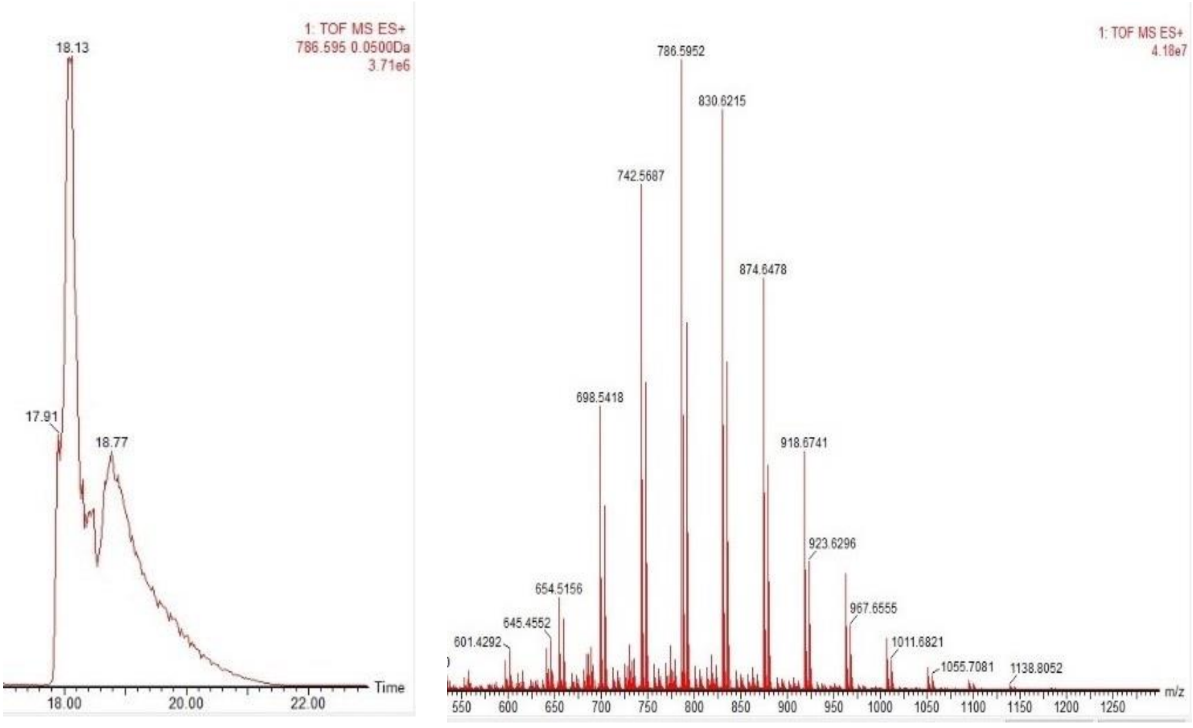

**Figure 9.** PEG-stearate chromatogram and Mass spectra of PEG-stearate

In contrast to PEG-oleate and PEG-stearate, the PEG-palmitate was separated at three different retention times: 18.18 minutes, 15.74 minutes, and 15.41 minutes. It means that a mobile phase (mobile phase A=water added 5 mM ammonium formate and mobile phase B=acetonitrile added 0.005% formic acid) used in the LC-MS/MS measurement was not good enough for the PEG-palmitate. Based on table 1, it was obvious that a mobile phase at a gradient time of 15 minutes (100% phase B) is more polar than a mobile phase at a gradient time of 19 minutes (95% phase A and 5% phase B). The group of PEG-palmitate molecules that produce more polar properties prefer to interact with a mobile phase B, while the group of PEG-palmitate molecules that produce less polar properties prefer to interact with a mobile phase A. Based on the values of m/z that has the highest abundance from each distribution m/z values of PEG-palmitate, obtained different molecular weights: 742.5669 g/mol, 685.5057 g/mol, and 734.5208 g/mol. PEG-palmitate mass spectra that appeared at a retention time of 18.18 minutes are shown in **Figure 10**.

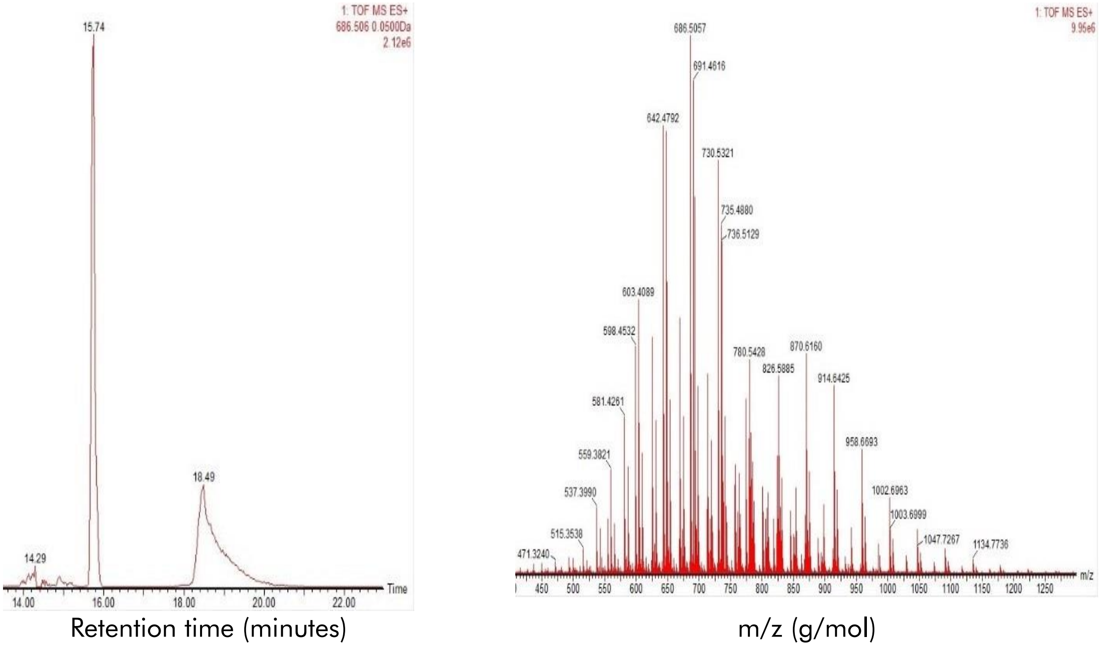

**Figure 10.** Chromatogram of PEG-palmitate and Mass spectra of PEG-palmitate (a retention time of 18.18 minutes)

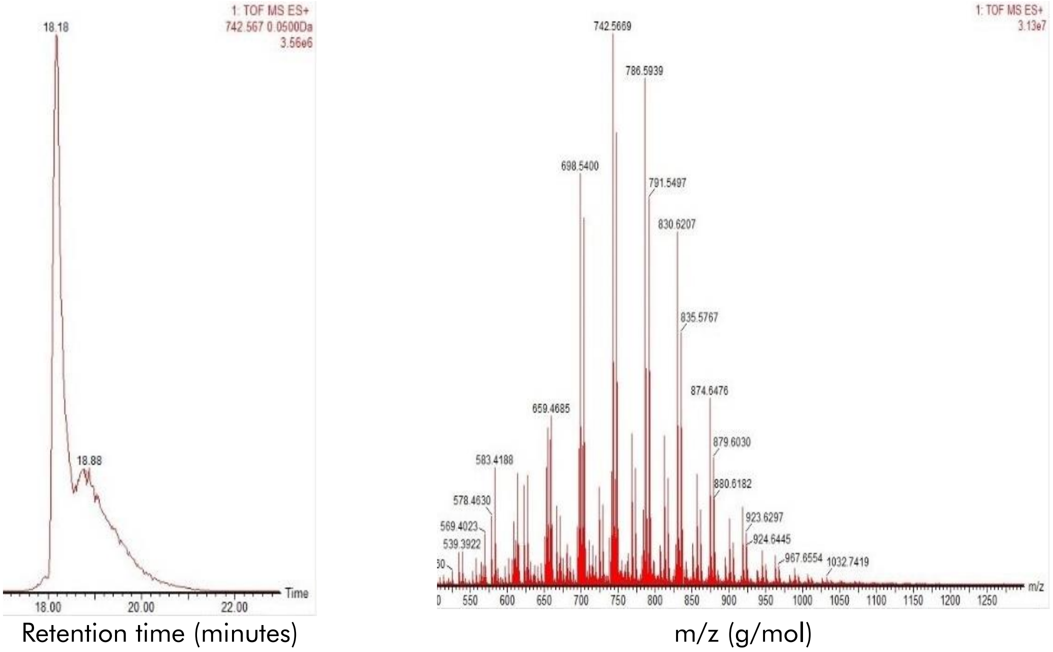

**Figure 11.** Chromatogram and mass spectra of PEG-palmitate at a retention time of 15.74 minutes.

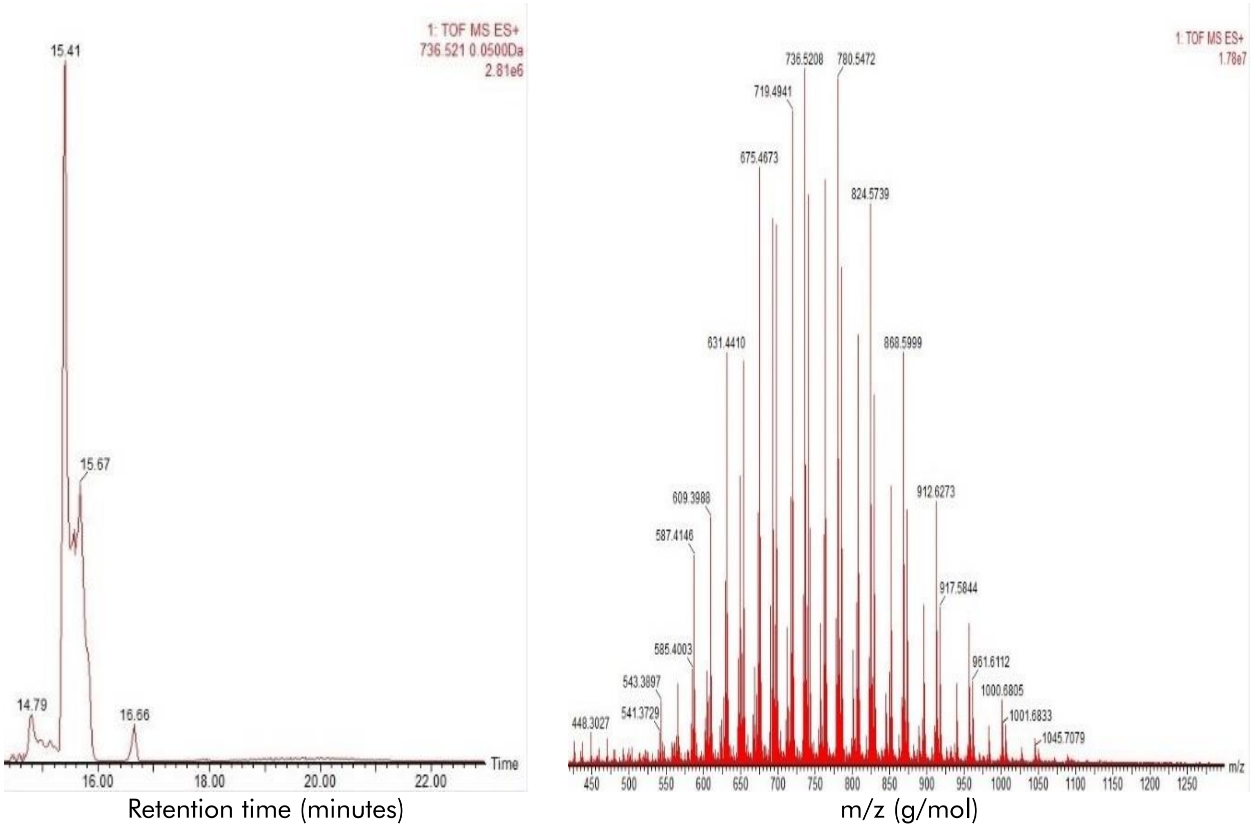

**Figure 12.** Chromatogram and Mass spectra of PEG-palmitate at a retention time of 15.41 minutes

Figure belows also shows PEG-palmitate at various retention times. PEG-palmitate mass spectra that appeared at a retention time of 15.74 minutes are shown in **Figure 11**. Meanwhile **Figure 12** shows PEG-palmitate mass spectra that appeared at a retention time of 15.41 minutes.

**Table 3** summarizes the results of the LC-MS/MS study in terms of retention time, percent area, most abundant m/z values, and molecular weights of PEG esters. Palmitic acid ($C_{16}H_{32}O_2$) has a shorter carbon chain than oleic acid ($C_{18}H_{34}O_2$) and stearic acid ($C_{18}H_{36}O_2$), then it combines with other PEG molecules more quickly to generate new ester compounds. As a result, the overall percent area of the PEG-palmitate is greater than the others.

### Pour Point values

Pour point measurements were carried out to see the effect of polyethylene glycol ester on crude oil samples which had an SG (specific gravity) value of 0.894 and an API (American Petroleum Institute) 26.659° API. The crude oil sample used is classified as a medium oil, which means it has quite a lot of heavy fractions.

The pour point measurement results show that the PEG-fatty acid product in the range of 0.1% to 1% has not been able to reduce the pour point of the crude oil sample yet . This is presumably because the hydrocarbon chains of fatty acids and the ether chains of PEG are too short to be applied to this crude oil sample so that the long alkyl groups interact less with long-chain paraffin waxes. Low molecular weight polymers may not have sufficient molecular volume to interfere with the co-crystallization of wax crystals (Ragunathan et al 2020; Cherukuvada et al 2016). Therefore, PPD compounds must have a structure similar to paraffin to interact with paraffin and have a polar group to prevent the meeting of paraffin molecules that will interact with each other (Borthakur et al 1995; Chi et al 2017).

**Table 3.** LC-MS/MS data analysis for PEG ester

| Product | A retention Time (minutes) | % Area | The Values of m/z (Da) that has Highest Abundance | Molecular Weight (g/mol) |
|---|---|---|---|---|
| PEG-oleate | 16.81 | 1.10 | 846.6154 | 845.6154 |
| PEG-stearate | 18.13 | 3.74 | 786.5952 | 785.5952 |
| PEG-palmitate | 18.18 | 5.38 | 742.5669 | 741.5669 |
| | 15.74 | 1.37 | 686.5057 | 685.5057 |
| | 15.41 | 2.99 | 735.5208 | 734.5208 |

**Figure 13**. Samples of crude oil and measurement of Pour point

**Tabel 4.** The results of the pour point measurement of crude oil samples with or without PEG ester

| Sample | Pour Point (°C) | | | | |
|---|---|---|---|---|---|
| | 0% Additive | 0.1% Additive | 0.3% Additive | 0.5% Additive | 1% Additive |
| *Crude Oil* | 36 | - | - | - | - |
| *Crude Oil* + Additive 1 | 36 | 36 | 36 | 36 | 36 |
| *Crude Oil* + Additive 2 | 36 | 36 | 36 | 36 | 36 |
| *Crude Oil* + Additive 3 | 36 | 36 | - | - | - |

Additive 1 = PEG400-oleate;
Additive 2 = PEG400-stearate;
Additive 3 = PEG400-palmitate

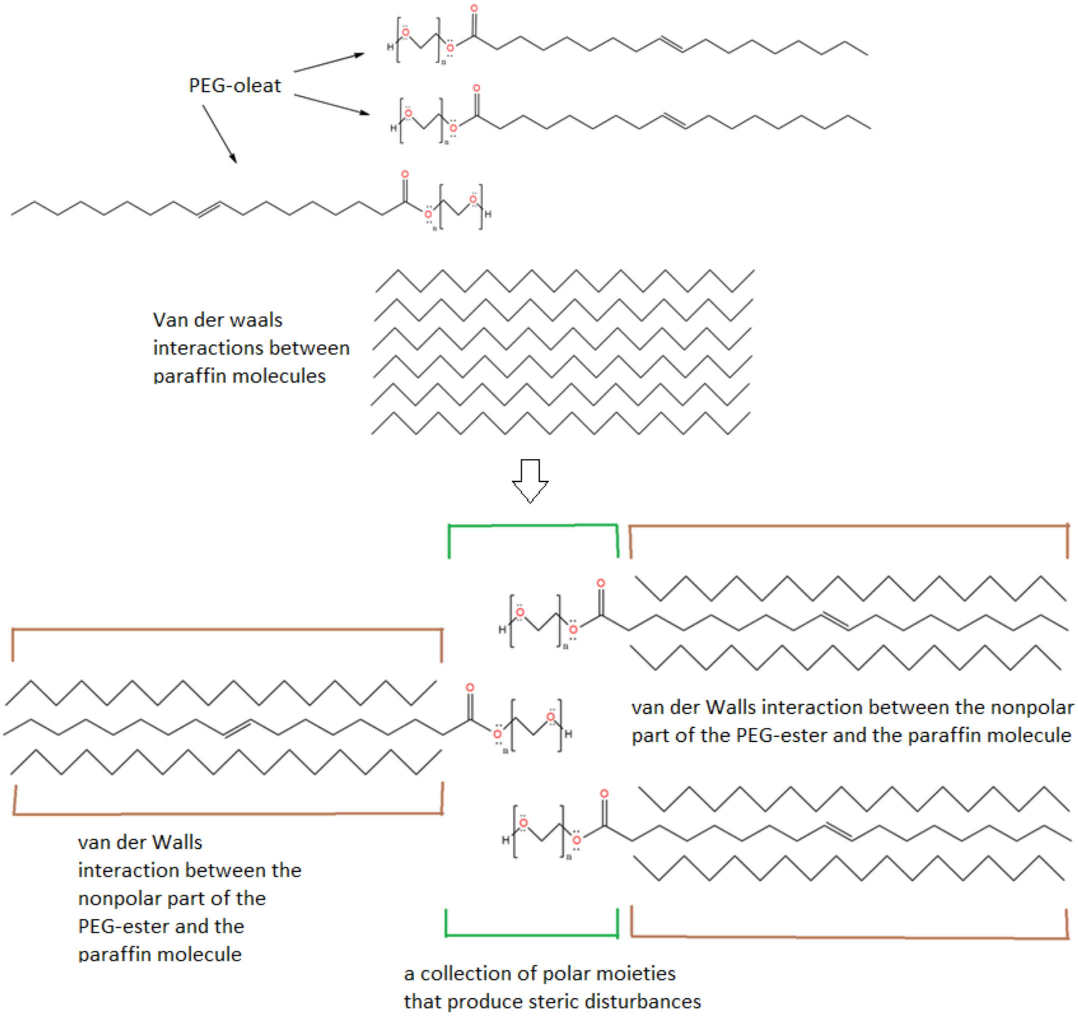

**Figure 14.** Schematic of inhibition of paraffin wax by PEG-oleate molecules

Two critical steps are involved in the suggested PEG ester's mechanism of prevention of paraffin wax deposition. First, the ethylene glycol group chain (polar moiety) of the PEG ester-containing oxygen atoms can help generate strong van der Waals interactions between the long alkyl paraffin molecules and the PEG ester. This case is due to the formation of a collection of polar moieties resulting in steric interference for interactions between paraffin molecules. As a result, the paraffin molecules split and the paraffin wax dissolves readily in the PEG ester, lowering wax gel strength and reducing wax deposition. Second, the long alkyl group of PEG ester interacts van der Waals with paraffin molecules so that wax crystallization is inhibited and then leads to a decrease in the pour point of the crude oil sample. **Figure 14**, for example, epicts a schematic of a PEG-oleate molecule inhibiting the deposition of paraffin wax.

## CONCLUSIONS

In this study, we have succeeded in synthesizing PEG-esters from oleic acid, palmitic acid and stearic acid through two methods with the best percent yield through reflux (92-96%). PEG-ester synthesis was confirmed by FTIR (the presence of an absorption band at a wave number of around 1100 $cm^{-1}$ that indicates the stretching vibration of the C-O ester) and LC-MS analysis showing monoester formation for PEG-oleate, while for PEG-stearate and PEG-palmitate a diester was formed. The molecular weight of PEG400-oleate was 845.6154 g/mol and, PEG400-stearate was 785.5952 g/mol. Meanwhile PEG400-palmitate produced three ester compounds with different molecular weights: 741.5669 g/mol, 685.5057 g/mol, and 734.5208 g/mol. The pour point measurement results show that the PEG-fatty acid product in the range of 0.1% to 1% has not been able to reduce the pour point of the crude oil sample.

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