



## Synthesis of Oleic Acid Derivatives as Pour Point Depressant (PPD)

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### Abstract

Crude oil is widely used worldwide as an energy source in various fields. Over the years, crude oil production has decreased due to one major problem that continues to occur, namely wax deposition. Wax deposits tend to occur due to the composition of the crude oil itself. Crude oil mostly consists of large amounts of hydrocarbon compounds, such as paraffins. Therefore, an additive, such as a pour point depressant (PPD), is needed to inhibit or prevent wax formation. This study compares the performance of various PPDs synthesized using oleic acid as a base material. The esterification of oleic acid with alcohols yielded PPD-Ester Butanol (96.72%) and PPD-Ester Decanol (72.21%). Further esterification with oleic acid resulted in PPD-Ester Butanol + Oleic Acid (47.30%) and PPD-Ester Decanol + Oleic Acid (22.56%). These derivatives can undergo additional reactions, such as epoxidation, diol formation, and esterification, to produce a PPD. Pour point measurements on crude oil samples were conducted following ASTM D-5853. The blank sample had a pour point of 39°C. PPD-Ester Decanol reduced the pour point by 3°C, while all PPD-Esters further esterified with oleic acid lowered it by 9°C. Chemical characterization via FTIR analysis confirmed the presence of C=C, C=O, and aliphatic C-H functional groups. GC-MS analysis of PPD-Ester Decanol + Oleic Acid (decyl 9-monooleate, 10-hydroxy oleate) identified three major compounds: 1-decanol, oleic acid, and decyl oleate. Physical characterization revealed that the synthesized PPDs had densities ranging from 850 to 1,066 kg/m<sup>3</sup>.

### 1. Introduction

Crude oil is one of the most valuable natural resources in the world. Crude oil can be processed into various products and used in various sectors, including transportation, industry, and energy production. Before crude oil can be processed, it must first be transported, typically via pipelines or tankers. While pipeline transportation is generally more practical due to its safety and efficiency, it presents challenges due to the high wax content in crude oil. When the temperature drops below the wax appearance temperature (WAT), wax begins to crystallize, separate from the oil, and adhere to the pipe walls [1, 2]. Paraffin wax is a saturated long-chain hydrocarbon compound with at least 15 or more carbon atoms per molecule [3, 4].

Crude oil becomes more viscous or solidifies due to wax deposition, resulting in a high pour point. The pour point is defined as the lowest temperature at which the oil can still flow before it solidifies [5]. Three methods can be used to prevent wax formation and reduce the pour point: mechanical, thermal, and chemical [6]. This study focuses on the chemical method, utilizing pour point depressants (PPDs) to inhibit wax formation in crude oil. PPDs are additives that lower the pour point of crude oil, preventing wax precipitation and thus reducing the pour point temperature [7]. Non-ionic surfactants, such as PPDs, have become a prominent topic of interest. Surfactants are surface-active compounds with a non-polar hydrophobic component and a polar hydrophilic part, typically consisting of 8–18 carbon atoms [8].

The carbon chain in the tail of surfactants can be linear, branched, or cyclic. At reservoir temperatures, these compounds are effective in forming emulsions, which can be broken down in refineries [9]. Commercial PPDs include ethylene vinyl acetate (EVA), polyethylene propylene (PE-PEP), polyethylene glycol ester (PEG), and polyethylene butene (PEB) [10]. Additionally, PPDs can be synthesized from various structures, often derived from fatty acids, which share similarities with the wax in crude oil, such as PPD esters [11]. Low molecular weight polymers may lack sufficient molecular volume to disrupt the co-crystallization of wax crystals [12, 13]. Therefore, PPD compounds must have a structure similar to paraffin to interact effectively with wax molecules while incorporating a polar group to prevent their aggregation [14, 15].

PEG ester is a non-ionic surfactant formed by the ethoxylation of fatty acids. The fatty acid's carbon chain is a non-polar group, while polyethylene glycol or alcohol monomers act as polar groups. Several researchers have synthesized PEG esters for pour point depression. El-Shamy *et al.* [16] synthesized C18E68 and C18E136 by reacting oleic acid with PEG in the presence of a *p*-TSA (*p*-Toluenesulfonic acid) catalyst, achieving pour point reductions of 6°C and 12°C, respectively, in fuel oil. Khidir *et al.* [17] developed ethoxylated non-ionic surfactants (C14E5, C16E5, and C16E7), reducing the pour point of fuel oil by 9°C, 12°C, and 15°C, respectively, at a 2000 ppm additive concentration.

Fatty acids react with alcohols to form esters through condensation reactions, where two molecules combine to form one, typically releasing a minor byproduct such as water (H<sub>2</sub>O). The esterification of fatty acids is reversible, involving both ester formation and hydrolysis [18]. The reaction typically produces a mixture of monoesters and diesters.

In this study, oleic acid is used as a base material for synthesizing a pour point depressant. Oleic acid (C<sub>18</sub>H<sub>34</sub>O<sub>2</sub>) contains alkene groups at C9 and C10 and a carboxylic acid group at C1. These functional groups can be modified through oxidation and esterification to enhance their effectiveness as a PPD.

## 2. Experimental

### 2.1. Materials

Oleic acid (technical), 30% hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), formic acid (CH<sub>2</sub>O<sub>2</sub>), 30% NaOH, decanol, butanol, *p*-TSA (*p*-Toluenesulfonic acid), methanol, acetone, and chloroform. All reagents were of analytical grade from Sigma-Aldrich. Ethyl acetate was obtained from commercial suppliers and used without further purification. Heavy crude oil was obtained from the Petroleum Lab of Universitas Pertamina.

### 2.2. Pour Point Depressant Synthesis

#### 2.2.1. Epoxidation

The initial step in the PPD synthesis was epoxidation via the reflux method. The reaction utilized oleic acid, 30% H<sub>2</sub>O<sub>2</sub>, and formic acid in a 1:0.6:22 ratio. The process began by mixing 15 mL of 30% H<sub>2</sub>O<sub>2</sub> with 257 mL of formic

acid, heating the mixture to 50–60°C, and stirring for 5 minutes. Then, 100 mL of oleic acid was added to the mixture in a three-necked flask and reacted at 70–80°C for 2 hours. After the reaction, the mixture was cooled to 20–25°C in an ice bath, and the phase separation was observed.

#### 2.2.2. Diol

In the second step of PPD synthesis, a diol was formed from the previously obtained oleic acid epoxide using a reflux method with 30% NaOH. The epoxide was mixed with 372 mL of 30% NaOH (maintaining a 1:1 ratio with the previous reaction volume) in a three-necked flask. The mixture was heated to 90°C and stirred with a magnetic stirrer for 1 hour. After the reaction, the mixture was cooled in an ice bath, inducing solidification.

#### 2.2.3. Esterification Using Fatty Alcohol

In the third step of the PPD synthesis, esterification was performed using the previously obtained oleic acid diol and alcohol (decanol or butanol) in a 1:3 ratio, along with 2% *p*-TSA, under reflux. The oleic acid diol was placed in a three-necked flask while the alcohol and *p*-TSA were mixed and preheated to ensure dissolution. The preheated mixture was then added to the oleic acid diol, and the esterification reaction proceeded for 4 hours at 110°C with a stirring speed of 400 rpm. After 4 hours, the esterification product was washed 1–2 times with distilled water using a separatory funnel to separate the organic and aqueous phases. The organic phase was then evaporated using a rotary evaporator at 80–90°C for approximately 30 minutes.

#### 2.2.4. Esterification Using Oleic Acid

In the final stage of PPD synthesis, further esterification was conducted by adding oleic acid to the ester obtained from the previous alcohol reaction. The ester was placed in a three-necked flask, and oleic acid was added in a 1:1 ratio for ester-decanol and 1:2 for ester-butanol. The reaction was conducted at 110°C for 2 hours at 400 rpm. The result was the final Pour Point Depressant (PPD).

### 2.3. Pour Point Test

The pour point test was conducted according to the ASTM D-5853 standard. The synthesized PPD was used as an additive and injected into various crude oil samples at doses ranging from 0% to 10%. The dosage amounts used in this test are listed in Table 1.

Table 1. Additive distribution

| % Additive | Volume (mL) |           |
|------------|-------------|-----------|
|            | PPD         | Crude oil |
| 0          | 0           | 5         |
| 5          | 0.25        | 4.75      |
| 7.5        | 0.375       | 4.625     |
| 10         | 0.5         | 4.5       |

## 2.4. Characterization

### 2.4.1. Density

Density was measured using a pycnometer. The empty pycnometer was weighed first, filled with the synthesized PPD sample, and weighed again. The same procedure was applied to determine the density of the crude oil sample.

### 2.4.2. FTIR

FTIR (Fourier-Transform Infrared Spectroscopy) characterization was performed to identify the functional groups in the oleic acid derivatives and to compare the differences in functional groups across each derivative reaction. The samples were analyzed using FTIR in ATR (Attenuated Total Reflectance) mode with a Thermo Fisher Scientific Nicolet iS5-iD7 instrument.

### 2.4.3. GC-MS

GC-MS (Gas Chromatography–Mass Spectrometry) analysis was performed using an Agilent 8890 to identify the compounds in the PPD samples derived from oleic acid reactions. The analysis was conducted with an initial temperature of 50°C, increasing at 12°C/min and ending at 300°C. A 10-μL sample was injected for analysis. This characterization was done on two final samples: PPD-Ester Decanol + Oleic Acid. Methanol was used as the solvent in a 1:5 volume ratio.

## 3. Results and Discussion

### 3.1. Pour Point Depressant Synthesis

Fatty acids, particularly oleic acid, are among the primary materials that can be synthesized into a PPD, and oleic acid was specifically used in this study. It was chosen due to its natural abundance and availability as an organic fatty acid found in various sources. Structurally, oleic acid contains an alkene group (C9=C10) and a carboxylic acid group, which can be modified to create new derivatives that may effectively lower the pour point of crude oil. Additionally, oleic acid is a widely produced fatty acid in the oleochemical industry and serves as a key raw material for various derivatives. In this study, its derivatives were synthesized through four reaction steps: epoxidation, diol formation, and two esterification stages, as outlined in Figure 1.

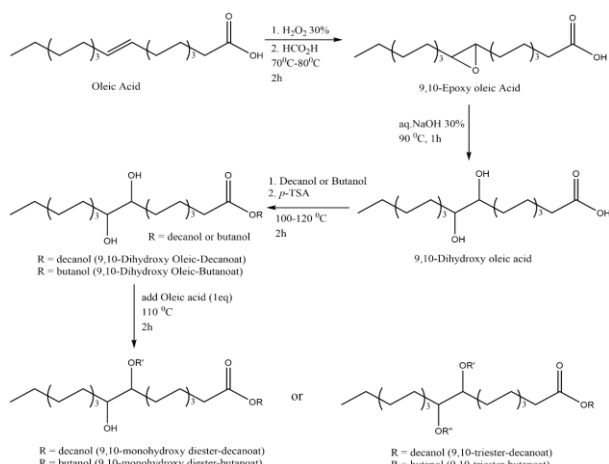


Figure 1. Synthesis of oleic acid derivatives

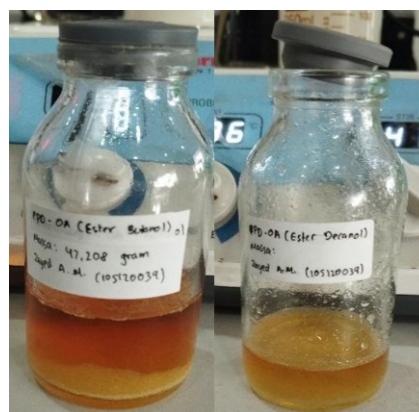


Figure 2. Product of esterification with fatty alcohol

### 3.1.1. Epoxidation

The first step in synthesizing oleic acid derivatives involved the epoxidation or formation of an oxirane/epoxide ring within the oleic acid molecule. Epoxidation is a reaction between an organic peracid and a double bond (such as the unsaturated fatty acids in vegetable oils) to form an oxirane (epoxide) compound. The key materials used in this step were oleic acid, formic acid, and 30% H<sub>2</sub>O<sub>2</sub>. Oleic acid served as raw material, formic acid acted as an acid catalyst, and 30% H<sub>2</sub>O<sub>2</sub> was used as the oxidizing agent. The equivalence ratio for this experiment was 1:0.6:22 (oleic acid:30% hydrogen peroxide: formic acid). Formic acid was chosen as the catalyst due to its relatively high reactivity, making it an effective activator for H<sub>2</sub>O<sub>2</sub>, thereby improving its ability to deliver oxygen without additional catalysts [19]. This reaction proceeds via a substitution mechanism, where the C=C double bond at C9-C10 in oleic acid is attacked by performic acid, forming an epoxide or oxirane ring.

### 3.1.2. Diol Formation

The next step in synthesizing oleic acid derivatives was the formation of a diol from the epoxidized oleic acid product, specifically 9,10-epoxy oleic acid. The diol was formed by reacting to the epoxide product with a strong base, such as 30% NaOH, in a 1:1 volume ratio. During this step, an acid-base reaction occurs where NaOH, acting as a strong base, hydrolyzes the epoxide ring. The hydroxide ion from NaOH, acting as a nucleophile, attacks the electrophilic carbon atoms in the epoxide ring, breaking the oxirane/epoxide ring and forming two hydroxyl (-OH) groups. The resulting product, 9,10-dihydroxy oleic acid, was obtained as a solid, yielding 121.40 grams after evaporation.

### 3.1.3. Esterification with Fatty Alcohol

The third step, esterification, involved reacting to the previously synthesized diol-oleic acid (9,10-dihydroxy oleic acid) with fatty alcohols such as decanol and butanol, along with 2% *p*-TSA based on the amount of alcohol. *p*-TSA served as an acid catalyst to accelerate the esterification process. Since esterification is a reversible reaction, it produces two products: oleic acid ester (9,10-dihydroxy oleic ester) and water as a byproduct. A Dean-Stark apparatus was intended to trap the water and prevent it from hydrolyzing the formed ester to optimize the ester yield. However, the water was not successfully

trapped in this reaction, so the reaction mixture was washed with distilled water instead. After washing and letting the mixture stand for about a day, the organic phase containing the oleic acid ester was collected and evaporated using a rotary evaporator. The percentage yield results are 96.72% for PPD-Ester Butanol and 72.21% for PPD-Ester Decanol through esterification with alcohols.

### 3.1.4. Esterification with Oleic Acid

The final step involved the addition of oleic acid to the 9,10-dihydroxy oleic ester product. This was a further esterification reaction aimed at reacting to the diol (C9-OH and C10-OH) in the 9,10-dihydroxy oleate with fatty alcohols (decanol and butanol). In the previous esterification, the alcohols preferentially reacted with the hydroxyl group of the carboxylic acid due to its higher nucleophilicity and ease of protonation compared to the hydroxyl groups in the diol. The reaction conditions for this step were the same as the previous esterification and were conducted under reflux. Further esterification with oleic acid yielded 47.30% for PPD-Ester Butanol + Oleic Acid and 122.56% for PPD-Ester Decanol + Oleic Acid.

## 3.2. Fourier Transform Infrared Spectroscopy (FTIR)

The identification of functional groups and types of vibrations in the oleic acid derivatives was conducted using the ATR method. The FTIR spectrum of oleic acid (Figure 4) was used as a reference for comparison with the spectra obtained from the oleic acid derivative reaction products.

### 3.2.1. Oleic Acid

Figure 4 displays several peaks corresponding to specific bonds and functional groups within its structure. The peak at  $3005\text{ cm}^{-1}$  corresponds to the C=C-H bond in the alkene group located at C9-C10 of oleic acid. The range between  $2900$  and  $2800\text{ cm}^{-1}$  indicates the stretching vibrations of aliphatic C-H bonds in the aliphatic carbon chain (alkane). The peak around  $1700\text{ cm}^{-1}$  corresponds to the stretching vibrations of the carbonyl (C=O) group in the carboxylic acid. The peak at  $1460\text{ cm}^{-1}$  represents the bending vibrations of C-H in the carboxylic acid group. The range between  $1300$  and  $1260\text{ cm}^{-1}$  shows the bending vibrations of the hydroxyl (O-H) group in the carboxylate group of oleic acid. The peak near  $930\text{ cm}^{-1}$  corresponds to the stretching vibrations of the C-O bond in the carboxylic acid group. Finally, the peak around  $730\text{ cm}^{-1}$  indicates the bending vibrations of the =C-H bond in the long alkyl chain. This spectrum serves as the baseline for comparison with the FTIR spectra of the oleic acid derivative reaction products.



Figure 3. Product of esterification with oleic acid

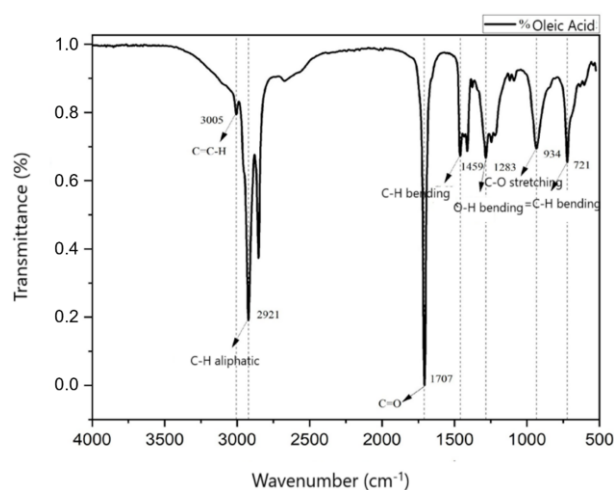


Figure 4. FTIR spectrum of oleic acid

### 3.2.2. Epoxide and Diol

The FTIR spectra analysis for the epoxidation and diol formation (Figure 5) stages reveals distinct functional groups. The spectrum of 9,10-epoxy oleic acid (black) shows key peaks at  $2920\text{ cm}^{-1}$ ,  $1708\text{ cm}^{-1}$ ,  $1212\text{ cm}^{-1}$ ,  $933\text{ cm}^{-1}$ , and  $720\text{ cm}^{-1}$ . The peak at  $2920\text{ cm}^{-1}$  corresponds to the stretching vibrations of aliphatic C-H bonds in the aliphatic carbon chain (alkane). The  $1708\text{ cm}^{-1}$  peak represents the stretching vibrations of the carbonyl (C=O) group in the carboxylic acid. The  $1212\text{ cm}^{-1}$  peak indicates the stretching vibrations of the epoxide or oxirane ring formed in this reaction. The peak around  $933\text{ cm}^{-1}$  corresponds to the stretching vibrations of the C-O bond in the carboxylic acid group, while the peak at  $720\text{ cm}^{-1}$  reflects the bending vibrations of the =C-H bond in the long alkyl chain.



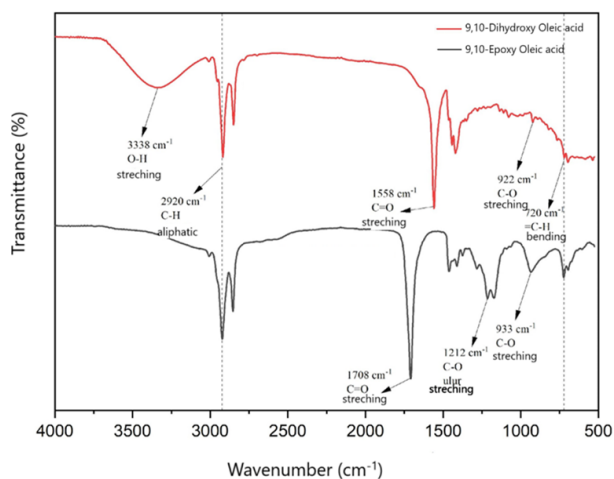


Figure 5. FTIR spectra of epoxidation and diol formation of oleic acid

In the spectrum of 9,10-dihydroxy oleic acid (red), peaks are observed at 3338  $\text{cm}^{-1}$ , 2920  $\text{cm}^{-1}$ , 1558  $\text{cm}^{-1}$ , 922  $\text{cm}^{-1}$ , and 720  $\text{cm}^{-1}$ . The 3338  $\text{cm}^{-1}$  peak corresponds to the stretching vibrations of the O-H bond formed during the reaction. The 2920  $\text{cm}^{-1}$  peak again indicates the stretching vibrations of aliphatic C-H bonds in the alkane chain. The 1558  $\text{cm}^{-1}$  peak represents the stretching vibrations of the carbonyl (C=O) group in the carboxylic acid. The slight reduction in this vibration compared to the previous reaction is likely due to hydrogen bonding interactions between hydroxyl groups formed during diol formation, as illustrated in Figure 5. The peak around 922  $\text{cm}^{-1}$  indicates the stretching vibrations of the C-O bond in the carboxylic acid group, and the 720  $\text{cm}^{-1}$  peak is associated with the bending vibrations of the =C-H bond in the long alkyl chain.

### 3.2.3. Esterification with Fatty Alcohol

From Figure 6, the functional groups in the esterification stages with alcohols, decanol, and butanol were analyzed. The spectrum of decyl 9,10-dihydroxy oleate (black) shows peaks at 3326  $\text{cm}^{-1}$ , 2920  $\text{cm}^{-1}$ , 1556  $\text{cm}^{-1}$ , 1056  $\text{cm}^{-1}$ , and 720  $\text{cm}^{-1}$ . The peak at 3326  $\text{cm}^{-1}$  corresponds to the O-H stretching vibration from the previous reaction. The peak at 2920  $\text{cm}^{-1}$  indicates the stretching vibration of C-H in aliphatic chains. The peak at 1556  $\text{cm}^{-1}$  represents the stretching vibration of the C=O carbonyl group in carboxylic acids. The peak around 1056  $\text{cm}^{-1}$  shows the C-O stretching vibration of the ester formed. The peak at 720  $\text{cm}^{-1}$  corresponds to the bending vibration of =C-H in long alkyl chains. These characteristic peaks confirm the successful formation of decyl 9,10-dihydroxy oleate, highlighting the presence of ester and hydroxyl functional groups in the product.

The spectrum of butyl 9,10-dihydroxy oleate (red) exhibits peaks at 3360  $\text{cm}^{-1}$ , 2920  $\text{cm}^{-1}$ , 1546  $\text{cm}^{-1}$ , 1070  $\text{cm}^{-1}$ , and 720  $\text{cm}^{-1}$ . The peak at 3360  $\text{cm}^{-1}$  shows the O-H stretching vibration from the previous reaction. The peak at 2920  $\text{cm}^{-1}$  is due to C-H stretching in aliphatic chains. The peak at 1546  $\text{cm}^{-1}$  indicates the C=O stretching vibration in carboxylic acids. The peak around 1070  $\text{cm}^{-1}$  represents the C-O stretching vibration of the ester. The peak at 720  $\text{cm}^{-1}$  shows the bending vibration of C-H bending in long alkyl chains.

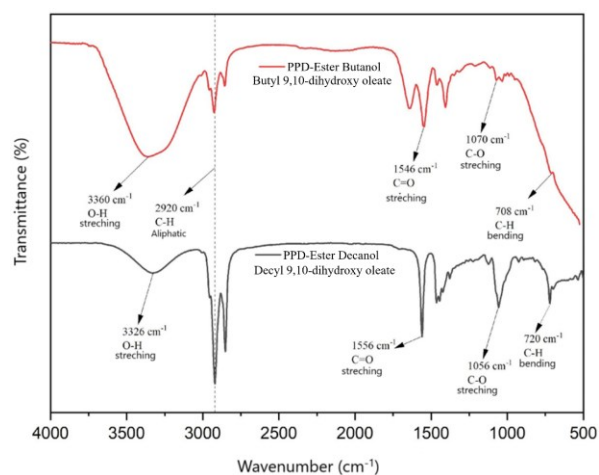


Figure 6. FTIR spectra of esterification with fatty alcohol (red = ester butanol, black = ester decanol)

### 3.2.4. Esterification with Oleic Acid

Figure 7 presents the functional group analysis of advanced esterification with oleic acid. The spectrum of decyl 9-monooleate, 10-hydroxy oleate (black) shows peaks at 3399  $\text{cm}^{-1}$ , 3005  $\text{cm}^{-1}$ , 2921  $\text{cm}^{-1}$ , 1710  $\text{cm}^{-1}$ , 1054  $\text{cm}^{-1}$ , and 721  $\text{cm}^{-1}$ . The peak at 3399  $\text{cm}^{-1}$  indicates O-H stretching, potentially from residual diol. The peak at 3005  $\text{cm}^{-1}$  is due to C=C-H stretching from the alkene group in oleic acid. The peak at 2921  $\text{cm}^{-1}$  shows C-H stretching in aliphatic chains. The peak at 1710  $\text{cm}^{-1}$  represents C=O stretching in carboxylic acids. The peak around 1054  $\text{cm}^{-1}$  corresponds to C-O stretching in the ester formed. The peak at 721  $\text{cm}^{-1}$  indicates bending vibration of =C-H in long alkyl chains.

The spectrum of butyl 9,10-dioleate oleate (red) exhibits peaks at 3399  $\text{cm}^{-1}$ , 3005  $\text{cm}^{-1}$ , 2921  $\text{cm}^{-1}$ , 1710  $\text{cm}^{-1}$ , 945  $\text{cm}^{-1}$ , and 721  $\text{cm}^{-1}$ . The peak at 3399  $\text{cm}^{-1}$  shows O-H stretching, likely from residual diol. The peak at 3005  $\text{cm}^{-1}$  indicates C=C-H stretching from the alkene group in oleic acid. The peak at 2921  $\text{cm}^{-1}$  represents C-H stretching in aliphatic chains. The peak at 1710  $\text{cm}^{-1}$  shows C=O stretching in carboxylic acids. The peak around 945  $\text{cm}^{-1}$  corresponds to C-O stretching in the ester. The peak at 721  $\text{cm}^{-1}$  indicates bending vibration of =C-H in long alkyl chains. A summary of the FTIR spectra for each stage of the process is provided in Table 2.

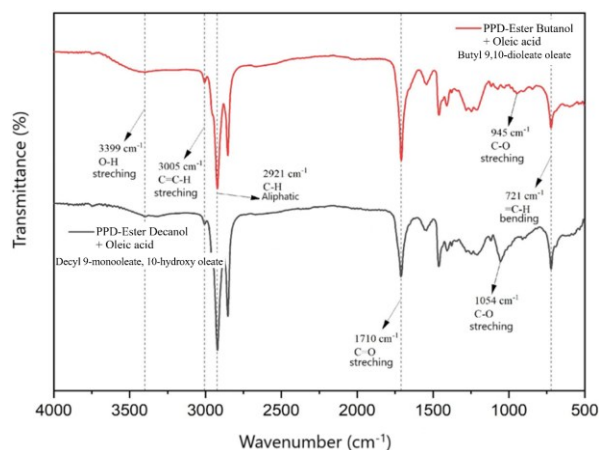


Figure 7. FTIR spectra of advanced esterification with oleic acid

Table 2. FTIR summary for each reaction

| Type of bond  | Type of vibration | Wavenumber (cm <sup>-1</sup> ) |                         |                           |                    |                    |                                 |                                 |
|---------------|-------------------|--------------------------------|-------------------------|---------------------------|--------------------|--------------------|---------------------------------|---------------------------------|
|               |                   | Oleic acid                     | 9, 10 epoxy-oleate-acid | 9,10 Dihydroxy-Oleic acid | PPD-Esther Decanol | PPD-Esther Butanol | PPD-Esther Decanol + Oleic acid | PPD-Esther Butanol + Oleic acid |
| O-H           | Stretching        | -                              | -                       | 3338                      | 3329               | 3358               | 3399                            | 3399                            |
| C-H aliphatic | Stretching        | 2921                           | 2922                    | 2918                      | 2919               | 2925               | 2922                            | 2921                            |
|               |                   | 2854                           | 2853                    | 2849                      | 2850               | 2855               | 2852                            | 2852                            |
| C=O           | Stretching        | 1706                           | 1708                    | 1558                      | 1559               | 1547               | 1710                            | 1709                            |
| C=C           | Stretching        | 3005                           | -                       | -                         | -                  | -                  | 3004                            | 3005                            |
| C-O           | Stretching        | 933                            | 1213                    | -                         | 1056               | 1031               | 1054                            | 945                             |
|               |                   |                                | 932                     | -                         | -                  | -                  | -                               | -                               |
| O-H           | Bending           | 1285                           | 1410                    | 1421                      | 1422               | 1410               | 1246                            | 1242                            |
| =C-H          | Bending           | 1450                           | 722                     | 695                       | 720                | 708                | 1461                            | 1460                            |
|               |                   | 719                            | -                       | -                         | -                  | -                  | 721                             | 721                             |

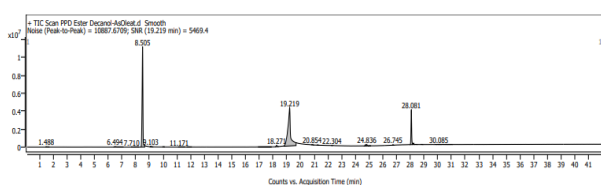


Figure 8. GC chromatogram of decyl 9-monooleate, 10-hydroxy oleate

Table 3. Major compounds identified in decyl 9-monooleate, 10-hydroxy oleate

| Peak number | Retention time (minute) | Molecule weight (g) | % Area | Description                    |
|-------------|-------------------------|---------------------|--------|--------------------------------|
| 8           | 8.08                    | 140.16              | 29.38  | 1-Decanol                      |
| 14          | 19.21                   | 280.26              | 48.36  | Octadecenoic acid / Oleic acid |
| 23          | 28.08                   | 422.42              | 22.26  | Decyl oleate                   |

3.3. GC-MS

GC-MS was used in this study to identify the compounds present in the oleic acid derivative samples, specifically in the PPD-Ester Decanol + Oleic Acid sample (Decyl 9-monooleate, 10-hydroxy oleate). The chromatogram obtained from this analysis is shown in Figure 8. Based on Figure 8, 32 peaks were observed, with retention times ranging from 1.48 to 31.03 minutes. Among these, three peaks are used to identify the major compounds in the PPD-Ester Decanol + Oleic Acid sample. The summary of the major compounds in the sample, based on these three peaks, is provided in Table 3.

3.4. Density

The density determination results are presented in Table 4, showing relatively similar values for each PPD, except for the centrifuged decanol PPD-ester. Density measurement determines the mass per unit volume of a sample. A higher density than crude oil benefits the synthesized PPD by enhancing the mixing process, promoting homogeneity, and increasing van der Waals interactions between PPD molecules and paraffin wax.

Table 4. Density of crude oil and synthesized PPD

| Sample                                       | Mass of empty pycnometer (g) | Mass of pycnometer + sample (g) | Density (ρ) (kg/m <sup>3</sup> ) |
|--|------------------------------|---------------------------------|----------------------------------|
| Crude Oil                                    | 13.667                       | 17.903                          | 844.8                            |
| PPD-Ester Butanol                            | 13.667                       | 18.722                          | 1,001.0                          |
| PPD-Ester Decanol (centrifuged)              | 13.667                       | 17.990                          | 864.6                            |
| PPD-Ester Butanol + Oleic Acid               | 12.321                       | 17.654                          | 1,066.6                          |
| PPD-Ester Decanol + Oleic Acid (centrifuged) | 12.321                       | 17.465                          | 1,028.8                          |
| PPD-Ester Decanol + Oleic Acid (solid)       | 12.321                       | 17.490                          | 1,033.8                          |

3.5. Pour Point Test

Pour point testing in this study was conducted using the ASTM D-5853 method, specifically designed for crude oil samples. The pour point test aimed to evaluate the effect of adding synthesized PPDs, derived from oleic acid reactions, on crude oil samples.

Pour point measurements of crude oil samples revealed that three of four synthesized PPDs lowered the pour point. The blank sample's pour point was 39°C, typical for heavy oil. The oleic acid injection did not alter the pour point. PPD-EB was ineffective, while PPD-ED reduced the pour point by 3°C to 36°C at 7.5% and 10% concentrations. PPD-Ester reacted with oleic acid and showed a significant reduction. PPD-EBOA and PPD-EDOA both lowered the pour point by 9°C to 30°C. The interaction between PPDs and the paraffin content in oil involves strong van der Waals forces. This interaction inhibits wax deposition and reduces the viscosity of crude oil.

Table 5. Pour point test result

| % PPD | Point depressant (°C) |             |         |         |            |            |
|-------|-----------------------|-------------|---------|---------|------------|------------|
|       | Blank                 | PPD variant |         |         |            |            |
|       | Crude oil             | +Oleic acid | +PPD-EB | +PPD-ED | +PPD-EB+OA | +PPD-ED+OA |
| 0     | 39                    | -           | -       | -       | -          | -          |
| 5     | -                     | 39          | 39      | 39      | 30         | 30         |
| 7.5   | -                     | 39          | 39      | 36      | 30         | 30         |
| 10    | -                     | 39          | 39      | 36      | 30         | 30         |

Total volume = 5 mL

EB: Ester Butanol

ED: Ester Decanol

OA: Oleic Acid

#### 4. Conclusion

Oleic acid derivatives were successfully synthesized with yields of 96.72% for PPD-Ester Butanol and 72.21% for PPD-Ester Decanol through esterification with alcohols. Further esterification with oleic acid yielded 47.30% for PPD-Ester Butanol + Oleic Acid and 22.56% for PPD-Ester Decanol + Oleic Acid. Pour point measurements on crude oil samples were conducted according to ASTM D-5853. The blank sample's pour point was 39°C. PPD-Ester Decanol reduced the pour point by 3°C, while all PPD-Esters further esterified with oleic acid reduced it by 9°C. Chemical characterization via FTIR analysis revealed functional groups such as C=C, C=O, and aliphatic C-H. GC-MS analysis of PPD-Ester Decanol + Oleic Acid (decyl 9-monooleate, 10-hydroxy oleate) identified three major compounds: 1-decanol, oleic acid, and decyl oleate. Physical characterization showed average densities of synthesized PPDs ranging from 850 to 1,066 kg/m<sup>3</sup>.

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