WAX AGGREGATION INHIBITION IN CRUDE OIL BY OXIRANE ESTER COPOLYMER

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ABSTRACT

Wax deposition can cause a serious problem in the distribution process of crude oil through a pipeline. At low temperatures, wax molecules can interact to form a wax aggregate. One way to reduce the wax aggregation is to introduce an additive compound into the crude oil. In this study, 15 crude oil models were prepared by mixing gasoline, kerosene, oil, wax, and asphaltene. Oxirane ester copolymer (OEC) additive was introduced into the crude oil models with various concentrations and volumes, and its effect on the crude oil models' pour point and viscosity were evaluated. OEC interactions with wax and asphaltene were observed by FTIR, and the wax aggregation process was observed using cross polarized microscopy (CPM). The optimum pour point of crude oil was reached at a temperature of $6^{\circ}C$ and optimum viscosity at 10 cSt for the selected model 4. OEC additions of 5% and 10% require 500 and 300 μL, respectively, to achieve the optima pour point and viscosity. OEC was able to inhibit the wax aggregation, as evidenced from the interaction between OEC-wax at 722 cm^{-1} and OEC-asphaltene at 1604 and 1494 cm^{-1} of FTIR spectra. The distribution of the wax aggregate was observed using CPM, with the value of the wax appearance temperature (WAT) at $28.7^{\circ}C$. This research can be the basis for designing or selecting a molecule for use as a pour point depressant in accordance with the characteristics of crude oil, particularly since each source of crude oil has different characteristics.

Keywords: Crude oil; Inhibition process; Oxirane ester copolymer; Pour point; Wax

1. INTRODUCTION

The main cause of clogged pipes in the distribution of crude oil is straight chain hydrocarbon (wax) with a high molecular weight (Ronningsen et al., 1991). When the crude oil temperature is below the wax appearance temperature (WAT), the wax solubility drastically decreases, and the wax deposits on the pipe wall. Wax crystals quickly form and trap the crude oil until it cannot flow at low temperatures and high wax contents (Soldi et al., 2007). Temperature decrease causes further wax deposits and forms interlocked crystals that can trap the crude oil (Elsharkawy et al., 2000). The main factor causing oil temperature decrease is the temperature difference between the oil and its environment. There are four mechanisms of deposited wax formation: molecular diffusion, Brownian diffusion, shear dispersion, and gravitational settling (Burger et al., 1981).

Minimizing wax deposition inside the pipe can be done with a thermal method, mechanical cleaning, and additives (Newberry, 1984; Siringi et al., 2014). A pour point depressant (PPD)

or wax modifier is a chemical additive that can reduce the pour point and viscosity of crude oil (Chanda et al., 1998). A good PPD has three requirements. First, the PPD has a hydrocarbon chain. Second, it has polar groups to inhibit wax aggregation. Third, it consists of a polymer that is able to interact with the wax crystals, and those intermolecular interactions hamper wax aggregation (Wang et al., 1999). Hydrocarbon compounds, which have a similar alkyl chain length with that of wax, will interact and inhibit wax crystallization. The polar group of PPD also inhibits the growth of wax crystals (Wuhua et al., 2010).

There have been several studies on wax aggregation inhibition using a PPD, such as polymethacrylate (Soldi et al., 2007), polyacrylic acid derivative (Jiang et al., 2006), and ethylene-vinyl acetate copolymer (Machado et al., 2001). Soldi et al. (2007) investigated the role of polymethacrylate as a PPD in diesel oil. They reported that an oil sample with a polymer additive concentration of 50 ppm is capable of reducing the pour point of diesel oil down to 22 $^{\circ}$C. The polymer PPD (comb like polymer) has two types of interactions: nucleation and co-crystallization. This type of PPD has the chain structure of paraffin wax and a polar group. The polar group is used to inhibit crystal aggregation and to form a gel-like structure (Hemant et al., 2008). The surfactant has hydrophobic and hydrophilic groups that are capable of adhering to the surface of the wax crystals, inhibiting wax molecule aggregation and maintaining the dispersal system (Ahn et al., 2005).

In this study, we focused on the inhibition of wax aggregation with the oxirane ester copolymer (OEC) additive. This compound has a long chain that can interact with the wax, while the ester and oxirane groups interact with the asphaltene to inhibit the formation of wax aggregates. The crude oils in this study were prepared by adding wax and asphaltene into petroleum fractions, such as gasoline, kerosene, and oil. Wax was added into the crude oil models because it is a major component of clogged pipes due to the formation of wax aggregates.

2. METHODOLOGY

2.1. Material
Samples of petroleum fractions (gasoline, kerosene, and oil) were generally purchased from commercial stores; the wax source was from paraffin wax; the asphaltene source was from black bitumen. They were used for the preparation of the crude oil model. Oxirane ester copolymer (OEC), used as an additive, was obtained from the company in Indonesia. Toluene, used as a solvent, was obtained from Merck.

2.2. Preparation of Crude Oil Model
Fifteen crude oil models were made through the Odebunmi method (Odebunmi et al., 2002) with the minor modification of mixing 2.40 g of gasoline, 1.64 g of kerosene, 4.36 g of oil, and 1.53 g of residue, respectively. The residue consists of wax and asphaltene, with a wax/asphaltene weight ratio of 100/0, 99/1, 95/5, 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80, 10/90, 5/95, 1/99, and 0/100. Hereafter, the crude oil models are denoted as models 1-15, respectively. With the different crude oil models, we can make comparisons and evaluate the effective inhibition of wax aggregation and the most stable dispersion model.

2.3. Physical Properties of Crude Oil Model
Crude oil pour point was determined by ASTM D 5853. Crude oil flowability was observed at decreasing intervals of 3.0°C, and pour point was determined. Crude oil viscosity was determined using a Brookfield viscometer. Water and crude oil density (ρ) were determined using a pycnometer. Their specific gravity and the American Petroleum Institute (API) gravity were determined by:

$$SG = \frac{\rho\ sampel}{\rho\ air} \tag{1}$$

$$API\ gravity = \frac{141.5}{SG} - 131.5 \tag{2}$$

2.4. Effect of Oxirane Ester Copolymer in a Crude Oil Model

Concentration variations of oxirane ester copolymer (OEC) were prepared at 2%, 5%, and 10% wt in toluene. OEC volumes of 20, 50, 70, 100, 300, 500, 700, and 1000 μL were added into 10 mL of crude oil, and their pour points were determined.

2.5. Characterization

High temperature gas chromatography (HTGC; Agilent Technology 7890A) was used to determine the wax carbon chain length. Wax appearance temperature (WAT) before and after the addition of OEC to the crude oil model were measured using cross polarized microscopy (CPM) employing a Nikon polarizing microscope L plan SLWD20i to observe the growth of wax aggregates. In this measurement, the sample in the capillary tube was put into the CPM compartment, heated at a rate of 5.0°C/min to 55.0°C, and the temperature stability was maintained. The cooling of the sample was done at a rate of -0.1°C/min to -10.0°C. Characterization of OEC and its interactions with wax and asphaltene were performed using FTIR spectroscopy (Shimadzu, Prestige 21).

3. RESULTS AND DISCUSSION

3.1. Preparation of Crude Oil Model

At room temperature, the crude oil models 1-3 were deposited and formed a two-phase system. A higher wax content leads to a shorter distance between wax molecules, facilitating hydrophobic bonds to form wax aggregates and, thus, a two-phase system. The wax has a length of carbon chain C_{26}-C_{41}, as characterized using HTGC. For crude oil models 4-15, for which the ratio of wax/asphaltene was reduced, the higher amount of asphaltene hardly causes wax aggregation because there is an interaction between the wax and the asphaltene that inhibits the interaction of wax intermolecules to produce a stable dispersion system like in a natural crude oil, as illustrated in Figure 1.
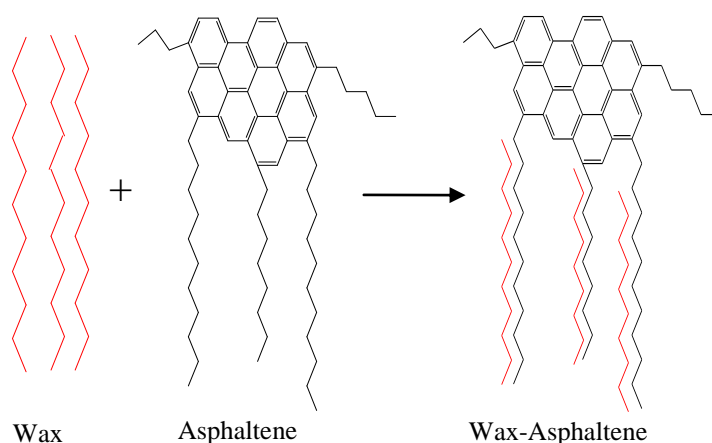

Figure 1 Illustration of interactions between the long alkyl chain of wax with asphaltene

3.2. Weight Ratio Effect of Wax/Asphaltene to Pour Point of Crude Oil

Model 1, which had the highest wax content, had the highest pour point at 25.0°C, because the close distance between wax molecules promotes aggregation and traps the crude oil. For models

2-11, the pour point decreases with wax content reduction, as shown in Figure 2, because the distance between the wax intermolecules increases. We note that crude oil models 12-15 had pour points below -10.0°C.
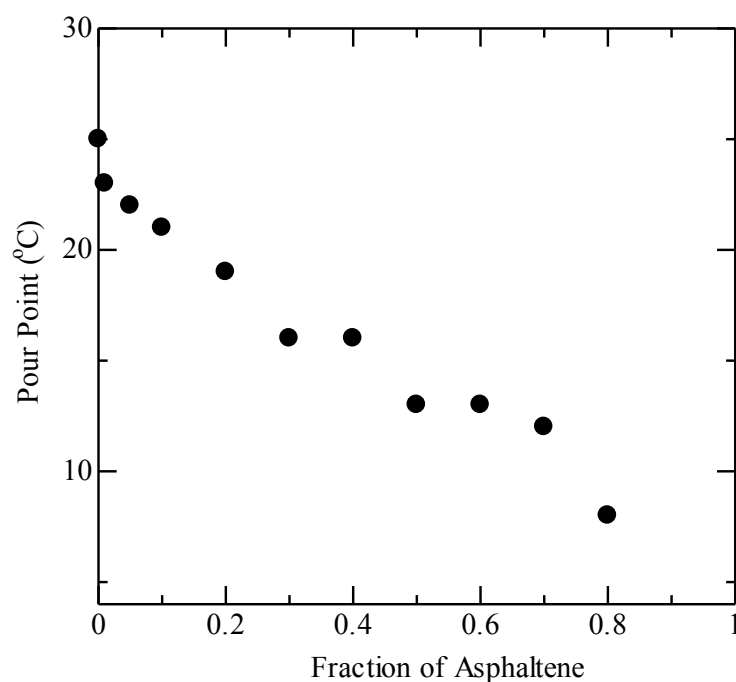

Figure 2 Fraction of asphaltene from wax-asphaltene mixture against the pour point of the crude oil model

3.3. Weight Ratio Effect of Wax/Asphaltene to Viscosity of Crude Oil

Crude oil models 4-11 were selected for viscosity measurements. Models 4, 5, 6-7, and 8-11 had viscosities of 30, 20, 15, 10 cSt, respectively. This suggests that the viscosity of crude oil decreases with a decreasing wax content. For the crude oil models 4-11, model 4 had the highest viscosity, as the highest amount of wax content caused the highest possibility for the wax intermolecular aggregations that trap the crude oil, making it more viscous. Crude oil model 4 was chosen to evaluate the effect of the OEC addition because it had the highest pour point and viscosity, a stable dispersion system with a density of 0.8216 g/mL, a specific gravity of 0.8257, and an API gravity of 39.8697. This crude oil model was categorized in light oil because the API gravity value is above 31.1.

3.4. OEC Addition Effect in Crude Oil Model

3.4.1. *Variation of OEC concentration against pour point of crude oil*

Figure 3 shows the decrease in the pour point of crude oil against the concentration and volume of the added OEC. The OEC molecules interact with the wax molecules, inhibiting the formation of the wax aggregates that trap the crude oil and leading to a decrease in the pour point. The optimum pour point decreases to 6.0°C with the addition of 300 μL OEC 10% or 500 μL OEC 5%, while the addition of 1000 μL OEC 2% decreases the pour point to 9.0°C.
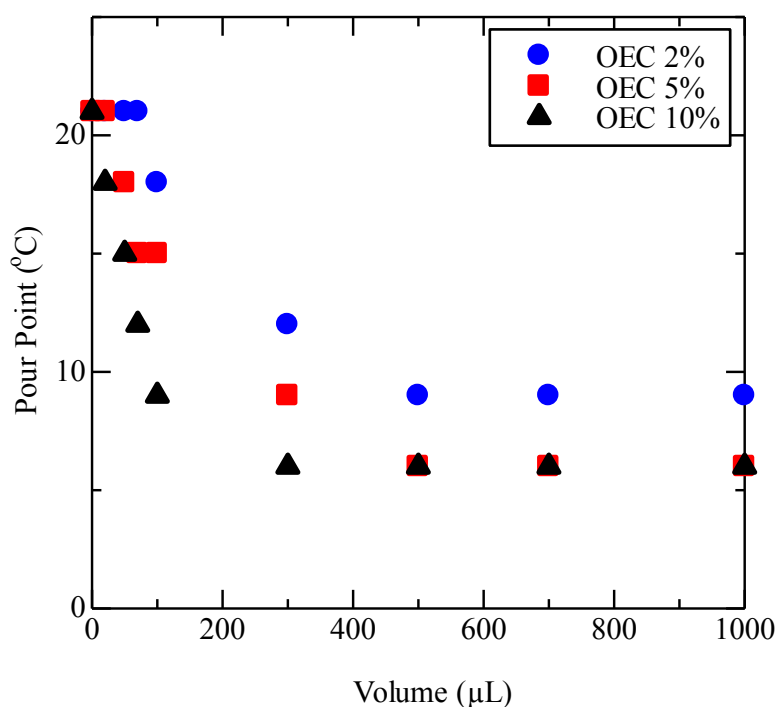
Figure 3 Variation of concentration and volume of OEC against pour point of crude oil

3.4.2. *Variation of OEC concentration against viscosity of crude oil*

The crude oil models' viscosities were measured at the added OEC volume conditions of: 1) 0μL, 2) 20μL, 3) at optimum pour point, and 4) 1000 μL at concentrations of OEC 2%, 5%, and 10%, as shown in Table 1. The higher the concentration and volume of OEC, the higher the possibility of interacting with the wax, inhibiting the aggregation of wax molecules. In this sense, the addition of OEC increases the shear rate of the molecules in crude oil, creating a decrease in viscosity.

Table 1 Crude oil viscosity values to volume additions of OEC 2%, 5%, and 10%

Volume (μL)	Crude oil viscosity (cSt)		
	OEC 2%	OEC 5%	OEC 10%
0	30	30	30
20	30	30	30
300	-	-	10
500	-	10	-
700	15	-	-
1000	15	10	10

3.5. Study of Wax Aggregation in Crude Oil Model using CPM

The wax aggregation process in crude oil can be studied through WAT measurements before and after OEC additions by using CPM to observe the growth of wax aggregates. Before the OEC addition, wax aggregate formation did not occur at 55.0-33.3°C (Figure 4a, dark area); the first wax aggregate was observed at 32.9°C, according to the WAT value of the crude oil, due to the interaction of the wax intermolecules (Figure 4b, light area). More wax aggregate was observed, and it was more homogenously distributed, at 21.0°C, forming networks and trapping the crude oil (Figure 4c). The network of wax aggregate almost covers the space of the entire

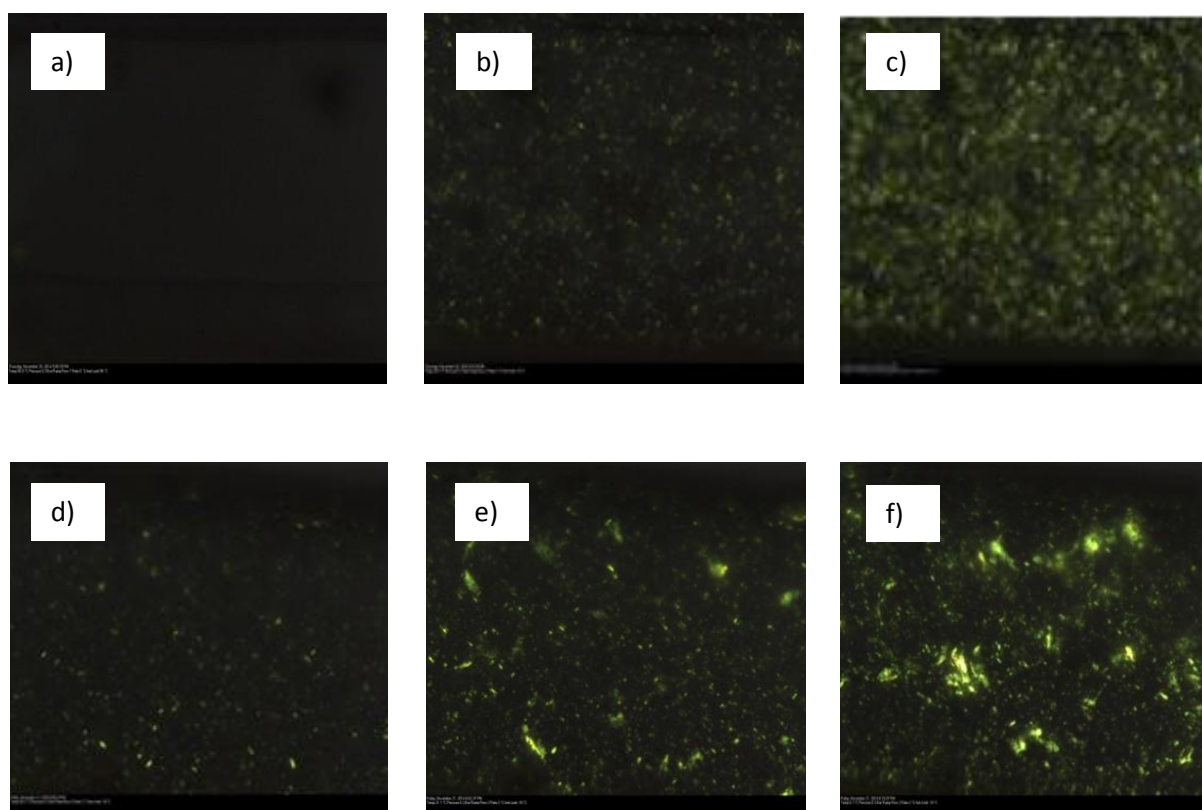sample, stopping the crude oil flow. This is consistent with the pour point of crude oil at 21.0°C.

Figure 4 Image of wax aggregate growth in crude oil using CPM before the additions of OEC at: (a) 55.0°C; (b) 32.9°C; (c) 21.0°C, and after the additions of OEC at: (d) 28.7°C; (e) 21.0°C; and (f) 6.0°C

We have evaluated the effect of OEC addition against wax aggregation inhibition in crude oil. Figures 4d, 4e, and 4f show images of wax aggregates in crude oil at the optimum condition with an addition of 300 μL OEC 10%. In our experimental conditions, the formation of wax aggregate did not occur at 55.0-29.0°C. Wax aggregate first formed at 28.7°C (Figure 4d), according to the WAT value of crude oil, with the addition of OEC. This value is lower than that in crude oil with an absence of OEC (32.9°C). The presence of OEC molecules inhibit wax aggregate growth through a hydrophobic interaction between long chains of the OEC alkyl group with wax molecules, lowering the WAT value. When the temperature is lowered to 21.0°C (Figure 4e), wax aggregate formation was smaller than that without the addition of OEC, indicating that the wax network is hampered due to the interaction of wax and OEC, enabling the crude oil to continue flowing. At lower temperatures, the wax molecular dynamics decreased, although it was inhibited with OEC. Wax aggregate growth at lower temperature was also observed. The temperature decrease causes a decrease in the intermolecular dynamics, and the interaction between the wax molecules and the OEC increases. As a result, the amount of wax aggregate formation increases. This issue was clearly evidenced for lowered temperatures down to 6°C. At this condition, the wax aggregate growth was observed to form a network of aggregates like a heterogeneous cluster that inhibited the movement of crude oil, causing it to no longer flow (Figure 4f). This value is the pour point of crude oil after OEC addition, and it is in agreement with the results determined using the pour point measurement method shown in Figure 3.

3.6. Interaction Study of OEC with Wax and Asphaltene in Crude Oil Model

The existence of OEC molecules in the wax-asphaltene crude oil model was characterized using FTIR spectrophotometer. The molecular structure of the OEC compound is shown in Figure 8. As shown in Figure 5, the FTIR spectrum of OEC shows vibrational bands at 2932 and 2851 cm^{-1}, related to the stretching vibration of the –CH group, and around 722 cm^{-1}, related to the vibrations of a long chain carbon of the hydrophobic group (Suryanaraya et al., 1990). The vibrational band at 1732 cm^{-1} is due to the –C=O of the ester group, while those at 1160 and 1054 cm^{-1} are attributed to the oxirane group, and those at 1604 and 1494 cm^{-1} are related to the aromatic group. Similarly, the FTIR spectrum of the wax molecules (Figure 5) shows the vibrational bands at 2918 and 2852 cm^{-1} are for stretching vibration, and the bands at 1467 and 1379 cm^{-1} are for the bending vibration of the -CH group. The frequency vibration of a long chain carbon of the hydrophobic group appears at 722 cm^{-1} (Suryanaraya et al., 1990). When wax was mixed with OEC (Figure 5), the vibrational band at 722 cm^{-1} strengthened due to the hydrophobic bond of the long chain carbon of both compounds. The new spectrum was also observed at 1744 cm^{-1}, related to the ester carbonyl group of the OEC molecule, which is large enough to shift from the ester carbonyl group of pure OEC at 1732 cm^{-1}. This shift is due to the interaction between the carbonyl group of wax and the long chain alkyl groups near the OEC carbonyl group, thus affecting the vibrational energy of the ester carbonyl group. The same thing was observed due to the interaction; a new spectral band appeared at 1606 and 1496 cm^{-1} for the aromatic ring of the OEC molecule on wax, and it shifted to 1604 and 1494 cm^{-1} for pure OEC. This shift is very small because the aromatic ring is located quite far from the alkyl chains' bond. The presence of OEC oxirane on the wax bond was shown with the appearance of a spectrum at 1170 and 1080 cm^{-1}, which shifted from 1160 and 1054 cm^{-1} of the pure OEC oxirane group due to the position of the oxirane group at the long chain alkyl terminal that interacted with the wax.
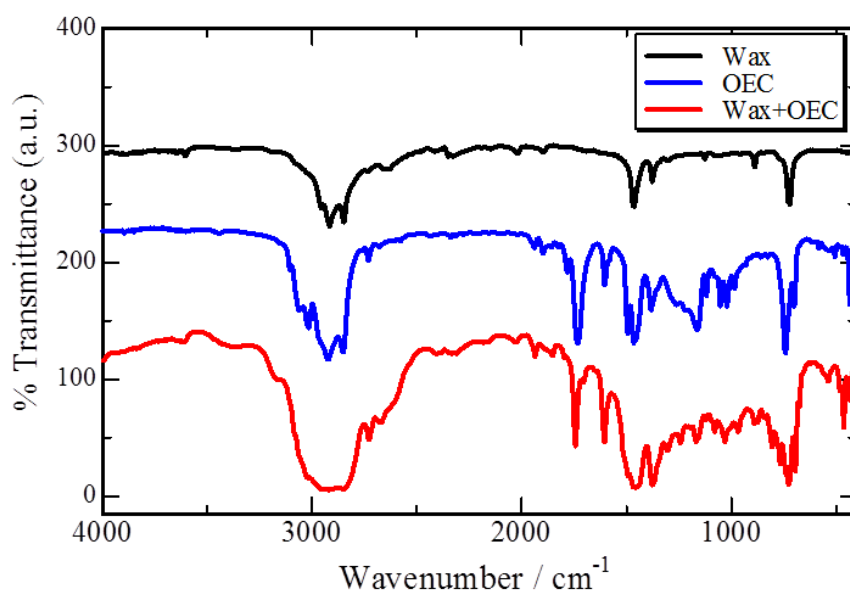

Figure 5 FTIR spectra of wax, OEC, and OEC-added wax

The interaction between the OEC additive and asphaltene was also studied through FTIR characterization, as shown in Figure 6. Asphaltene shows the spectrum at 2925 and 2854 cm^{-1} due to the stretching vibration of the -CH group and at 1460 and 1378 cm^{-1} due to the bending vibrations of the -CH group. Spectral bands at 1607 and 1492 cm^{-1} indicate the presence of an aromatic ring. Weak spectral bands at 722 and 1744 cm^{-1} are related to low cross sections of long alkyl chains and the carbonyl group, respectively. When asphaltene was added into OEC,

the strengthening of spectral bands at 1605 and 1494 cm^{-1} indicate the interaction of the aromatic groups from both compounds. However, the increase in intensity of bands at 722 and 1744 cm^{-1} are related to additional long alkyl chains and the OEC carbonyl group, respectively.
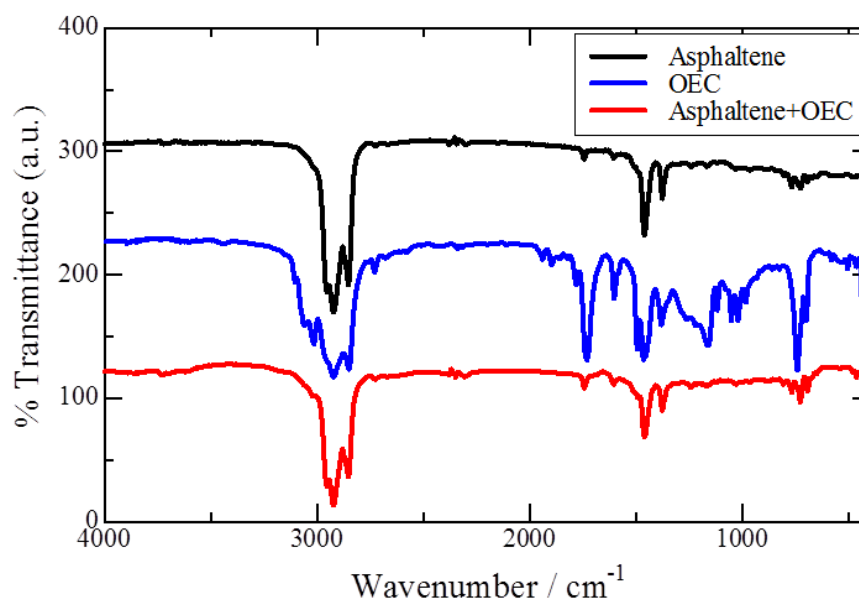

Figure 6 FTIR spectra of asphaltene, OEC, and OEC-added asphaltene

Interactions between OEC with wax and asphaltene in a crude oil system were also observed by FTIR, as shown in Figure 7. The spectrum of the crude oil model is similar with that of wax or asphaltene. The OEC's interaction on the wax was mainly characterized by the strengthening of the spectrum at 722 cm^{-1}, due to the hydrophobic bond of the long chain alkane from both compounds, while the OEC attached on the asphaltene was particularly characterized by the strengthening of spectra at 1604 and 1494 cm^{-1}, related to the interaction of the aromatic groups from both compounds.
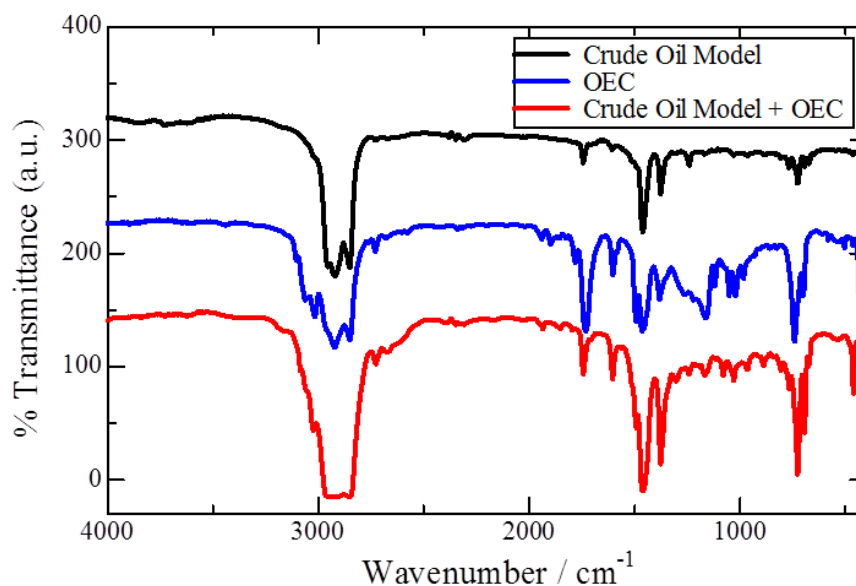

Figure 7 FTIR spectra of crude oil model, OEC, and OEC-added crude oil model

The appearance of an additional strong band of the ester carbonyl group at 1743 cm^{-1}, which was shifted from 1732 cm^{-1}, and those of the oxirane group at 1168 and 1078 cm^{-1} blue, shifted from 1160 and 1054 cm^{-1}, confirmed the presence of OEC interaction with wax and asphaltene in the crude oil model. The presences of gasoline, kerosene, and oil in crude oil showed the strengthening of vibrational bands due to the stretching vibrations of the -CH group at 2925 and 2854 cm^{-1} and the bending vibrations of the -CH group at 1460 and 1378 cm^{-1}. The main constituents of the three compounds are the alkane hydrocarbon compounds, which act as a natural solvent for wax, asphaltene, and OEC. These solvents indicate the crude oil flow was blocked by a wax aggregate network, and this network could be inhibited in the presence of asphaltene and the OEC additive.

From the overall characterizations, we proposed that the OEC additives interact with wax on its long chain of the alkyl group, while they interact with asphaltene via their aromatic groups, as shown in Figure 8. These interactions inhibit the wax aggregate formation, resulting in the reductions in the crude oil model's pour point, viscosity, and WAT value.
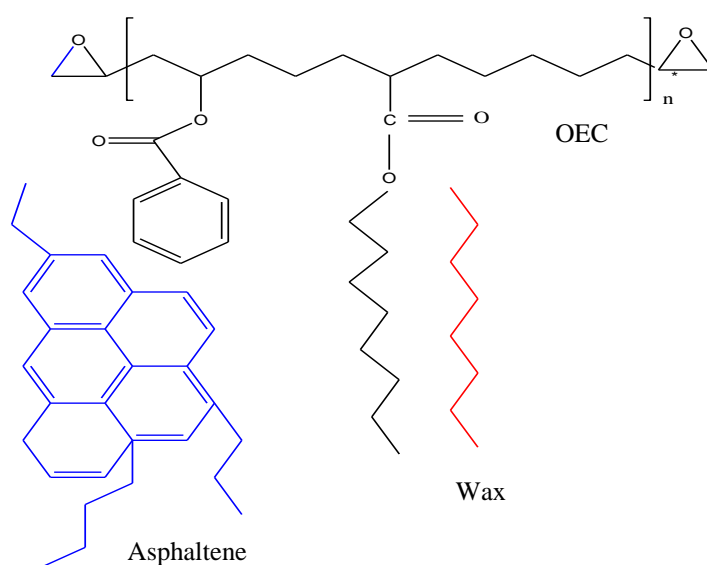

Figure 8 Proposed interaction illustration of OEC with wax and asphaltene

4.   CONCLUSION

The inhibition of wax aggregation in a crude oil model with OEC has been studied using FTIR, CPM, WAT, pour point, and viscosity measurements. We found that the weight ratio of wax/asphaltene had a significant effect upon the value of the crude oil's pour point and viscosity. The higher amount of asphaltene hardly causes wax to aggregate, thus it produces a stable dispersion system. The addition of OEC in the selected crude oil model, which contains a weight ratio of wax/asphaltene = 90/10, is capable of decreasing the pour point from 21.0 to 6.0°C, the viscosity from 30 to 10 cSt, and the WAT value from 32.9 to 28.7°C. From the experimental results, we proposed the interaction mechanism in which the OEC in crude oil could interact with wax on its long chain of the alkyl group, while it interacts with asphaltene via its aromatic groups. These interactions inhibit wax aggregate formation and decreases the crude oil's pour point, viscosity, and WAT value.

5.   ACKNOWLEDGEMENT

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