Comparison of pour point depressant (PPD) ethylene-vinyl acetate (EVA) and nano-montmorillonite

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Abstract. One of the problems with oil production is stuck of oil transportation flow in the pipeline caused by wax deposits. The high wax content in crude oil causes the oil viscosity value to increase so that crude oil has High Pour Point Oil (HPPO) properties. In this research, using crude oil sample with initial pour point of 31°C and viscosity of 556 cP. This samples are classified as heavy oil. Therefore, this sample is suitable for use as an experiment in this research. There are several methods to deal with HPPO. One chemical method used to overcome this problem is adding Pour Point Depressant (PPD) to crude oil. This PPD functions to decrease pour point value by binding wax crystals in crude oil. In this study, two types of PPD were compared, Ethylene-Vinyl Acetate (EVA) and Nano-Montmorillonite (Nano-MMT). Both can reduce the pour point value on crude oil, but PPD EVA shows a more excellent reduction than nano-MMT. The results show that EVA is better at binding crystals than nano-MMT. After the injection of 400 ppm EVA, the pour point value of crude oil could be decreased up to 24°C, and the viscosity also decreased by 185 cP.

1. Introduction
In general, the type of crude oil in Indonesia is a heavy oil classified as high pour point, some examples of crude oil with the HPPO category can be seen in Table 1. With the highest pour point value at a temperature of 39 °C. Operating conditions below the pour point temperature will impact the production shift that causes it to record the flow due to blockage from the wax deposits in the pipeline to the crude oil storage. If this happens, then the volatile components contained in crude oil will be evaporated so that the concentration of heavy fraction of crude oil increases. It is caused by a decrease in pressure which causes the driving efficiency and flow of heavy fractions to decrease. The flow of petroleum causes the possibility of forming wax deposits quickly because the crude oil contains wax or paraffin, asphaltene, and resin.

Table 1. Examples of petroleum fields in Indonesia that have HPPO characteristics.

| No. | Name of Fields       | Wax Content (%) | Pour point (°C) | References |
|-----|----------------------|-----------------|-----------------|------------|
| 1.  | Pinag, Riau          | n.a             | 39              | [1]        |
| 2.  | Minas, Riau          | 10.8            | 36 – 38         | [2]        |
| 3.  | Duri, Riau           | 16              | 22              | [2]        |
| 4.  | Sepanjang, East Java | 24.9            | 49              | [3]        |
Paraffin or wax is a colorless, odorless, crystalline substance that can be solid or semi-solid. Paraffin is not easy to react with other chemical compounds (inert), but at high temperatures, a small part will be oxidized or broken (cracking), insoluble in water and alcohol but soluble in petroleum and benzene fractions. Paraffin is a highly saturated hydrocarbon compound (paraffin). In the distillation process, it is also distilled after gas oil. The resulting wax is classified into several types according to the melting point: 45-52°C, 55-57°C, and 63-66°C. Two main parameters affect the solubility of wax in oil under ambient conditions, namely temperature, and composition, while pressure has a minimal effect on wax formation in oil compared to the two parameters above. The flow of crude oil containing wax, with several indicators analyzed such as Wax Appearance Temperature (WAT), pour point temperature (PP) or cloud point temperature (CP), and gel strength.

This wax component can be dissolved in petroleum (crude oil) and condensate in a liquid phase. The solubility of paraffin wax is very sensitive to temperature changes. Temperature changes are factors that affect the process of formation of wax crystals. Paraffin wax remains dissolved in crude oil while in the reservoir and is in equilibrium with petroleum in thermodynamics. Similar to the asphaltene deposition event, when the thermodynamic equilibrium begins to be disturbed, such as a change in temperature or pressure, the paraffin will crystallize or begin to precipitate due to the loss of the volatile light end in petroleum, where the volatile fraction in petroleum seems to if acts as a solvent for paraffin wax. When this mixed fluid begins to cool, each wax component will separate (become insoluble) until finally, the wax component with a high molecular weight will solidify (solidify). The event where the wax crystals first form at a specific temperature is called the onset of wax crystallization or better known as the cloud point or Wax Appearance Temperature (WAT). When the reservoir fluid temperature drops to a temperature T, paraffin hydrocarbons with a solidification temperature greater than T will tend to precipitate and separate from the solution. The following is a schematic illustration of the thermodynamics of a wax deposit.

The P-T of crude oil describes about the process of wax formation, where the blue area with a low temperature is the area for the formation of wax. Provides an interesting review of the wax deposit measurement technique and states that there is a serious problem in the field with the presence of wax during production, so that plugging is often encountered in the tubing pipeline and some areas—surface production equipment [6]. Due to too many wax deposits in the piping system, pigging activities will be carried out more often. Wax crystals, when they appear, will change the flow behavior of an oil fluid from Newtonian to non-Newtonian conditions. Wax crystals will also cause the oil's viscosity to flow in the pipeline by increasing energy consumption and decreasing pumping capacity. In addition, wax deposits also increase the pipe's roughness and reduce the pipe's cross-sectional area, resulting in increased pressure drop in the pipeline system.

Three factors contribute to the formation of wax deposits in flowing systems including flow rate, temperature difference, cooling rate, and the surface condition [7]. The wax can form a precipitate or crystal as the flow temperature decreases below the cloud point or Wax Appearance Temperature (WAT). This phenomenon can impede flow in a piping system by triggering non-Newtonian fluid behavior. The viscosity of petroleum can increase as the operating temperature reaches the pour point (the minimum temperature at which the liquid phase becomes semi-solid and can flow). Therefore, the
newly deposited paraffin wax layer begins to stick, which can further narrow the area of the pipe [8]. Of course, this can cause various technical problems, so it is necessary to prevent wax deposition in the piping system. One way that can be humiliated in dealing with wax deposition is to use Pour Point Depressant (PPD) as a chemical method that aims to reduce the value of the pour point and viscosity of crude oil with several advantages, such as saving costs, energy, and production time [9,10,11].

Wax inhibitors, commonly referred to as PPD (Pour point depressants), need to be added to crude oil before the wax crystallizes, which is wax inhibitors can only work effectively in a very narrow range, which also depends on the composition of the oil. Therefore, it is necessary to design different treatments for each field with different petroleum compositions. Fang, 2012 describes a strong relationship between the specific efficiency of PPD and the composition of crude oil. PPD can effectively change the structure and morphology of wax crystals to prevent wax deposits that can form a rigid three-dimensional network at low temperatures. Conventional PPDs are homo- or copolymers of a wide variety of monomers. Ethylene-vinyl acetate (EVA) copolymer is the most commonly used copolymer. In modern theory, the mechanism of EVA as PPD includes adsorption, co-crystallization, nucleation, and improving the solubility of wax in petroleum. The higher the vinyl acetate composition increased, the more polarity of the polymer and dissolved in the oil. However, increasing vinyl acetate can reduce co-crystallization in PPD with wax. EVA with 18-30% vinyl acetate is commonly used as PPD [13,14].

EVA (Ethyl Vinyl Acetate) is a copolymer made from two different types of monomers, namely ethylene and vinyl acetate. The first ethylene copolymers, including EVA, were synthesized and patented in 1930 IC-1 Great Britain in the same laboratory where polyethylene was discovered [14]. EVA copolymers are synthesized through the copolymerization process of ethylene and vinyl acetate at high pressure and temperature and by the bulk polymerization process [9]. Bulk polymerization is the most frequently used technique for producing EVA copolymers containing up to 50% vinyl acetate. Another copolymer used as PPD is nano-montmorillonite (MMT). The commonly used method is to use pure EVA or another PPD, namely nano-montmorillonite (MMT). A new generation of PPDs based on nanotechnology, including nanocomposites, has attracted much attention in recent years. Nano-silica and modified montmorillonite nano-clay have been very populated in recent studies [15]. Montmorillonite is a type of clay that is widely found in bentonite rocks with the chemical formula (Na, Ca)(Al, Mg)₆(Si₂O₁₀)₂(OH)₆·nH₂O (Hydrated Sodium Calcium Aluminum-Magnesium Silicate Hydroxide) [16]. See the advantages of PPD EVA and MMT in reducing pour point and viscosity values of crude oil, with high pour point and viscosity values. so that we will compare the two performances of the PPD in order to increase the effectiveness of the production [17,18,19].

2. Methodology

Look at The advantages of PPD EVA and MMT in reducing pour point and viscosity values of crude oil, with high pour point and viscosity values. Therefore, in this study, we will compare this study. The following tools and materials were used, Viscometer Ostwald Cannon-Fenske for Transparent Liquid, measuring cup, oil bath, Cleveland Open Cup Apparatus, Magnetic Stirrer, Stirrer rod, sample crude oil, PPD Ethylene-Vinyl Acetate, PPD nano-Montmorillonite. Meanwhile, the initial step is to heat the crude oil sample to a temperature of 50°C, then pour it into 200 ml cylindrical bottles. Then add PPD into crude oil, with variables PPD EVA and MMT with the same dose of 0 ppm, 200 ppm, 300 ppm, 400 ppm, and 500 ppm. Next, pour point and viscosity analysis was performed on the oil sample—the two performances of the PPD in order to increase the effectiveness of the production.

For the preparation of PPD EVA material which has a melting point temperature of 80°C – 120°C, which means that for this initial step, the PVA that will be used in the study is up to a temperature above the melting point for 2 hours so that all EVA compounds can be ensured to melt completely. Then EVA is dissolved into petroleum with a predetermined variable dose. The initial treatment that needs to be done for PPD MMT is to put MMT into a beaker glass, pour toluene into a beaker glass that already contains MMT, then stir using a magnetic stirrer while heated at 80°C for 2 hours. After two hours, continued heating at a temperature of 120°C until the toluene in the beaker evaporated. After that, nano-MMT is obtained, which is ready to be mixed into the crude oil sample.
2.1. Pour point analysis

Pour point is defined as a temperature point when oil does not flow when cooled under certain conditions. The crude oil sample is placed in a closed tube then the tube is inserted into the cooling mixture (substance) where there is no direct contact between the tube containing the oil and the refrigerant used, namely ice and water [20]. Determination of pour point can be used equation,

\[
\text{Pour Point} = \text{Temperature} + 3 \quad \text{..................................................}(1)
\]

Cleveland open cup apparatus for pour point measurement on oil samples have a several part, there are:

1. Sample to be tested
2. Thermometer
3. Pour point detector
4. Test jar
5. Cooling medium
6. Inlet cooling medium
7. Outlet cooling medium
8. Jacket
9. Temperature detector of cooling medium
10. Air cavity

Firstly, the oil sample is filtered from dissolved substances in it can be removed, and then the sample is inserted into a test cylinder which is equipped with a cork and a thermometer to the mark. The capillary tip of the thermometer should be submerged approximately 3 mm from the surface of the oil sample. Furthermore, the test cylinder is put into a cooling bath with a temperature far below the pour point temperature of the oil sample. Every 3°C decrease in temperature, the biodiesel change was observed by flowing the oil sample horizontally. If there was no movement for 5 seconds, then this value was the measured pour point value.

2.2. Viscosity analysis

The fluid's viscosity is related to the resistance to the forces that move the fluid in one layer against another. The viscosity produced by force in the dyne striking two horizontal planes a distance of 1 unit between them flows a viscous fluid. The unit of viscosity is dyne second/cm² which is proportional to 1 poise (dynamic unit), while the kinematic viscosity has units of cm²/second. Oil viscosity is highly dependent on temperature pressure. While the tool used to determine the viscosity is the Ostwald Viscometer type Viscometer Cannon-Fenske for Transparent Liquid. The sample to be tested for viscosity is inserted into the Ostwald viscometer, then blows the sample using a rubber bulb until the sample is at the top of the boundary mark, then the sample is allowed to drop, and records the time it takes to pass the two marks. The time it takes to pass that mark will be recorded as “t.” This time is used to measure the viscosity of the sample solution at each concentration. Clean the viscometer tube with toluene, dry it and blow it with air to clean it from toluene.

3. Result and discussion

The crude oil sample used has properties with a property in high pour point value or can also be referred to as (High Pour Point Oil) of 31°C, and other physical characteristics can be seen in the Table 2.

| Properties                    | Methods       | Analysis Result |
|-------------------------------|---------------|-----------------|
| Temperature of measurement    |               | 30 °C           |
| SG                            |               | 0.844           |
| Density at 15°C               | ASTM D-1298   | 0.8539          |
| API Gravity at 60 °F          | ASTM D-187    | 33.71           |
| Water content (%vol)          | ASTM D-95     | -               |
| BS&W (%vol)                   |               | 0.2             |
| Pour point                    | ASTM D-96     | 31 °C           |
| Viscosity                     |               | 556 cP          |
Figure 1. The relationship between EVA and nano-MMT PPD Dosage on Pour point in crude oil samples.

Figure 1 shows the effect of EVA and nano-Montmorillonite copolymer PPD doses, which reduced the pour point value significantly. So it can be concluded that the Pour point value decreases with the addition of pour point depressant EVA chemicals. The addition of a bit of chemical pour point depressant EVA can reduce the viscosity value of crude oil. The alkyl group causes it on the pour point depressant absorbs the wax crystal content in the oil and prevents the growth of wax crystal formation; in addition to the addition of chemical pour point depressant prevents the absorption of oil by the wax crystals. Wax can become crystals due to paraffin, which interacts and lock into each other at low temperatures.

Meanwhile, the PPD nano-MMT succeeded in reducing the pour point value in the crude oil sample. The pour point value of the crude oil samples decreased from 31°C to 30°C, 28°C, 25°C, and 24°C. These phenomena can happen because the nano-MMT molecules absorb the wax crystal content in crude oil and prevent hardened wax deposits from forming, hindering the transportation of crude oil.

Figure 2. The relationship between EVA and nano-Montmorillonite PPD Dosage on the viscosity of crude oil samples
Viscosity is a measure of the viscous fluid which states the size of the impact in the liquid. The greater the viscosity value in a fluid, the more difficult it is for a fluid to flow and the harder it is for an object to move within it. In Figure 2 shows us that both of PPDs can reduce the viscosity of the crude oil sample. At a dose of 200 ppm, the viscosity is decreased to 445 cP for EVA PPD and 512 cP for nano-MMT PPD. Meanwhile, at 300 pm, there was a decrease in viscosity to 300 cP for PPD EVA and 380 cP for PPD nano-MMT. Then at a dose of 400 ppm, there was a decrease in viscosity to 185 cP for PPD EVA and 240 cP for PPD nano-MMT. Furthermore, at a dose of 500 ppm, there was a decrease in viscosity to 150 cP for PPD EVA and 210 cP for PPD nano-MMT. It can be concluded that there is a decrease in every PPD dose added. It is caused by the presence of PPD in the sample, thereby reducing the viscosity value.

The decrease in the viscosity value shown in nano-MMT was not as significant as the decrease in the value indicated by EVA because EVA molecules are better at binding wax crystals than nano-MMT. The wax crystals' content, abundant in crude oil, is the leading cause of hardened wax crystal deposits and clogging transportation pipelines. When PPD is mixed in oil samples, PPD will bind to wax crystals, preventing precipitation. In addition to PPD EVA to pour point and viscosity, the higher the dose of PPD given, the lower the viscosity and pour point of the sample. In general, the ambient temperature in the piping system is around 27-30°C, which means that pour point temperatures below 27°C can be recommended. Then the PPD EVA dose of 400 ppm can be chosen to be advised, which sees the pour point value, which decreases by 26%, and viscosity by 185 cP with a decrease of 67%, where crude oil with a viscosity can flow well. While the addition of PPD nano-MMT to the pour point and also the viscosity of the sample. The more doses added to the oil mixture, the lower the pour point and viscosity. Similar to EVA, injection at a dose of 400 ppm is recommended because it is seen from the 19% decrease in pour point and 57% decrease in viscosity which is the best result among the other doses. In addition to PPD EVA to pour point and also viscosity.

4. Conclusion
The viscosity value of the oil will decrease according to the number of doses of PPD mixed into the oil. More PPD molecules because it binds to wax crystals in the oil content. PPD ethylene-vinyl acetate (EVA) showed better results in lowering the pour point of oil than nano-Montmorillonite (nano-MMT). Crude oil added the optimum dose of PPD EVA at 400 ppm with a decrease in pour point of 26% and a decrease in viscosity of 67%.

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