Comparative study of wax inhibitor performance for pour-point reduction of oil from Sirikit Oilfield in Thailand

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Abstract. In petroleum industries, waxy crude oil is normally found in petroleum production. Wax formation and precipitation during pipeline transport of waxy crude oils can cause several challenges, including wax deposition and flow reduction which adversely impacts pipeline performance in oil and gas production. To overcome the wax deposition problem, the small amount of chemicals like wax inhibitors can provide an effective preventative measure. One of this mechanism is to reduce the pour point temperature. In this work, oil from Sirikit Oilfield in Thailand is selected for this study. The wax inhibitors are selected and studied the performance for pour-point reduction. These chemicals are Polyalkyl methacrylate (PAMA), Poly(maleic anhydride-alt-1-octadecane) (PMAO), Polyalkyl methacrylate-co-ethylene glycol (PAMAEG) and Copolymers of maleic anhydride (CPMA) with the concentration ranging from 100 to 1000 ppm. Also, n-pentane with the concentration of 5-20 % by weight is used as a solvent for wax inhibitors. The results from this study show that n-pentane can reduce the pour point to 39.41 % compared to the original oil. Furthermore, among the polymer group, PMAO can reduce the lowest pour point to 52.82 %. In addition, the mixed solvents of polymer with n-pentane can provide relatively less effect on pour-point reduction. The mixture of n-pentane with PMAO can lower the pour point to a certain level of 54.96 % compared to the original oil. This study can be applied to use in the real field to prevent wax deposition in the pipeline transportation for oil production.

1. Introduction
Waxy crude oils contain some amounts of wax and paraffin. When the temperature decreases, the wax starts to precipitate and forms the crystals [1]. In the presence of other forms of hydrocarbon such as the cyclic hydrocarbons, the structure of wax molecules can change from linear and/or branching to cyclic form including aromatic ones. This can result in the serious effects on the melting points and on the wax solubility in crude oil [2]. An evaluation of the effect of some parameters in wax precipitation can mitigate this problem [3]. The crystal formation of these molecules could be the reason for the solid wax formation in crude oil; thus, resulting in the reduction of its fluidity [4]. Furthermore, the severity of wax deposition problem is also relied on the type of crude oil and on the composition of the wax molecules in the crude oil. The pour point of the oil portion is also the important characteristic of crude oil that can lead to flow assurance in oil production and transportation.
The wax formation in crude oil with high pour-point temperature can cause major problems in production, transportation and storage of oil including an increase in oil viscosity and pressure drop in pipeline, a high yield stress for flow return, wax deposition on the pipeline surface and a decrease in equipment performance for oil production; thus increasing the costs of oil production [5].

Recently, some studies have discussed on pour point reduction, but generally it is on the basis on wax deposition and pour-point reduction that researchers have divided the commonly used methods to solve the problem of wax deposition into three groups: 1) mechanical methods, 2) thermal method by using heat and 3) chemical method by using solvents to removal wax [6]. In these current years, most research works have focused mainly on chemical methods to prevent wax precipitation even though they cannot completely prevent wax precipitation in pipelines. Therefore, chemical additives will be the one of the main factors for the performance of chemical method especially with the mechanism of wax crystal modifiers (inhibitors) and pour point depressants [7].

In recent studies, many researchers have investigated the effect of additives on crude oils or a mixture of them as discussed above. For this study, many additives such as Poly(maleic anhydride-alt-1-octadecane) (PMAO), Polyalkyl methacrylate (PAMA), Polyalkyl methacrylate-co-ethylene glycol (PAMAEG) and Copolymers of maleic anhydride (CPMA) with the concentration ranging from 100 to 1000 ppm will be studied as a wax inhibitors for pour-point reduction. Also, n-pentane with the concentration of 5-20 % by weight is used as a solvent in crude oil.

Therefore, the objective of this research is to investigate and compare the effects of different additives on the pour-point temperature of oil sample from Sirikit Oilfield. Moreover, the effect of concentration of each additives on pour-point reduction is also studied. The result of this study can be used as a fundamental data for additives screening for pour-point reduction in the real field in the future.

2. Materials and methods

2.1 Materials

The oil for this study is obtained from the PTT Exploration and Production Public Company Limited, Sirikit Oilfield in Thailand with the density 0.85 g/cm³ at 70 °C. The oil composition from Sirikit Oilfield is presented in Table 1. The main oil composition is C16-C20 ranging for 21.63 %. N-pentane is purchased from Ajax Company with AR grade. Polymers like poly(maleic anhydride-alt-1-octadecane) (PMAO), polyalkyl methacrylate (PAMA), polyalkyl methacrylate-co-ethylene glycol (PAMAEG) and copolymers of maleic anhydride (CPMA) for this work are ordered from Sigma Aldrich Company. The chemical structure of these additives are illustrated in Figure 1.

| Percent by weight (%) | Percent by weight (%) |
|-----------------------|-----------------------|
| C6-C10                | 17.6                  |
| C11-C15               | 16.8                  |
| C16-C20               | 21.6                  |
| C21-C25               | 18.1                  |
| C26-C30               | 16.2                  |
| C31-C35               | 9.7                   |
2.2 Experimental procedures
Initially, to do the pour-point measurement, the procedure is arranged to follow the Standard Test Method for Pour Point of Crude Oils or ASTM D97, as presented below:

The crude oil sample is set to pretreat the oil for testing and it is cooled inside a cooling bath in order to form the paraffin wax crystals. It is kept at about 9 °C above the expected pour point. For every 3 °C, the test container is removed and tilted to check for the surface movement. When the sample does not flow when tilted, the container is held horizontally for 5 sec. If it does not flow, 3 °C is added to the corresponding temperature and the result is the pour point temperature. However, it should be warned that the flow of the sample can be affected by its viscosity. Therefore, the pour point may give a misleading result of the properties of the oil.

3. Results and discussion
3.1 Effect of N-pentane on pour-point reduction
The concentration of n-pentane for this study is ranged from 5-20 % weight. The results is presented in Figure 2. From the results, it is clearly seen that the pour-point temperature is reduced from 37.3 °C to 22.6 °C or 39.4% as the n-pentane concentration increases because of the wax and heavier fractions in the crude oil can dissolve more in n-pentane; thus making the oil more flowable.

3.2 Effect of additives on pour-point reduction
The concentration of polymeric additives for this study are varied from 100-1000 ppm. The effect of additives on pour-point reduction are shown in Figure 3-6 for single additives and a mixture with n-pentane. It can be seen that among these polymers, PMAO can reduce the pour-point temperature to the lower level for 52.8% at 1,000 ppm concentration followed by PAMA, CPMA, PAMAEG and EVAGMA for 40.8%, 37.5%, 30.8% and 29.5%, respectively.

Furthermore, the effects of polymer combined with solvent, 20% n-pentane, are also investigated and presented in the figure. From the results, the pour-point temperature is reduced with an increase in polymer concentration. Moreover, like that of single additive, the pour-point temperature can be lowered with the mixed additives at the concentration of 1000 ppm of PMAO for 55.0% followed by PAMA, CPMA, PAMAEG and EVAGMA for 48.5%, 46.4%, 46.1% and 43.7%, respectively.
Figure 2. Effect of N-pentane on pour-point reduction.

Figure 3. Effect of PMAO on pour-point reduction.

Figure 4. Effect of PAMA on pour-point reduction.

Figure 5. Effect of PAMAEG on pour-point reduction.

Figure 6. Effect of CPMA on pour-point reduction.

It can be concluded that adding n-pentane can increase the performance of polymer additive for pour-point reduction. The reason is that polymer can prohibit the formation of wax. At the same time, the solvent can dissolve the heavier fraction into liquid. Therefore, the oil can flow in the pipeline.

4. Conclusions
In the petroleum production, wax formation and precipitation can be found in production and transportation from waxy crude oil causing oil flow reduction. To solve this problem, the small amount of wax inhibitors or solvent can prevent wax deposition, reduce the pour point temperature and increase
flow assurance. In this study, oil from Sirikit Oilfield in Thailand is selected to evaluate and compare the performance of four polymers for reducing pour-point temperature. These chemicals are Polyalkyl methacrylate (PAMA), Poly(maleic anhydride-alt-1-octadecane) (PMAO), Polyalkyl methacrylate-co-ethylene glycol (PAMAEG) and Copolymers of maleic anhydride (CPMA) with the concentration ranging from 100 to 1000 ppm. In addition, n-pentane with 5-20 % by weight is provided as a solvent for wax inhibitors. The results present that n-pentane can reduce the pour point to 39.41 % compared to the original oil. Moreover, among the polymer additives, PMAO can provide the lowest pour point reduction to 52.82 % for a single chemical. Also, the mixed solvents of polymer with n-pentane can provide relatively less effect on pour-point reduction. The mixture of n-pentane with PMAO can lower the pour point to a certain level of 54.96 % but can increase more performance with other polymers. This work can be used as a fundamental data to apply in the real field to prevent wax deposition in the pipeline transportation.

5. Acknowledgement
The authors would like to acknowledge the Chevron Thailand Exploration and Production, Co., Ltd. for financial support. Also, the authors would like to thank PTT Exploration and Production Public Company Limited for oil sample.

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