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Optimization Study on the Effects of Shear Rate and Concentration of Inhibitor on Wax and Asphaltene Deposition from Crude Oil using Copolymer and Aromatic Compounds

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In this study, the effects of shear rate and an ethylene-vinyl acetate (EVA)-based wax inhibitor towards the viscosity of crude oil was investigated. The viscosity of crude oil decreased when the shear rate increased and the most effective shear rate (in terms of rotational speed) was 100 rpm, which could reduce viscosity as high as 62.96% compared to the lowest shear rate applied (20 rpm). The EVA-based wax inhibitor could reach up to 80.66% of viscosity reduction of crude oil original viscosity when the weight percentage of EVA, methylcyclohexane (MCH) and *para*-xylene (PX) were 10.00%, 45.78% and 44.22%, respectively. PX was used as the asphaltene depressant along with the inhibitor. An optimization study evaluated that the most optimum conditions were found to be 10.00%, 40.09% and 49.90% respectively for EVA, MCH and PX.

Key words: Wax inhibitor, shear rate, viscosity, ethylene-vinyl acetate (EVA), optimization

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Crude oil, which plays an important role as an energy source, is depleting around the world. Crude oil is a mixture of numerous hydrocarbon chains. However, the mixture of the carbon and hydrogen chains also contain other elements, such as sulphur, nitrogen and oxygen [1-9]. Due to the different percentages of the hydrocarbon chains in crude oil, the physical and chemical properties also vary widely.

Heavy straight chain paraffinic waxes are hydrocarbons that contain carbon atoms ranging from C18 to C36, while microcrystalline waxes consist of branched and cyclic hydrocarbons where the carbon atoms range from C30 to C60. Gelling of wax within the pipelines below the wax appearance temperature (WAT) will inhibit the flow of crude oil by causing the fluid to act as non-Newtonian fluid where the viscosity of crude oil increases as temperature reaches its pour point [10,11]. On the other hand, when the temperature of the pipeline walls is below the WAT, the formation and deposition of a layer of paraffin molecules will be promoted [2-12]. This layer can grow over time which will cause the diameter of the pipelines to decrease and constrict the flow of crude oil [13]. This problem usually arises in deep-sea environments as the temperature of the water in the subsea can reach as low as 5ºC, even in warm climate [14].

A few methods to control and manage wax deposition have been practised by oil production companies to manage the problems that arise due to wax deposition. The strategies implemented are based on one or combination of several methods, such as pipeline pigging, thermal insulation and pipeline heating, and chemical (inhibitor) injection [4,13,14]. There are several drawbacks to pipeline pigging such as identifying the solid formation and the specific location of the precipitation, the cost for maintenance which is quite high considering the pipelines which are underground and having to halt all operations throughout the maintenance process which may take a very long duration and loss of profit. Thus, it is suggested to perform such maintenance less perform. There is a very logical relationship between temperature and paraffin solubility. The removal of paraffin deposits from downhole tubular and piping equipment is usually done using high temperatures to dissolve the deposited wax. The most common way of thermal treatment is the use of hot oil or hot water, while less commonly used methods are based on direct burning, explosives and electricity [15]. Chemical treatment is the most commonly used treatment of all, owing to the fact that it eradicates the deposits in the shortest possible time and also alters the flow properties of waxy crude oil, resulting in prevention and inhibition of paraffinic deposition at low temperatures. Chemical methods also act as very effective remediation via the use of solvents which were also found to be a good and powerful treatment for deposition in production strings and also may be applied to remediate formation damage. Many researches had been conducted over the years to formulate inhibitors that can give maximum efficiency [2-21].

Wax prevention techniques have gained an increased interest by researchers. Wax inhibitors such as pour point depressants and wax dispersants are used to chemically modify the wax solid structure thus reducing the tendency of wax crystals to interlock and form three dimensional network growths [16-18]. Wax inhibitors or wax crystal modifiers are chemical compounds that have the same chemical structures as the wax that is precipitating. This type of materials will agglomerate with wax by occupying the hydrocarbon chains of wax molecules on the crystal lattice. As an addition, the inhibitor will hinder the wax crystal growth, which in turn reduces the pour point of crude oil [19].

The most widely used polymer as wax inhibitor is ethylene-vinyl acetate (EVA). The chemical structure of EVA has a straight chain which consists of a polyethylene portion of various lengths that are dependent on the number of the vinyl acetate groups. EVA has been highly recognized to have the ability to control the size of wax formed [19,20]. Nonetheless, the optimum conditions for the highest reduction in viscosity have not been widely considered.

On the other hand, asphaltenes are commonly defined as the heavy fraction from the oil constituents that are insoluble in low boiling point paraffin (n-pentane and n-heptane) but soluble in aromatics (toluene) [21]. If asphaltenes are present in abundant in crude oil, they will give a significant effect on the behavior of the oil. It is found that dilution of crude oil with aromatic solvents, especially toluene, will depress the flocculation of asphaltenes in crude oil [22,23]. However, other types of aromatic solvents have not been extensively investigated.

The aim of this study was to investigate the effectiveness of wax and asphaltene inhibitors in reducing the viscosity of crude oil and to evaluate the most efficient composition of EVA, methylcyclohexane (MCH) and *para*-xylene (PX) in reducing wax and asphaltene formation. In selecting the suitable solvents, it is known that wax inhibitors are usually a combination of active compounds dissolved in organic solvents. It is found that dilution of crude oil with aromatic solvents, especially toluene and xylene will depress the flocculation of asphaltene in crude oil [22,23]. A method that is useful for developing multiple parameters together with their interactions is response surface methodology (RSM) [2,3,7,24,25]. RSM is a method that utilizes the collection of mathematical and statistical data for improvement and optimization of a process. In this study, the optimization of the viscosity of crude oil was done by RSM using D-optimal. The analysis of the results was used to determine the optimum combination for the inhibitor and the shear rate to give maximum reduction in viscosity.

METHODOLOGY

Preparation of crude oil

The crude oil used in this research was obtained from Sabah platform, Malaysia. Thus, the type of crude oil is known as Malaysian crude oil where it contains higher fractions of asphaltene compared to wax fraction. Prior to the experiment, the crude oil was heated in an oven at 90°C overnight to melt any primitively formed wax crystals and asphaltene agglomerates [2,3,5,6].

Preparation of inhibitor

EVA with 40wt% of vinyl acetate (EVA40), MCH and PX were obtained from Sigma-Aldrich with purity >99%. Prior to mixing of the inhibitor, EVA40, MCH and PX were heated in a water bath at 50°C. The individual chemicals, EVA, MCH and PX were measured separately of their respective weight in accordance to the manipulated percentage composition. EVA, MCH and PX were measured in grams of mass. The total weight of inhibitor used was 2% of the weight of crude oil used [2,3,5,6].

Viscosity experiment

The sample and the inhibitor were mixed and shaken for about 30 s. The mixed sample was then placed in the oven for 15 min to allow the reaction to take place. Using an ice bath, the sample's temperature was reduced to 5ºC to imitate the subsea environment [2,3,5,6]. Viscosity measurement was conducted using Brookfield Programmable Viscometer DV-II + Rheometer. The equipment was arranged as shown in Figure 1.

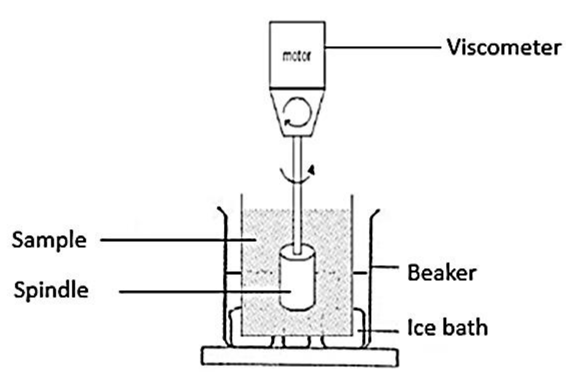

Figure 1. The schematic diagram of the experiment.

The viscosity of each sample was tested using three different rotational speed, 20 rpm, 50 rpm and 100 rpm. The configurations for the viscometer are shown in Table 1.

Design of experiments using RSM

Using Design Expert 7.0 program, the optimization of the viscosity of crude oil can be done using RSM by using D-optimal. The parameters involved in the optimization were concentration of EVA, MCH and PX and rotational speed.

The software was used to generate 16 runs for combinations of three variables listed in Table 2. The operating parameters for the experiment were followed the 16 combinations.

RESULTS AND DISCUSSION

Effects of shear on wax and asphaltene deposition

The viscosity of crude oil affected by the stirrer speed, which can also be treated as shear rate, is presented in Figure 2.

Table 1. Independent variables and their coded levels using user defined design.

Spindle size	**63**
Rotational speed	20, 50, 100 rpm
Readings	Viscosity (cP) Torque (%)

Table 2. Independent variables and their coded levels using D-optimal.

Independent variables	**Range and levels**		
	-1	0	+1
Concentration of EVA (wt%)	10	40	70
Concentration of MCH (wt%)	10	40	70
Concentration of PX (wt%)	10	40	70
Rotational speed (RPM)	20	60	100

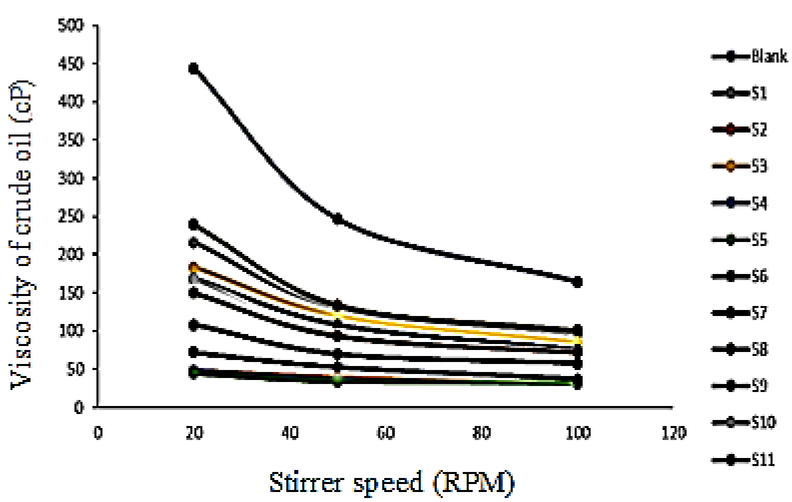

Figure 2. Viscosity of crude oil against stirrer speed.

The trend is not the reflection of the performance of the inhibitor. Instead, it is purely the result of the effect of shear rate towards the viscosity of crude oil for different combinations of wax inhibitor. It can be observed that the viscosity of crude oil decreases with the increase of the shear rate. This is due to the decreasing wax deposition with increasing shear rate [7,26-28]. As shown in Figure 2, 100 rpm of shear rate produced the best result for all samples, which was up to 62.96% of viscosity reduction compared to at 20 rpm when performed with blank crude oil. At 0 rpm, or also called as zero-shear, the viscosity is very high or impossible to measure. This is because the decrease in viscosity can only be measured starting from a very low shear rate [26].

As proven by previous studies, EVA has been commonly used as crystal modifiers as it has the ability to control the size of wax crystals formed. This could also significantly reduce the size of wax crystals and turn the shape of crystals from plate-like to spherical with denser morphology [16,17,19].

Development of regression model equations using mixture design in D-optimal

The model in terms of actual responses of viscosity of crude oil at 100 rpm was regressed by mainly considering the significant terms and expressed by equation 1:

$$Viscosity\ (cP) = -1.15145A - 0.55703B + 1.36018C + 0.04023AB + 0.03AC - 0.0228BC + 1.44 \times 10^{-3}ABC - 1.52 \times 10^{-4}AB(A-B) + 7.599 \times 10^{-4}AC(A-C) + 6.69 \times 10^{-4}BC(B-C) \quad (1)$$

where A, B and C represent weight percentage of EVA, MCH and PX, respectively.

Effects of inhibitor on wax and asphaltene deposition

Table 3 shows that there is no specific trend for combinations of parameters to give the greatest effect towards the viscosity of crude oil. The highest viscosity observed was in sample 8, where the weight percentage were 33.38%, 33.29% and 33.33% of EVA, MCH and PX respectively, which gave the result of 100.8 cP. On the other hand, viscosity was the lowest for sample 4, which was 31.8 cP at 10.00%, 45.78% and 44.22% of EVA, MCH and PX, respectively. These observations were obtained based on RSM, which is expressed by equation 1. The reduction of the viscosity when it was the lowest could reach up to 80.66% reduction from the original viscosity.

Statistical analysis

Based on the results of the analysis of variance (ANOVA), it was proven that the model was extremely significant ($p = 0.001$) and the coefficient determination R^2 was 0.9840, which indicated 98.40% of the variability in the response and can be explained by the model and less than 2% of the total variations could not be explained by the model. The adjusted determination coefficient value (Adj. R^2 = 0.9601) was within reasonable agreement with the predicted R^2 of 0.9840 and it also strongly indicated the significance of the model.

Table 3. Viscosity of crude oil for combinations of EVA, MCH and PX.

Sample	Weight percentage (wt%)			Viscosity (cP)
	EVA	MCH	PX	
Blank	-	-	-	164.4
1	51.41	19.79	28.80	96.0
2	10.00	79.99	10.01	32.4
3	42.53	10.00	47.47	85.2
4	10.00	45.78	44.22	31.8
5	10.02	10.00	79.98	33.3
6	20.00	23.12	56.86	37.2
7	58.87	31.13	10.00	57.6
8	33.38	33.29	33.33	100.8
9	40.81	49.19	10.00	75.6
10	70.00	10.33	19.67	72.0
11	19.03	58.21	22.76	73.2

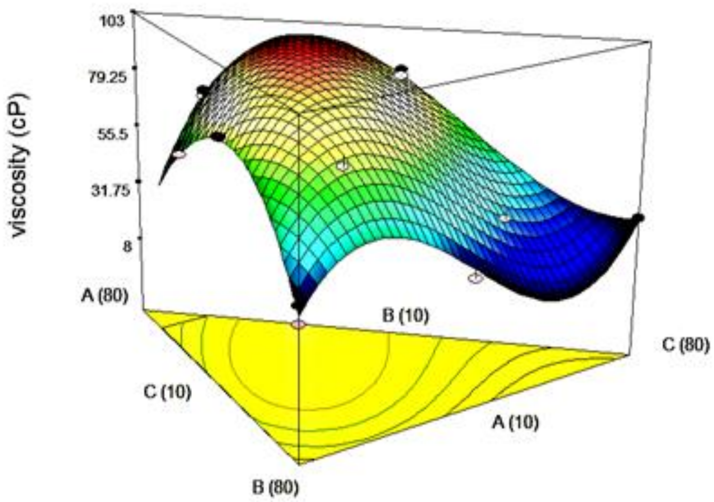

Figure 3. Response surface curve (3D plots) of viscosity (cP) of crude oil for the combination of EVA (wt%), MCH (wt%) and PX (wt%) as wax and asphaltene inhibitor.

Effects of individual variables and their interactions

It was revealed that linear mixture components (A, B, C) and their interactions [AB, AC, ABC, AC(A-C) and BC(B-C)] are significant model terms as their p-values were less than 0.0500. Term B, which represented the weight percentage of MCH did not give significant effects as it was solely used to assist the melting of EVA only [11]. It did not serve any purpose in inhibiting the wax or asphaltene deposition. Figure 3 shows the three-dimensional (3D) plots of the combined effects of the three parameters for the viscosity of crude oil.

Figure 3 shows the effect of weight percentage of EVA (A), MCH (B) and PX (C) on the viscosity of crude oil. Terms A and C, and the combination of these two parameters (AC) gave the greatest effect on this model as A (EVA) is the polymer that works as the inhibitor and C (PX) functions as the asphaltene depressant [14,19].

Process optimization

The optimization of the combination of EVA, MCH and PX to improve the viscosity of crude oil was carried out by using Design-Expert software 7.0 (Stat-Ease, Inc., Minneapolis, MN 55413, USA). The optimum combination for the three variables is presented in Table 4. Under these optimization conditions, the viscosity obtained was 23.6 cP. The deviation of the result obtained from the predicted optimized combination is about 7.6%. Nonetheless, this optimized conditions further increased the viscosity reduction up to 85.64%.

It was discovered that the efficiency of the inhibitor to improve the flow can go as high as 36.6% viscosity reduction. However, in this study it was found that the optimized conditions could further reduce the viscosity up to 85.64%. Thus, the result agrees with the hypothesis that the chemical inhibitors studied improved the flow assurance of crude oil.

Table 4. Optimized condition for every parameter.

Variables	Target/Goal	Optimized condition
EVA (wt%)	In range	10.000
MCH (wt%)	In range	40.097
PX (wt%)	In range	49.903
Responses		
Viscosity of crude oil (cP)	Minimize	21.932
Desirability	1.000	

CONCLUSION

In a nutshell, applying shear rate on crude oil reduces viscosity as shear rate increases. The best shear rate observed in this study was 100 rpm. Usage of EVA-based wax inhibitor will assist the inhibition of wax in crude oil. The result could reduce viscosity up to 80.66% of the original viscosity. PX has been observed to aid in depressing the asphaltene formation along the wax. Three parameters, EVA, MCH and PX, as wax and asphaltene inhibitors, were optimized to give the lowest viscosity of crude oil. The results from the optimized conditions showed a deviation of 7.6% from the predicted viscosity.

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