Development of Demulsifier for Malaysian crude oil – Effect of ASP and Polymer flooding

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Abstract
With growing global demand and depleting reserve for crude oil, Enhanced Oil Recovery (EOR) takes center stage in research industry. Chemical EOR method can be implemented easily because it needs fewer facilities to add chemicals in injection water. Among the chemical methods, alkaline-surfactant-polymer (ASP) is the most prominent method because it works on the synergy of alkaline, surfactant and polymer. The combination of these three components are the next generation technology designed to provide tolerance to extreme salinity and also produces higher mobility control in the EOR crude. In this study, a synthetic surfactant is injected simultaneously with alkaline chemicals such as sodium carbonate into the Malaysian crude during the bottle test to create EOR emulsion. Besides that, water soluble polymer was also injected with the mixture of alkali and surfactant to increase the viscosity of the sample as well as to improve the mobility of the flood fronts. However it was found that, the emulsion formed will be higher and tighter when the amount of ASP added increases. Thus, determining the right concentration of ASP in the injected water will give an effective separation of emulsion in crude oil processing.

Keywords— crude oil; ASP flooding; EOR; emulsion

I. INTRODUCTION
Crude oil is usually produced with water, which causes several problems during oil production [1]. Water emulsion that is produced during crude oil processing cause
operational interruption in the gas-oil separating plants such as tripping and shorting of the separating equipment. Moreover, the formation of emulsions is a very costly problem, which increases the capital cost in pipeline and processing equipment, because the volume of dispersed water occupies valuable space and causes high shear and turbulence near the wellbore, over valves or in other process equipment. Emulsions should be treated to eliminate the water emulsion in order to meet crude requirement and to reduce corrosion in crude oil processing. Therefore, the proposed solution is to develop a novel demulsifier to eliminate emulsion and separate water from oil efficiently.

However, in early years there was a clear decline in the oil production globally. To increase the oil production, EOR techniques have shown a marked improvement in the extraction of crude. The EOR method can be done by gas injection, chemical injection, ultrasonic stimulation, microbial injection or thermal recovery [2]. This research paper focuses on chemical injection of Alkaline Surfactant Polymer (ASP) technique.

ASP flooding consists of a complex mixture of chemicals injected to the crude in order to obtain low interfacial tension between the oil and the rock formation [3]. This is done by increasing the viscosity of injected fluid and decreasing the oil in water mobility ratio between the injectant and the displaced oil [4]. However, the main problem that arises from ASP flooding is the production of the tight micro-emulsion which influences the emulsion stability [5]. Emulsion that is created by chemical flooding is difficult to break because of the extremely high concentration of the polymer additive, which tightly bind with the oil and water. The additive can decrease the size of oil droplets, increase the surface charge of oil droplets and increase the film elasticity [6].

Generally, polymer flooding gives a major increase in oil recovery compared to water flooding techniques. Polymer flood technique is done by mixing and injecting polymer together with other additives like surfactant into the brine. When only water is injected into a reservoir, usually the layers with higher permeability will flow to the lower pressure area of the producing wells. If the oil has a higher viscosity compared to the injected water, the water will pass through this oil. Thus, the results will be lower sweep efficiency and a loss in recovery [7]. To improve the sweep efficiency, polymer injection is done. Besides that, polymer injection is able to decrease the mobility contrast between water and oil.

II. OBJECTIVES

The main objective of this research paper is to formulate a suitable demulsifier for Malaysian crude oil type. The sub-objective is to determine the effect of ASP and polymer on the emulsion formation.
III. MATERIALS AND METHODOLOGY

Material
Experimental work was carried out on Malaysian crude oil which was supplied by PETRONAS Research Sdn Bhd (PRSB) together with the base demulsifiers that were used in the formulation. EOR emulsion is created by alkaline surfactant polymer which is used in the injected water.

Preparation of Injected water with ASP
Injected water is prepared based on the formulation given by PRSB. The salts content used in the brine preparation was made up of NaCl, NaHCO3, Na2SO4, CaCl2.2H2O, MgCl2.6H2O, KCl, BaCl2.2H2O, and SrCl2.6H2O at specific mass percent. Then, 25mL of ASP mixture was added into 1 L of prepared brine.

Demulsifier formulation
Finding a right demulsifier that works well is often done by trial and error. Demulsifier composition can be obtained by simply mixing the base demulsifier and solvents in certain ratios until a homogeneous solution is obtained without visible suspended particles, cloud or sediment.

Emulsion Tendency Test
The emulsion tendency test is conducted via the bottle test method. To create the emulsion, the dehydration tubes are filled with various percentages of brine water and crude. The test is conducted at 20%, 40%, 60% and 80% water cut. Followed by the tubes being inserted into the water bath for 10 minutes at 38°C to homogenize the sample. The tubes are then placed in a horizontal shaker and left for shaking at 300 rpm for 5 minutes. Finally, the tubes are kept in the water bath for 30 minutes at 38°C to produce a homogeneous sample with a tight emulsion mix. This is then proceed to the emulsification test.

Demulsification
The demulsification test is carried out using the bottle test. Here the tubes are filled with crude and brine at specific ratios and shaken for 5 minutes at a speed of 300 rpm for thorough mixing of the emulsion. Similar process conditions are followed as the emulsion tendency test. To the prepared sample above, selected demulsifier formulation is added using a microliter syringe pre-set to deliver the required test concentration. A blank (without demulsifier formulation) is also done and subjected to the same handling conditions as mentioned above. All the test samples were examined periodically to record the demulsification rate, quality of water, volume of emulsion and solid precipitation, if any.
IV. RESULTS AND DISCUSSION

A. Chemical flooding screening on Malaysian crude

Two EOR scenarios; the polymer flooding and alkaline-surfactant-polymer flooding (ASP), were tested. For the purpose 60 % water cut was analyzed as per recommendation of PRSB using 10, 30, 50 and 70% surfactant formulation. Figure 1 and Figure 2 below, represent the ASP and polymer flooding results respectively. From the results obtained, it can be clearly seen that ASP flooding has a better resolution (emulsion breaking tendency) than the polymer flooding method in general. In ASP flooding 10% formulation produces a clear separation within 10 minutes residence time. For the polymer flooding, the emulsion was unresolved and demulsifiers were unable to break the emulsion and separate the oil from water within the 30 minutes residence time specification.

Figure 1 below shows the influence of ASP concentration on stability of synthetic W/O crude oil emulsions. Increasing ASP concentration increases emulsion layer. This indicates that synthetic W/O crude oil emulsion tends to be tighter when ASP concentration increases.

Figure 2 below illustrates the results from the polymer flooding screening on Malaysian crude at 60% water cut. Polymer flooding is generally used to improve the oil to water mobility ratio. To conduct this test, about 1000 ppm of the polymer is injected into 1 L of brine solution and 6 ml if this solution is injected into the 40 ml Malaysian crude along with 54mL of produced water. From the results obtained, it can be observed that the blank sample has lesser emulsion and better water quality compared to the sample containing polymer. Besides that, the emulsion layer increases with increase in polymer content.

The injected water with polymer present increase the stability of oil droplets. The main function of the polymer is to increase the viscosity of the aqueous phase. Polymers are partially hydrolyzed polyacrylamide and hydrophobically modified product which contains a lot of anion and cation [7]. It has a strong hydrophilic group which is able to absorb on the oil-water interface, whereby reducing the interfacial tension and it improves the stability of the emulsion [8] for EOR purposes. In the aqueous solutions, the hydrophobic group usually reduce its exposure to the solvent, which cause the formation of micelles above its critical micelle concentration. These phenomena increases the hydrodynamic size of the polymer which than increases the viscosity of the solution which in turn improves the stability of produced liquid and making it difficult to be treated.
Figure 1: Alkali-surfactant polymer flooding screening at 60% water cut for Malaysian crude

![ASP flooding screening](image)

Figure 2: Polymer flooding screening at 60% water cut for Malaysian crude

![Polymer flooding screening](image)

B. Demulsification Test

Table 1 summarizes the results obtained from treated with 10% of ASP flooding and untreated (blank) emulsion samples. From the same table it can be observed that the untreated oil sample after 30 minutes has 9% unresolved emulsion whereas for the treated, no emulsion was detected for the same time duration. Besides that, the water quality for the treated sample was clear and contains about 37 ppm of oil in water. The use of deoiler in this case is not required.
Table 2 above exhibits the results of Enhanced oil recovery (EOR) emulsion tendency test after 30 minutes of residence time for Baram crude with 70% of ASP Flooding. The emulsion developed before treating is 38% whereas the treated has 0 emulsion within 10 minutes of residence time. To treat this emulsion, 300ppm of demulsifier B is used. This indicates that oil miscibility is much higher with higher ASP Flooding. Thus, it requires higher concentration of demulsifier to treat the emulsion. In other word, the crude with higher percentage of ASP requires higher concentration of demulsifier to treat it.

Table 1: EOR emulsion for Malaysian using 60% water cut with (S:PW) ratio of 10:90

<table>
<thead>
<tr>
<th>Screening Parameter</th>
<th>Emulsion treatment studied at 30 minutes residence time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Untreated</td>
</tr>
<tr>
<td>Demulsifier Concentration (ppm)</td>
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<tr>
<td>Emulsion (%)</td>
<td>9</td>
</tr>
<tr>
<td>Water Quality</td>
<td>Oily</td>
</tr>
<tr>
<td>Water content</td>
<td>Too low to be detected</td>
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</tbody>
</table>

Table 2: EOR emulsion for Baram using 60% water cut with (S:PW) ratio of 70:30

<table>
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<th>Screening Parameter</th>
<th>Emulsion treatment studied at 30 minutes residence time</th>
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<tbody>
<tr>
<td></td>
<td>Untreated</td>
</tr>
<tr>
<td>Demulsifier Concentration (ppm)</td>
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</tr>
<tr>
<td>Emulsion (%)</td>
<td>38</td>
</tr>
<tr>
<td>Water Quality</td>
<td>Oily</td>
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<td>Water content</td>
<td>-</td>
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V. CONCLUSION

This study describes on determining whether polymer flooding and ASP flooding influences the formation of emulsion on a laboratory scale. The results from the findings demonstrate that polymer has the ability to stabilize the emulsion and causing difficulty in treatment. The interaction between polymer molecules and the solid surface causes the polymer molecules to be bound closely to the surface of the solid by physical adsorption and hydrogen bonding which makes the emulsion tighter [9]. Thus, the level of emulsion formed depends on polymer molecular weight, polymer concentration, surfactant, alkali concentration and brine salinity [10]. Besides that, to treat the tight emulsion of the EOR crude, the right formulation of demulsifier also is required.

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REFERENCES


