PALM OIL-BASED METHYL ESTER SULPHONATE AS AN OIL WELL STIMULATION AGENT

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ABSTRACT

Methyl ester sulphonate (MES) is a surfactant (surface-active agent) that can reduce interfacial tension between water and oil. The compound can be diluted not only in water but also in oil. MES surfactant can be used in chemical stimulation processes to increase and enhance oil recovery (EOR) from reservoirs by reducing the interfacial tension between the oil and water formation. One of the success criteria in surfactant application as a stimulation agent is its effect on the interfacial value between oil and water droplets in a particular saline condition. Hence, the palm oil-based MES oil well stimulation agent was tested in three saline conditions before it was injected into the core. This study was aimed at determining the total oil recovery from a crude oil reservoir after injection of the palm oil-based MES stimulation agent into the core. The formulation of the palm oil-based MES as a stimulation agent consists of 70% palm oil-based MES, 20% solvent, 7% non-ionic surfactant and 3% co-solvent. Using 0.5% and 1% concentrations of the stimulation agent tested at 10 000, 20 000 and 30 000 ppm water salinity, the interfacial tension between oil and water was reduced to 10^{-4} dyne cm^{-1}. The total oil recovery with a 0.5% concentration of the palm oil-based MES stimulation agent was between 88% and 94%. However, the total oil recovery increased in the range of 90%-99% with the injection of a 1% palm oil-based MES stimulation agent into the core. Based on these results, the palm oil-based MES surfactant can be used effectively as a stimulation agent in a real crude oil reservoir.

Keywords: MES, palm oil, oil well stimulation agent.

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INTRODUCTION

The capability of a surfactant in decreasing interfacial tension has been used to enhance oil recovery from crude oil reservoirs over the last few years, especially for chemical stimulation that is associated with the injection of chemical material into the oil reservoir. Chemical stimulation studies are aimed at increasing the oil well productivity, which may have declined due to a decrease in reservoir permeability. The low permeability in turn can be caused by changes in wettability and capillary pressures which bring about water blocking as well as blocked reservoir pores during drilling activities (Allen and Roberts, 1993; Mulyadi, 2000).

According to Watkins (2001), petroleum sulphonate is one of the surface-active agents which have been used as an oil well stimulation agent. Utilization of petroleum sulphonate surfactant as an oil well stimulation agent, however, has some weaknesses, among which are: the tendency to clot in water with a high level of hardness, and its detergency characteristic which tends to decrease drastically at high water salinity. Most of the water formations of an oil well reservoir have high water salinity and hardness.

Methyl ester sulphonate (MES) is an anionic surfactant that can be produced from vegetable oils, and can be used to substitute the petroleum

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sulphonate surfactant. MES surfactant was produced by reacting methyl ester and sodium bisulphite in a ratio of 1:1.5 at 100°C for about 4.5 hr (Pore, 1976). According to Matheson (1996), utilization of MES surfactant as a surface-active agent has some benefits in terms of renewability, biodegradability, dispersion ability, detergency characteristic in hard water, high calcium tolerance and an ability to maintain enzyme activity. To produce MES, we can use palm oil as one of the raw materials.

The utilization of MES surfactant as a stimulation agent for oil wells should be adjusted to suit the reservoir conditions where the surfactant will be applied. The most important factor that can influence the performance of the surfactant as an oil well stimulation agent is the water salinity during the stimulation process. For this reason, we conducted the research to find out the interfacial tension of palm oil-based MES as a stimulation agent at concentrations of 0.5% and 0.1% with water salinity levels of 10 000, 20 000 and 30 000 ppm. The total oil recovery from core samples of an oil well using palm oil-based MES as a stimulation agent was also determined.

METHODOLOGY

Surfactant Preparation

Surfactant preparation was done through the sulphonation process of palm methyl ester with sodium bisulphite in a batch system reactor at 100°C for 4.5 hr. After the sulphonation reaction was completed, the crude sulphonated methyl ester was subjected to centrifugation at 1500 rpm for 30 min in order to separate the unreacted sodium bisulphite from the crude MES. The crude MES was purified by adding 35% (v/v) methanol, and leaving it at 50°C for 1.5 hr. The methanol was then evaporated off by heating the MES reaction mixture for another 10 min at 70°C-80°C. Purified MES was then neutralized by using 20% NaOH, and heating the MES for 30 min at 55°C. A stimulation agent was formulated by incorporating the purified MES with a carrier, an additive and a solvent. The formula consisted of 70% palm oil-based MES, 20% solvent as the carrier, 7% non-ionic surfactant and 3% co-solvent.

Performance of Palm Oil-based MES as an Oil Well Stimulation Agent

Interfacial tension. A study on the palm oil-based MES as an oil well stimulation agent was conducted using concentrations of 0.5% and 1% (w/w). The performance of the palm oil-based MES as a stimulation agent was based on the capability of the agent in reducing the interfacial tension in order to obtain a high total oil recovery. Interfacial tension tests were conducted using a spinning drop tensiometer in saline conditions of 10 000, 20 000 and 30 000 ppm.

Core characteristics. Before the stimulation agent is used in the field, we have to check its performance in the laboratory using a core. Six cores were sampled from the field where the stimulation agent will be applied. Reservoir formation differs from one field to another in two important characteristics of the core, *i.e*. porosity and permeability. The higher porosity and permeability of the core the more fluid can be adsorbed by the core (Monicard, 1980).

Total oil recovery. The dynamic core adsorption test was used to assess the total oil recovery at the tertiary phase. This test has to be done as a feasibility indicator before the surfactant injection is applied in the reservoir.

RESULTS AND DISCUSSION

Palm Oil-based MES Surfactant

As a surfactant can reduce the interfacial tension between water and oil, it can be used to reduce the capillary pressure of the oil that is trapped in the pores of the reservoir formation which is made up of sandstone. The injection of the surfactant into the reservoir can increase the possibility of releasing oil droplets trapped in the sandstone of the reservoir formation.

MES is an ionic surfactant which has a negative hydrophilic group that is best used in reservoir sandstone. The ability of MES surfactant to reduce the interfacial tension between oil and water is due to its capability in decreasing the adhesive power between two different polarity phases. A decrease in adhesive power occurs because surfactants have two different functional groups in one molecule, namely, the hydrophilic (dissolves easily in water) and the hydrophobic (dissolves easily in oil) groups. The hydrophilic surfactant group will react with water, while the hydrophobic surfactant group will react with the oil which is non-polar.

The palm oil-based MES surfactant that we prepared could lower the interfacial tension between oil and water by 99.96% from 30-dyne cm^{-1} to only 1.34×10^{-2} dyne cm^{-1}. This shows that the performance of the palm oil-based MES in decreasing the interfacial tension between the oil and water phases is promising; thus, it can be used as an oil well stimulation agent.

Palm Oil-based MES Performance as an Oil Well Stimulation Agent

Interfacial tension (IFT). One of the important parameters in the assessment of enhanced oil Recovery (EOR) from crude oil is interfacial tension. The value of IFT between the oil and water formation after the addition of the palm oil-based MES stimulation agent has first to be analysed before it is applied in EOR process in order to make sure that the stimulation agent is appropriate for the reservoir conditions. Using an inappropriate stimulation agent can lead to the formation of a sludge emulsion that blocks the reservoir pores and causes formation damage, resulting in not being able to pump out the crude oil from the oil well.

The surfactant, which consists of two functional groups of different polarities (hydrophilic and hydrophobic), can decrease IFT of oil and water. The MES surfactant that has a general formula of RSO_3H can dissociate to form RSO_3^- and H^+ ions in water. The RSO_3^- ion will touch the surface of oil bubbles and influence the binding of the oil molecules. At the same time, the surfactant will also be in contact with the rock. This interaction will influence the adhesion force between the oil bubbles and the reservoir formation. As a result, the binding effect among the oil bubbles will be strong enough to form an oil bank that can be forced out and produce the crude oil. However, the adhesion force between the oil and the rock will decrease, thus lowering the capillary pressure that occurs in the narrower area of the pores.

The results of IFT analysis using 0.5% and 1% concentrations of the stimulation agent at water salinity levels of 10 000, 20 000 and 30 000 ppm are shown in *Figure 1*. At the 0.5% concentration of the stimulation agent, the lowest IFT was 2.45 x 10^{-4} dyne cm^{-1} in a water salinity of 10 000 ppm, and the highest IFT was 8.38 x 10^{-4} dyne cm^{-1} in a water salinity of 30 000 ppm. At the 0.1% concentration of the stimulation agent, the lowest IFT was 2.23 x 10^{-4} dyne cm^{-1} in a water salinity of 10 000 ppm, and the highest IFT was 8.14 x 10^{-4} dyne cm^{-1} when salinity was 30 000 ppm. The increase in IFT value was caused by the formation of disalt molecules that were formed because of the reaction between MES and Na^+ ion of NaCl in the saline solution.

The changes in pattern for IFT values at a 0.5% concentration of stimulation agent were in accordance with Equation 1:

$$Y = 0.0003\ X - 5 \times 120^{-5}\ (\text{dyne cm}^{-1})$$

and those at the 1% concentration were in accordance with Equation 2:

$$Y = 0.0003\ X - 7 \times 10^{-5}\ (\text{dyne cm}^{-1}),$$

where Y is IFT value and X is salinity.

According to Krumrine *et al.* (1982), generally an IFT value lower than 10^{-1} dyne cm^{-1} will be enough to remove most of the crude oil from the pores of a reservoir formation. In fact, if IFT value is lower than 10^{-3} dyne cm^{-1}, the crude oil can be removed completely. IFT value from using the palm oil-based MES oil well stimulation agent was about 10^{-4} dyne cm^{-1}. This means that this oil well stimulation agent will be able to remove the crude oil effectively from the reservoir formation.

Core characteristics. Porosity of the six core samples ranged from 18.11% to 35.35% in the six core samples, while permeability ranged from 172.53 millidarcy to 2665.11 millidarcy (*Table 1*).

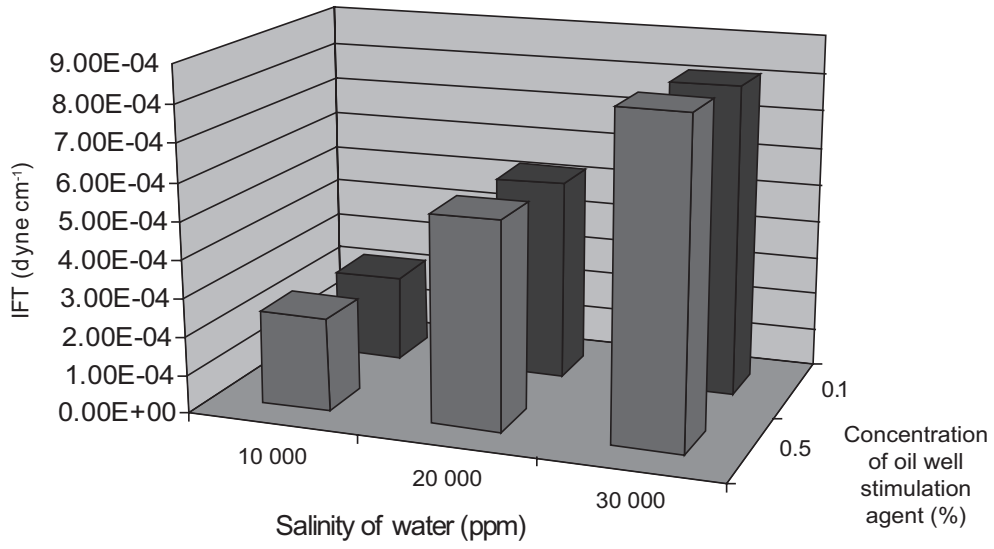

Figure 1. IFT values resulting from stimulation agent concentrations of 0.5% and 1% at water salinity levels of 10 000, 20 000 and 30 000 ppm.

TABLE 1. TOTAL OIL RECOVERY FROM SIX CORE SAMPLES

No.	Sample ID	Porosity (%)	Permeability (milidarcy)	Salinity (ppm)	Concentration of oil well stimulant (%)	Oil recovery after water injection (%)	Oil recovery after surfactant injection (%)	Total recovery (%)
1	30B	23.99	316.43	10 000	0.5	31.25	62.5	93.75
2	40B	21.37	301.32	-	1.0	21.88	75	96.88
3	65B	18.11	172.53	20 000	0.5	40.0	50.0	90.0
4	E1	21.28	1 950.80	-	1.0	21.43	71.43	92.86
5	2I	19.74	314.05	30 000	0.5	20.0	68.0	88.0
6	19B	35.35	2 665.11	-	1.0	40.0	50.0	90.0

Total oil recovery. Results of the oil recovery test are shown in *Table 1*. It may be seen that the higher the concentration of the injected oil well stimulation agent, the higher the total oil recovery. At 0.5% concentration, the total oil recovery was between 88% and 93.75%, while at 1% concentration, the total oil recovery was in the range of 90% to 96.88%. With a total oil recovery between 88% and 96.88%, we can conclude that the palm oil-based MES can be used successfully as a stimulation agent not only at the 1% concentration but also at the 0.5% concentration. The values of total oil recovery (88%-96.88%) indicate that the palm oil-based MES oil well stimulation agent injected into the cores was effective in decreasing interfacial tension between the oil and water formation, thereby enabling the oil that was trapped in the cores to be pushed out of the core pores. This proved that the palm oil-based MES stimulation agent is effective in increasing the recovery of the oil that is trapped in the reservoir formation.

CONCLUSION

The effectiveness of the palm oil-based MES stimulation agent in decreasing the interfacial tension is influenced by the salinity of the water formation. The interfacial tension will increase proportionally with an increase in water salinity. The values of interfacial tension between oil and water when using concentrations of 0.5% and 1% palm oil-based MES stimulation agent at water salinity levels of 10 000, 20 000 and 30 000 ppm were in the region of 10^{-4} dyne cm^{-1}. This indicates that the stimulation agent was very effective in increasing the total oil recovery. From the dynamic adsorption test, the total oil recovery after the water and surfactant injections was between 88% and 96.75%.

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REFERENCES

ALLEN, T O and ROBERTS, A P (1993). Production operations 2: well completions, workover and stimulation. *Oil & Gas Consultants International (OGCI).* OGCI Inc., Tulsa, Oklahoma, USA.

KRUMRINE, P H; FALCONE, Jr, J S and CAMPBELL, T C (1982). Surfactant flooding: the effect of alkaline additives on IFT, surfactant adsorption and recovery efficiency. *SPE J., 197*: 503-513.

MATHESON, K L (1996). Surfactant raw materials: classification, synthesis, and uses. *Soap and Detergents: A Theoretical and Practical Review* (Spitz, L ed.). AOCS Press, Champaign, Illinois.

MONICARD, R P (1980). *Properties of Reservoir Rocks: Core Analysis*. Gulf Publishing Company, Texas.

MULYADI (2000). Surfactant for oil well stimulation agent. *Oilfield and Maintenance Chemicals.* PT Mulino Ciptanusa, Jakarta.

PORE, J (1976). Sulfated and solfonated oils. *Oils and Fats* (Karlenskind, A ed.). Manual Intercept Ltd., New York.

WATKINS, C (2001). All eyes are on Texas. *Inform, 12*: 1152-1159.