Science and Technology Indonesia
e-ISSN:2580-4391 p-ISSN:2580-4405
Vol. 4, No. 2, April 2019

Research Paper

Production Methyl Ester Sulfonate (MES) Based Rubber Seeds as one of Chemical Injection Solution in Enhanced Oil Recovery (EOR) Process

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Abstract
One attempt to increase the recovery of oil from a reservoir is by injecting the surfactant. Surfactant is used for lowered tension interfaces (interfacial tension) between oil and water so able bring oil exit pores reservoir. It is a good opportunity for develop type surfactant based oil vegetable that is from oil seed rubber. As known from the chemical composition in oil seed rubber contain olein amounted to 39.45 % wt, which is almost approaching value olein from petrochemicals based by 40.7 %. For produce suitable surfactants with characteristics required by oil industry, then do formulation with combine MES surfactant produced with ingredients additives other as appropriate to produce a capable formula for give best performance to be applied on oil industry. From the test result, the MES from the rubber seed oil obtained has fulfilled the surfactant requirement with the value from soaking % crude oil recovery value is 0,815 % - 3,91 % with the best value is 3,91 %, pH value is 7,2 -8,2, density value is 1,006 - 1,065, the compability test result, both catalyst can be used because there is no difference and show positive results that there is no precipitate and clear colored of MES surfactant and also for Interfacial Tension test result is 0.373 - 0.254 dyne/cm.

Keywords
Surfactants, MES Production, Rubber Seed Oil

Received: 30 Juli 2018, Accepted: 8 April 2019
https://doi.org/10.26554/sti.2019.4.2.52-56

1. INTRODUCTION

The rest of oil in the reservoir during production process using natural driving force (primary recovery) that cannot be produced ranges from 60 to 70% of the original oil volume. Once the reservoir with natural driving force (primary recovery) and secondary recovery has been unable to push the oil to rise to the surface, advanced stage method of enhanced oil recovery known as Enhanced Oil Recovery (EOR) (Lake, 1989) is needed to bring out residual oil for production phase. One of the EOR methods is chemical injection using surfactant (Taber et al., 1997). Surfactant injection is one way to drain residual oil remains in the reservoir by injecting an active substance into the reservoir, thereby reducing interfacial tension of oil-water trapped within the pores of reservoir rock. In order to drain the remaining oil optimally, it requires surfactant type which in accordance with the conditions of water reservoir formation as well as type of reservoir rock itself. Currently, common surfactant type used in petroleum industry is a petroleum-based surfactant. The nature of several petroleum-based surfactant is not resistant to water formation with high levels of salinity and temperature, while oil wells in Indonesia mostly contain up to 10,000 ppm salinity and temperature of 60-120°C. This is an excellent opportunity to develop rubber seed oil-based surfactant, especially in South Sumatra region.

One kind of potential surfactant to be developed is methyl ester sulfonate (MES) surfactant which made by vegetable oil from rubber seed. MES surfactant is capable to be applied in petroleum industry given MES surfactant has more advantages compare to petrochemical-based surfactant (linear alkylbenzene-sulfonate, LAS) including its renewable feature, good biodegradability (Roberts et al., 2008), lower production costs (approximately 57% lower from production costs of LAS surfactant), good dispersion characteristic, good detergency especially on hard water (Watkins, 2001); at lower concentration, MES detergency power is the same as petroleum sulfonate (Matheson, 1996). EOR requires formula with more specific requirements, including: ultralow interfacial tension (< 10^{-2} dyne/cm), compatible with water formation and stable against reservoir temperature and high salinity, pH range 6-8, has phase III (middle phase) or phase II (above), and incremental oil recovery ranges 15-20% of original oil in place (OOIP) (Pithapurwala et al., 1986). Once surfactant having ultralow interfacial tension (< 10^{-2} dyne/cm), it can be presumed to be able to increase oil recovery for about 10-20%.

Assessed by chemical composition contained in rubber seed oil, it contains olein amounted for 39.45% which is close to the olein value of oil palm of 40.7%. Currently, MES from rubber seed oil has been used for EOR in some oil and gas fields in Indonesia. The comparison of chemical composition may become a big opportunity to develop rubber seed oil-based MES. MES surfactant is an anionic surfactant with general structure of RCH $(CO_2CH_3)SO_3$, generated through the process of sulfonation of fatty acid methyl esters ($RCH_2CO_2CH_3$) (Roberts et al., 2008; Watkins, 2001) with alternative reagents sulfuric acid (H_2SO_4), oleum (a solution of SO_3 in H_2SO_4), sulfur trioxide (SO_3), NH_2SO_3H, and $ClSO_3H$ (Hambali et al., 2009). To produce the best quality of MES product, some important treatments that should be considered include : mole ratio, reaction temperature, concentration of complementary sulfonate groups, neutralization time, catalyst type and concentration, pH and temperature neutralization Matheson (1996), depend on the product application. Under these conditions, the study aims to produce rubber seed oil-based MES surfactant as chemical injection solution in renewable EOR and formulate the optimum surfactant composition in accordance with reservoir conditions.

2. EXPERIMENTAL SECTION

2.1 Materials

Materials used in this study namely: rubber seed oil, KOH, CaO, methanol, NaCl, Aquadest, Na_2CO_3, H_2SO_4, NaOH, and other chemicals for analysis. The equipment used include: magnetic stirrer, hot plate, glass beaker, spatula, separating funnel, measuring cups, thermometer, Erlenmeyer, nixer glasses, bath, analytical balance digital, reactor for transesterification process, Whatman filter paper 41, as well as glasses and tools for other analysis.

2.2 Methods

2.2.1 Research Stages

The research was conducted in the following stages: preparation of raw material, methyl ester from rubber seed oil, transesterification process using KOH catalyst-based reactor, transesterification process using CaO catalyst-based reactor, produce Methyl Ester Sulfonate, formulate surfactant, and surfactant formulation performance test on the conditions of carbonate field of reservoir.

2.2.2 Preparation of raw material, methyl ester from rubber seed

At this stage, preparation of raw material methyl ester of rubber seed oil olein used hydrolysis process. In this process, rubber seed is separated from the shell then cut into thin pieces and dried to eliminate the levels of cyanide (HCN) in rubber seed. Once it was dry, rubber seed is crushed to spill out the oil. The fine seeds are stored into the reactor and mixed with water at a ratio of 1:1. Then heated in temperature of 120°C. This process lasted for 1 hours or until water in the reactor evaporated and separated the slag and rubber oil. Let the rubber seed oil sedimented in the reactor. Then poured the oil into a bottle. The physical and chemical properties of rubber seed oil olein is then analyzed, including iodine number, saponification number, acid value and free fatty acids.

2.2.3 Transesterification process using KOH catalyst and CaO catalyst

In transesterification process, 15% (v/v) methanol is added from the total raw material rubber seed, then processed and mixed with 1% KOH solution to form methoxide. Then rubber seed oil and methoxide solution mixed with transesterification reactor. The transesterification process lasted for 1 hour at 60°C with stirring technique. Furthermore, the separation process is carried out based on specific gravity to separate crude methyl ester and glycerol and then washed with 30% (v/v) warm water of the total crude methyl ester which was about to be purified, for three times. Last, drying process is conducted to reduce water and methanol content in the methyl ester washery to produce pure methyl ester. Repeat the steps in the transesterification process for the CaO catalyst. Physical and chemical properties of the resulting methyl esters is analyzed, including its acid number, iodine number, saponification, density, level of ester, free fatty acid content, total glycerol and water content.

2.2.4 Preparation of Methyl Ester Sulfonate

Prepare a set of reflux tools, namely and a flask with round base, ball cooler, thermometer, neck flask cover, oil bath and hot plate stirrer. 100 ml of methyl ester and magnetic stirrer added to the flask. Heat and stir under temperature of 100-120°C, then sulfuric acid (98%) is dropped to the solution until reaching volume of 12,5 ml. This reaction process runs for 1 hour. MES purification process is done by adding 20% (v/v) methanol into MES, then continue with neutralization process using 20% NaOH with reaction temperature of 55°C and stir using magnetic stirrer until pH 7.

2.2.5 Surfactant Formulation

MES surfactant that have been produced is used as raw material in the process of surfactant formulation. The additives used include Na_2CO_3 and NaOH. Both of these additives are mixed with the formula:

- Determination of salinity performed on the MES surfactant concentration of 0.1 to 0.5% with variations in salinity water injection of 10,000, 15,000 and 20,000 ppm. The analysis includes immersion, density, pH, compatibility and interface stress.
- Selection of additif to determine type and concentration of best additif in providing the lowest interfacial tension marked by percentage of largest percentage crude oil recovery. At this stage used two types of additives namely NaOH and Na_2CO_3, with concentrations according to the amount of MES dissolved.

3. RESULTS AND DISCUSSION

Olein is a raw material in the manufacture of rubber seed oil-based MES surfactant. To obtain olein, there are several production methods of rubber seed oil one of which is hydrolysis process conducted in this study. Hydrolysis is a type of chemical reaction that occurs between water and other compounds. During the reaction, chemical bond breaks into two molecules, causing them to rupture.

3.1 Transesterification process using KOH catalyst and CaO catalyst

Once rubber seed oil is obtained the next stage is esterifying rubber seed into metyl ester (ME). After ME is obtained, transesterification process is conducted to transform ester into other ester forms through the exchange of alkoxy group. The presence of a catalyst (either acid or strong base) is able to accelerate the achievement of equilibrium. In the production of good quality methyl ester (ME) with high yield rate of 98 %, the indicator includes acid number, iodine number, saponification, density, ester content, free fatty acid content, total glycerol and water content as shown in Table 1.

3.2 Preparation of Methyl Ester Sulfonate

The subsequent process of Methyl Ester produced in the transesterification process is converting Methyl Ester to Methyl Ester Sulfonate. Where in this method Methyl Ester is reacted with H_2SO_4 (98%) of 12.5 ml and heated for 1 hour at a temperature of 100 - 120 °C with stirring. After that is done purification process by adding 20% methanol from MES formed and then neutralized using NaOH as much as 20% of MES formed. The results of the sulfonation process with the final MES result in a liquid form with dark black color having a pH of 7.1 and density 0,959 gr/ml for MES formed from ME using CaO catalyst and having a pH of 8.0 and density 0,9003 gr/ml for MES formed from ME using a KOH catalyst.

3.3 Surfactant Formulation and Testing

MES produced by sulfonation process is then formulated using MES concentration 0.1 – 0.5 %, additive Na_2CO_3 and NaOH with salinity of 10,000 ppm; 15,000 ppm and 20,000 ppm. The purpose of surfactant formulation is to get the optimal recovery percentage in accordance with the conditions of carbonate reservoir. The analysis includes immersion, density, pH, compatibility and interface stress. The following figures shows results of surfactant formulation which closely achieve the nature of carbonate core.

Based on Figure. 1, Figure. 2 and Figure. 3 it can be seen that for a salinity level of 10,000 ppm and 20,000 ppm in MES surfactant injection water used very well using a KOH catalyst because it can produce a good% recovery. Whereas for a salinity level of 15,000 ppm in MES surfactant water injection is excellent using CaO catalysts because it can produce better% recovery than KOH catalysts. From the results obtained at MES concentrations when compared between using a KOH catalyst with CaO, the best average recovery rate was at a salinity level of 10,000 ppm and the most effective percentage with a formulation dose of 0.5% MES using a KOH catalyst of 3.91%. But if seen from the overall comparison of the three graphs above comparison can be

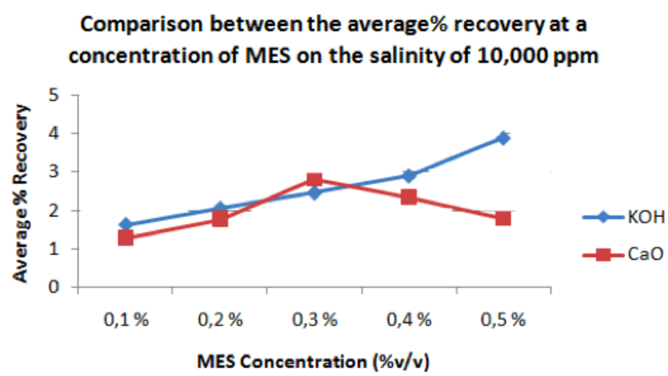

Figure 1. Graph of Comparison of MES Concentrations (between KOH Catalyst and CaO) to % Recovery Average Crude Oil at Salinity 10,000 ppm

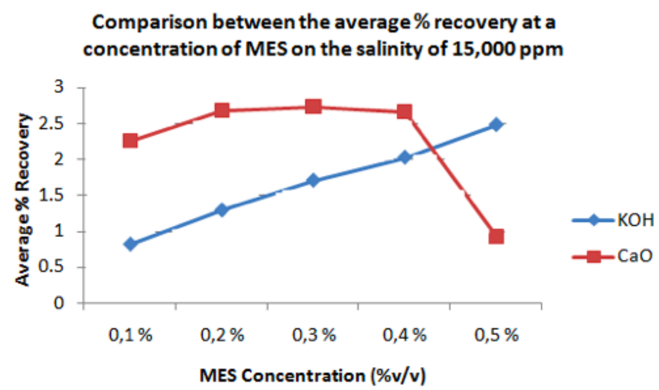

Figure 2. Graph of Comparison of MES Concentrations (between KOH Catalyst and CaO) to % Recovery Average Crude Oil at Salinity 15,000 ppm

concluded that the performance of MES solution by using KOH catalyst is better when compared with MES using CaO catalyst.

Results from pH testing where the results obtained ranged from 7.2 to 8.2. From this it can be seen that the pH produced at the time of measurement obtained an alkaline pH after MES solution was mixed with injection water containing various types of salinity. Increased salinity and MES concentrations did not significantly affect the pH value. It can be concluded that salinity has no effect on pH value as the same is also mentioned by Mira (2011).

The density for MES using a KOH catalyst was 0.903 gr/ml while the density for MES using a CaO catalyst was 0.959 gr/ml. The results obtained ranged from 1.01 - 1.025 gr/ml. This suggests that the resulting MES either by using CaO and KOH catalysts can be injected because of the density generated above from the water density value so that the injected surfactant position can be below the water surface and capable of pushing the existing oil within the pores of the rock. From the measurement of the density of the MES surfactant formulations showed that the addition of salinity also made the addition of density values. This

Table 1. Analysis result of methyl ester used KOH and CaO catalyst

Analysis	Unit	Specification Min	Specification Max	Rubber Seed Oil	ME rubber seed (KOH)	ME rubber seed (CaO)
Free Fatty Acid	%	-	3	0,26	0,28	0,31
Acid Number	mg KOH/g	-	0,8	0,53	0,55	0,61
Iodine Number	mg Iod/g	-	115	92,13	91,62	93,45
Saponification	mg KOH/g	-	500	205,40	200,63	210,57
Density at 15 °C	g/cm3	0,840	0,890	0,9060	0,8718	0,8856
Water Content	%	-	0,25	0,01	0,01	0,01
Total Glycerol	%-massa	-	0,24	-	0,20	0,19
Ester Content	%-massa	96,5	-	-	97,9	98,0

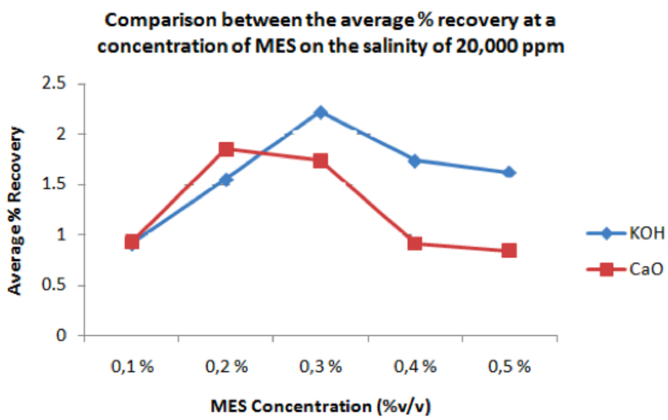

Figure 3. Graph of Comparison of MES Concentrations (between KOH Catalyst and CaO) to % Recovery Average Crude Oil at Salinity 20,000 ppm

is influenced by the higher levels of salinity, the more minerals it contains. As stated in the research of Mira (2011) that the more surfactant concentration addition, the higher the density value produced. Increasing the density of this surfactant solution has implications for the increasing density difference between oil and surfactant solution when measuring the interface voltage value using Spinning Drop Tensiometer.

The compatibility test was performed to determine the ability of MES surfactant formulation under reservoir conditions. This is done to determine the changes that occur in the MES surfactant formulation if injected into the reservoir. The average reservoir has temperatures ranging from 170°F - 185°F. Thus, in this compatibility test, it is carried out by storing surfactant formulations at temperatures ranging from 170°F - 185°F for 24 hours. The compatibility test is carried out by inserting 10 ml of MES surfactant formulation into the test tube, then storing the test tube in the oven at 185 °F for 24 hours. After 24 hours, then observed the changes that occur visually. The results of the compatibility test performed show positive results. Of the two types of catalysts used did not look the difference and the compatibility test performed successfully and showed a positive result, that is not formed precipitate and surfactant MES clear color. Then both types of catalysts can be used in the manufacture of Methyl Ester.

Measurements of MES surfactant capability in reducing the interface oil value of oil with water are performed by using injection water and oil from oil wells. This is done to see the response of the injection water interface voltage and the oil used after the addition of the surfactant sample. The result of oil interface interface value analysis with water after addition of MES surfactant sample using injection water gives range 0.254 until 0.341 dyne/cm. In MES solution using a KOH catalyst the best interfacial stress values obtained were 0.254 dyne/cm at 0.5% MES concentration with 10,000 ppm salinity. While in MES solution using CaO catalyst, the best interfacial stress value obtained was 0.275 dyne/cm at a MES concentration of 0.3% at salinity of 10,000 ppm. When compared between the two values we get the best interfacial stress values obtained from the MES solution by using a KOH catalyst.

4. CONCLUSIONS

From the test results obtained the best catalyst used in the manufacture of Methyl Ester from rubber seeds oil is KOH with ester levels produced reached 97.9%. From the results obtained at MES concentrations when compared between using a KOH catalyst with CaO, the best average recovery rate was at a salinity level of 10,000 ppm and the most effective percentage with a formulation dose of 0.5% MES using a KOH catalyst of 3, 91%. From the test results, the MES of rubber seed oil has met the requirements as surfactant with the result of immersion test parameters is % recovery crude oil obtained by 0.815% - 3.91% with maximum yield obtained of 3.91%, the pH is obtained about 7.2 - 8.2, density of 1.006 - 1.025 gr/ml, the compatibility test of both catalysts can be used because there is no difference and show positive results that there is no precipitate and surfactant MES clear color as well as testing the interfacial stress obtained results 0.254 - 0.373 dyne/cm.

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