

Optimizing Surfactant Polymer Flooding: Integrated Study from Molecular Dynamics Simulation to Chemical Cost per Incremental Oil

Yani F. Alli^{*1}, Usman², Iqbal Fauzi³, Anis N. Utami⁴, and Arif Bagus Prasetyo⁵

¹BPMGB “LEMIGAS”, ²BRIN, ³PERTAMINA EP, ^{4,5}SKK MIGAS

* Email: yani.alli@esdm.go.id

Abstract. The effectiveness of surfactant formulation to extract the trapped oil in the mature oil field has been studied for many years, especially in Indonesia where the majority of oil fields are on declining stage. The main objective of this research was to demonstrate how to develop excellent surfactant formulation along with polymer to maximize the production of oil. Surfactant formulation that in charge for lowering the interfacial tension (IFT) of oil and water, decrease the capillary forces and generating mobile oil consists of local biosurfactant derived from palm oil and commercially available co-surfactant to obtain synergistic mechanism of oil and water, whereas polymer is added to reduce the mobility ratio between displacing fluid and displaced fluid for improving sweep efficiency. The study starting with molecular dynamics simulation to screen the potential biosurfactant and synthesizing the selected one. Synthesized biosurfactant was tested including IFT measurements, and phase behavior investigation at several formulations with various ratio and concentration of biosurfactant and co-surfactant to obtain the best surfactant formulation. Polymer was then added to evaluate the surfactant performances in representative standard core. The cost effective of surfactant polymer formulation to increase the oil production was also calculated. It was found that surfactant formulation which exhibiting the lowest IFT and the highest microemulsion consist of biosurfactant and co-surfactant with the ratio 1:1 (OFTD11) at a given salinity. A series of flooding experiment utilizing varies surfactant polymer formulation which performed on sandstone standard core showed that OFTD11 was able to obtain maximum oil recovery with injection of 0.3 PV surfactant polymer followed by 0.6 PV polymer resulting in recovery factor as high as 45.19 %IOIP (initial oil in place). It showed that the volume of microemulsion formation is directly proportional to the recovery factor of chemical flood, indicate the importance of microemulsion for optimum oil recovery. This high performance of chemical injection described from chemical injection cost as low as 1.42 USD/bbl chemicals injected or 4.52 USD/barrel incremental oil with the price of biosurfactant 4.17 USD/kg, co-surfactant 4.25 USD/kg and polymer 3.3 USD/kg. Systematic methods begin with molecular dynamics simulation to the economical chemical cost are required on developing the suitable chemical formulation that is specific for certain reservoir in order to achieve the cost effective chemical EOR application

Keyword(s): enhanced oil recovery, biosurfactant, chemical injection, chemical cost

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1 Introduction

The needs of crude oil as main resources of energy still become an issue in the middle of higher prices of oil. And it is predicted that demand of energy worldwide increased by 30% from 2010 to 2040¹. While conventional oil process can only produce about 30% of original oil in place through natural flow and lifting oil², EOR technology has become one of the keys to boost oil production in the mature oil field³.

One of the popular methods is through chemical injection that utilizing chemicals such as surfactant⁴, polymer⁵, and alkaline⁶. These chemicals are expecting to interact with reservoir materials and change the characteristic of reservoir fluid and rock⁷.

While surfactant role is to release the trapped oil in the reservoir⁸, polymer is added to improve the mobility ratio of oil and water and lead the mobile oil into the production well⁹. Several laboratory experiments should be performed prior to the field injection in order to obtain the most effective chemical formula to be applied in the large scale.

The study of chemical formulation is starting with molecular dynamic simulation to predict the suitable molecular structure of surfactant based on the nature of crude oil and water in targeted field. Followed by the production of surfactant, laboratory experiment to analyze the compatibility of surfactant with the brine and other materials was performed comprehensively. And finally, the ability of chemical formula to increase oil production and the economical calculation were conducted to evaluate the feasibility of the project.

2 Data and Method

A series of experiment must be conducted to obtain the most suitable chemical for certain reservoir characteristic. Through the molecular dynamic simulation, the most promising molecular structure surfactant was selected, then followed by the producing surfactant in the laboratory scale. Analysis and evaluation were then completed to determine performance and ability of surfactant to enhanced oil recovery.

2.1 *Molecular dynamic simulation*

Molecular dynamic simulation study was performed using software GROMACS to design molecular structure of surfactant that expect to have the best performance with certain reservoir characteristic of fluid and rock. Selection was based on the calculation of the ability of surfactant to decrease IFT and also the ability to form emulsification as the main character of the surfactant.

2.2 *Synthesizing surfactant*

Based on the molecular dynamic simulation, potential specific molecular surfactant was synthesized by esterification and eterification of derived palm oil with hydrophilic substances polyethylene glycol to produce non-ionic biosurfactant using Dean-Stark and bubbling nitrogen methods. Synthesized surfactant was then analyze through a series of EOR laboratory experiment.



2.3 *Interfacial tension measurement*

The most important role of surfactant to decrease interfacial tension was measured using Spinning Tensiometer TX500 C/D. IFT tube was filled with surfactant solution and then oil as much as 2 μL was injected into the tube and placed in the IFT unit. Measurement was run at 6000 rpm at reservoir temperature 60 $^{\circ}\text{C}$.

2.4 *Phase behavior evaluation*

Surfactant formula that is having the ultralow IFT was adequate to follow the next experiment, phase behavior analysis. Surfactant formula at 2 mL and oil at 2 mL were injected to the burning closed measuring pipet. The level of water was recorded at initial and after mixing for 1 to 7 days. The equilibrium state of water and oil was observed regularly.

2.5 *Rheology measurement*

The characteristic of polymer to improve mobilization ratio by increasing viscosity of brine was measured using Brookfield DVIII. Polymer was mixed with brine at certain concentration and put into the tube for 16 mL. Run the program at shear rate 7 s^{-1} and temperature 60 $^{\circ}\text{C}$. Record viscosity of polymer after reached equilibrium state.

2.6 *Filtration ratio analysis*

The possibility of polymer to form plugging in the core was analyzed by filtration ratio (FR) analysis. For 120 mL of polymer was let to flow through filter paper size 3.0 μL with under pressure 30 psig. Time (t) to collect every 10 mL of polymer until 100 mL was recorded. FR value was then calculated with equation:
$$\text{FR} = \frac{T_{100} - T_{80}}{T_{40} - T_{20}}$$

2.7 *Thermal stability test*

One of the most important characteristics of polymer to be applied as chemical injection is the resistance of polymer to the heat since the chemical will be thermally exposed for several months during flow to the production well. Polymer was put in the oven at 6 $^{\circ}\text{C}$ for 3 months, and the viscosity was regularly measured and compared with the initial viscosity at day 0.

2.8 *Coreflooding test*

Surfactant formula that is pass all screening process were further analyze by coreflooding experiment. Standard and native core that conditioning at the reservoir temperature and pressure was injected by oil to get an initial oil in place (IOIP) and then aging for several hours. Saturated oil core was then injected with brine until reached residual oil saturation (Sor) to mimic the waterflood process and then followed by the injection of chemical with certain design injection and then flush with brine until reached 100% watercut. The production of oil was recorded regularly.

2.9 *Economical calculation*

In order to apply EOR project, economically value of the project must be well considered. Using rough calculation, with the parameter of chemical price and the results of laboratory test, cost chemical per

incremental oil was then calculated for every surfactant polymer formulation to obtain the cost-effective chemical.

3 Result and Discussion

3.1 Molecular dynamic simulation

Based on molecular dynamic simulation, it was found that surfactant Oleic-polyethylene glycol 400 can achieve the lowest IFT compared with the other polyethylene glycol from 50 to 400 and also compared with other hydrophobic chain such as palmitic acid. Whereas the average of contact (emulsification) between oil and surfactant, Oleic-PEG400 also was having the highest number compared to other molecular structure. It is therefore, Oleic-PEG400 was then synthesize for the next experiment, measurement of EOR parameter.

3.2 Synthesizing surfactant

Ester surfactant oleic-PEG400 was the synthesized from the raw material oleic acid and polyethylene glycol 400 using bubbling nitrogen. However, compatibility of surfactant cannot meet the criteria, since layer separation was found for 2 hours. Oleil glycidil PEG400 (OGP4) was then produced to encounter the compatibility issue as well as to increase the thermal stability of surfactant due to the eter functional group. OGP4 was synthesize via two step eterification. The first step was to react oleil alcohol with epychlorohydrin to get intermediate product oleil glycidil eter, followed by the reaction with polyethylene glycol 400 to produce OGP4.

3.3 Rheology polymer

Several tests were conducted to select the best polymer for chemical formulation in the target reservoir. Viscosity of selected polymer and various surfactant in the given brine was measured in the reservoir temperature 60 °C and shear rate 7 s⁻¹. Due to the oil viscosity at 2.88 cP, target viscosity of surfactant polymer is at 10 cP to confront with possibility of thermal degradation and adsorption issue. It showed that viscosity of all polymers increased as the concentration increased and the target concentration of polymer for SP flood is at 1250 ppm (Figure 1).

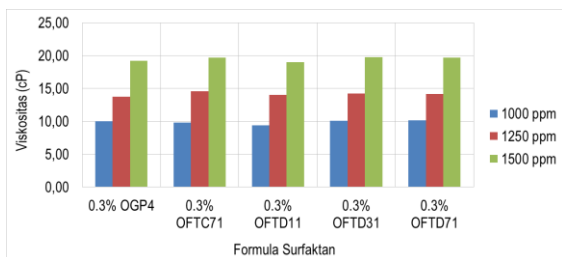


Figure 1. Polymer viscosity of surfactant polymer

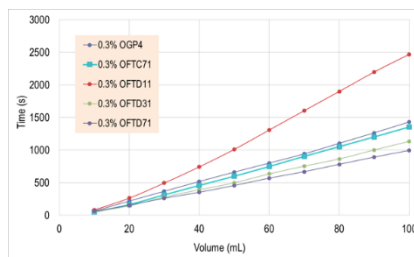


Figure 2. Filtration ratio of surfactant polymer

3.4 Filtration test

To ensure the flow of polymer in the core, filtration ratio value of polymer should be less than 1.2 which indicate that polymer is able to flow in the pore throath without plugging. The filtration ratio for all polymers showed that four polymers were having filtration ratio less than 1.2 (Figure 2).

3.5 Interfacial tension measurement

IFT measurement was then conducted to the mixture of formula surfactant and selected polymer at 1250 ppm. Formula surfactant was obtained by mixing main surfactant OGP4 with co-surfactant B to D with the ratio stated at the number of the formula. It showed that formula surfactant that having ultralow IFT 10^{-3} dyne/cm were OGP4 (main surfactant), OFTC71, OFTD11, OFTD31, and OFTD71 (Table 1).

Table 1. Thermal stability of surfactant polymer with various surfactant formula

TIME (DAYS)	Polymer FP3630S 1250 ppm										
	No Surf	0.3% OGP4		0.3% OFTC71		0.3% OFTD11		0.3% OFTD31		0.3% OFTD71	
	Visc (cP)	Visc (cP)	IFT (dyne/cm)	Visc (cP)	IFT (dyne/cm)	Visc (cP)	IFT (dyne/cm)	Visc (cP)	IFT (dyne/cm)	Visc (cP)	IFT (dyne/cm)
0	14.08	14.42	7.87E-03	14.50	5.32E-04	14.50	2.09E-03	13.34	5.33E-04	13.90	9.93E-04
14	9.27	10.90	6.37E-03	9.77	6.16E-04	10.55	5.26E-04	9.68	4.34E-04	10.25	2.60E-03
30	11.93	8.30	7.40E-03	9.50	7.41E-04	8.61	9.87E-04	7.37	6.17E-04	7.49	1.30E-03
60	19.03	5.81	8.53E-03	7.02	5.32E-04	8.75	1.44E-03	5.07	7.42E-04	7.20	1.85E-03
90	11.52	13.76	9.06E-03	8.12	1.68E-03	8.09	8.35E-04	8.61	1.31E-03	5.22	2.31E-03

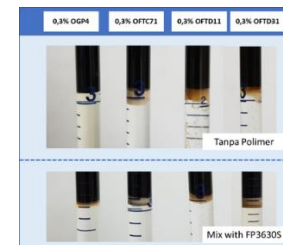


Figure 3. Phase behaviour of surfactant polymer in various surfactant

3.6 Thermal stability test

For the thermal stability test of surfactant polymer, it showed that viscosity of polymers showed degradation from initial viscosity of 14 cP to the range of 5 – 13 cP, whereas the IFT of formula surfactant showed stable in the level of 10^{-3} dyne/cm for 3 months and suitable for chemical injection (Table 1).

3.7 Phase behavior evaluation

All formula surfactant that was pass IFT test was then further analyzed by phase behavior evaluation. Phase behavior results showed that formula surfactant polymer that generated the highest amount of microemulsion were OFTD11 and OFTD31 (Figure 3). These two formula and main surfactant OGP4 was then selected to be chemical injection in the coreflood test.

3.8 Coreflooding test

The first step of coreflooding test was performed using standard core Bentheimer for three formula OGP4, OFTD31 and OFTD11. All formula surfactant was at 0.3% mixed with polymer at 1250 ppm to obtain viscosity ± 10 cP, whereas drive polymer concentration was at 2000 ppm to get viscosity ± 25 cP. Coreflood test was done by injecting 0.3 PV surfactant polymer, followed by 0.6 PV polymer. The results on the picture showed that injection of formula surfactant OFTD31 were able to increase the oil recovery at 35.74 %IOIP or 84.98 %ROIP (Figure 4), followed by formula OFTD11 with recovery factor 45.19 %IOIP or 84.98 %ROIP (Figure 5), indicated the high potential of formula surfactant to be injected in the field scale.

3.9 Economical calculation

Rough economical calculation based on the laboratory results showed that with the price of OGP4 as main surfactant in the range of 3.15 – 5.20 USD/kg, co-surfactant FTD 4.25 USD/kg and polymer FP3630 3.30 USD/kg was able to achieve chemical injection cost as low as 2.95 – 3.44 USD/ barrel incremental oil.

However, the injection of chemical in the native core should be performed to obtain the more representative data.

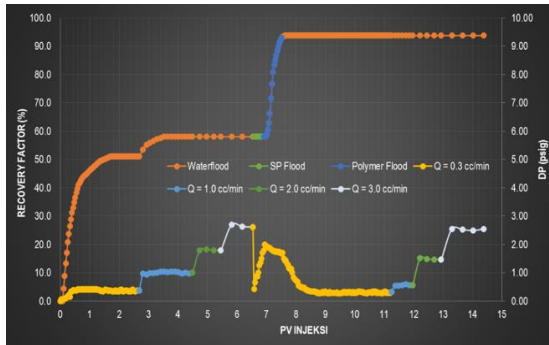


Figure 4. Coreflood test surfactant polymer OFTD31

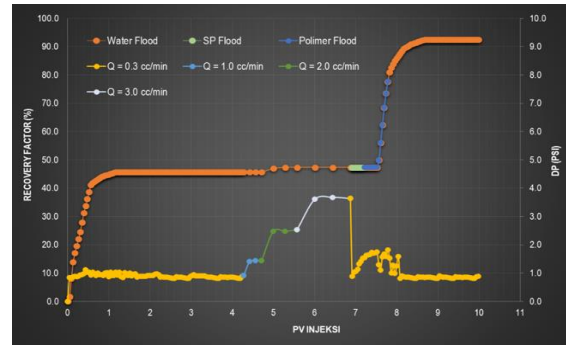


Figure 5. Coreflood test surfactant polymer OFTD11

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