Palm oil anionic surfactants based emulsion breaker
(Case study of emulsions breaker at Semanggi Field production wells)

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Abstract. The presence of emulsion in oil production process is undesirable. The emulsion will increase the production costs, transportation and costs related to emulsion separation process between water and oil. The development of palm oil-based surfactant as an emulsion breaker needs to be conducted given the availability of abundant raw materials in Indonesia and as an alternative to petroleum-based surfactant. The purpose of this study is to produce palm oil-based emulsion breaker, assessing the effect of additive application to the emulsion breaker and analyze the performance of the emulsion breaker. This research was conducted by formulating palm oil anionic surfactant in water formation with the addition of co-surfactant additive and co-solvent. Palm oil anionic surfactant-based emulsion breaker with 0.5% concentration in water can reduce 50% of emulsions with the interfacial tension (IFT) of 2.33x10⁻² dyne/cm. The addition of co-solvent (toluene: xylene) is able to remove the emulsion formed with a lower IFT namely 10⁻³ dyne/cm. The resulting emulsion breaker is capable to remove the emulsion between water and oil. The performance test of emulsion breaker show that the emulsion is able to maintain its performance at reservoir temperature with no indicate of plugging and the value generated incremental oil recovery values is 13%.

1. Introduction
Semanggi field is one of active oil fields in Indonesia, located in Cepu, Central Java. Semanggi field reservoir temperature is 50 °C and composed of Sandstone rock formations. The main problem of the petroleum industry especially at Semanggi field is the decrease in production caused by several factors, among other the old age of oil fields, formation damage and emulsions formation between oil and water formation. The emulsion of oil and water will cause a decrease in productivity. The emulsion would lead to increase the costs and production time as well as low oil production. Problems of productivity decline and emulsion formation at Semanggi field has been addressed by oil wells stimulation. Oil wells stimulation is injection of a certain amount of chemical compounds on the production wells to increase the productivity of produced oil. Oil well stimulation consists of three stages, namely reinjection, soaking and reproduction of the same oil wells. The injection process is expected able to increase the oil production. The process of stimulation in this study was conducted by injecting the emulsion breaker into production wells, a mixture of chemical compounds that can break the emulsion formed between oil and water formations.
The application of emulsion breaker in the petroleum industry has been developed. The applied emulsion breaker is include TOMAC (triocyl methyl ammonium chloride), trietanilamin, polyethylene glycol, and fatty acid ethoxylate with effectiveness reaches 49-55% in emulsion separation [1]. Some of the emulsion is petroleum-based surfactant. Such surfactants are not environmental friendly, having limited raw materials at a high price. The development of palm oil-based surfactants can be used as a solution for petroleum-based surfactants as emulsion breaker formula in oil well stimulation process. High oil production in Indonesia led to the abundant availability of raw materials, where the palm oil plantations in 2015 are 11 million ha with a total production of 31.3 million tonnes [2]. Due to the reasons, palm oil-based surfactant is necessary to be developed.

In this study, co-surfactant and co-solvent was used as additives in the emulsion breaker. Addition of additive was conducted to improve the emulsion breaker effectiveness to break the emulsion formed between oil and water formations. The selection of non-ionic co-surfactants is because of its use as an emulsion breaker in petroleum industry and the selection of aromatic hydrocarbons co-solvent is due to the ability in destabilizing rigid layer as barrier between the oil and water formations. The produce of emulsion breaker must be able to show a good performance as indicated by thermal resistance, filtration ratio value and oil recovery in the performance test of emulsion breaker formula.

2. Materials and Methods

2.1 Materials and Tools
Materials used in this research is oil and formation water from Semanggi oilfield (SMG-P12), palm oil anionic surfactant, nonionic surfactant (APG and ethoxylate), Whatman 41 filter paper (20-25 μm), stainless steel strainer 20 μm, core Berea 100 md, xylene, toluene and chemicals materials for laboratory analysis. The tools used in this study are the analytical balance, hot plate stirrer, rotary oven, microscopes, pH meters and centrifuges.

2.2 Selection of Surfactant Concentration
Formulation process of emulsion breaker was started by dissolving the amount of palm oil anionic surfactant in the interval of 0.5, 1, and 1.5% into formation water as solvent media. Surfactant solution is stirred with a speed of 100-200 rpm at room temperature for 30 minutes. The best concentration was determined with compatibility test (pH, density, droplet size, absorbance and transmission), IFT measurement and observation of emulsion formation (at interval of 5 and 10 minutes). The concentration of surfactant that completely dissolves, have the lowest IFT values, and able to eliminate the emulsion formed was selected as the best surfactant concentration to dissolve in water formation.

2.3 Selection of Additives
Additives mixing into surfactant formulation are intended to eliminate the emulsions formed in crude oil. This study used two types of additives namely co-surfactant and co-solvent. Determining of the best additive is based on IFT measurement and observation of the emulsion formation after the additives addition.

2.4 Performance tests
Performance tests were conducted to obtain the best emulsion breaker performance from the mixing of anionic surfactant with additives. The resulting performance test will illustrate the effectiveness of the emulsion breaker before implemented in Semanggi Field. Performance test of emulsion breaker formula is includes thermal stability test, filtration test and core flood test.
3. Result

3.1 Surfactant Concentration
The first stage to produce emulsion breaker is the selection of surfactant concentration to get the best surfactant concentration as emulsion breaker. Surfactants used in this study are anionic surfactant. The best surfactant concentration was selected based on the compatibility test, IFT measurement, and observation of the percentage of the emulsion.

3.1.1 Compatibility test
Compatibility test is performed to determine compatibility between the surfactant solution with formation water from the reservoir. The results of compatibility test are presented in Table 1.

| Surfactant Concentration (%) | pH       | Density (g/cm³) | Droplet Size (µm) | Absorbance | Transmission (%T) |
|-----------------------------|----------|----------------|-------------------|------------|------------------|
| 0.5                         | 8.6±0.01 | 1.00±4.00E-05   | 1.61 ± 0.28       | 0.85 ± 0.01| 14.3 ± 0.35      |
| 1                           | 8.6±0.01 | 1.00±5.00E-05   | 2.36 ± 0.62       | 1.35 ± 0.07| 4.5 ± 0.71       |
| 1.5                         | 8.5±0.01 | 1.00±4.00E-05   | 3.55 ± 0.13       | 2.28 ± 0.05| 0.54 ± 0.05      |

Results of compatibility test showed that the tested surfactant concentration is compatible to water formation. It is characterized by perfect dissolved in formation water and there is no sediment or lumps in the surfactant solution before and after heating at a reservoir temperature of 50°C. The compatibility test is also showed that anionic surfactant concentration of 0.5% is the best concentration for emulsion breaker formula. Use of anionic surfactant 0.5% was generating alkaline solution, low density, and very small droplet size that has good solubility in formation water. Absorbance and transmission measurements is also show that the concentration of anionic surfactant 0.5% generating clear and not cloudy solution as indicated by low absorbance values and high transmission values. A surfactant solution that clear, compatible and does not produce sediment or floating material is a solution that can be used in oil wells stimulation. In a compatibility test, the more compatible surfactant solution produced, the more effective to be used in oil wells and the decline in the IFT [3].

3.1.2 Interfacial Tension (IFT)
Results of IFT testing indicate that increasing of anionic surfactant concentration greater than 0.5% will increase the IFT produced. Increasing of the surfactant concentration shows that surfactant concentrations 0.5% are the concentration of micelle formed and known as CMC (critical micelle concentration). When CMC condition is reached, IFT measurements will stable or increase. This is because the addition of the surfactant more than 0.5% is no longer able to improve the interface performance. Surfactant has been saturated and prefer to form micelle at water phase that influence on IFT [4].
Figure 1. The Effect of anionic surfactant concentration on IFT

Figure 2. Effect of settling time on the emulsion percentage

Observations of emulsion on the resulting formulation solution was performed at reservoir temperature 50°C. Observation of the emulsion formed (Figure 2) shows that the control (oil and formation water) produce an emulsion of 0.2 mL or 2% after storage at rotary oven. The addition of anionic surfactant by 0.5 and 1% in formation water indicates the emulsion percentage 1% and 5% with the addition of surfactant 1.5%. Anionic and nonionic surfactants can be used as demulsifier [5]. Surfactants that dissolved into formation water when in contact with oil, slowly will destabilize the emulsion between oil and water, which leads to changes in the free energy around the oil surface and surfactant solutions and in turn will reduce rigidity of the film on the surface of oil and water emulsion.

The results of compatibility test, IFT measurement and observation of the emulsion showed that surfactant concentrations 0.5% is the best surfactant concentrations to emulsion breaker. The concentration of 0.5% is compatible to water formation. Measurement of IFT showed the lowest measurement and observation of the emulsion showed that in just 5 minutes was able to produce the lowest percentage of emulsion. Under these conditions, surfactant concentrations 0.5% serves as the best concentration of palm oil anionic surfactants based emulsion breaker.

3.2 Selection of Additive
Additives are chemical compounds that added to emulsion breaker solution. The additives used in this study are co-surfactant and co-solvent. The addition of additives to emulsion breaker solution is intended to eliminate the emulsion. The first stage is begins with co-surfactant addition and then followed by co-solvent when co-surfactant addition does not show better results. Selection of the best additives is based on IFT measurement and emulsion observations.
3.2.1 Co-surfactant
Interfacial tension (IFT) observation shows that the addition of co-surfactant into the emulsion breaker solution does not provide the better results (Figure 3). IFT is increased after the addition of co-surfactant either ethoxylate or APG surfactants namely 7.48x10^{-2} and 4.17x10^{-2} dyne/cm, respectively. Increasing of IFT may be caused by the type of nonionic surfactant added was not able to improve detergency of emulsion breaker.

![Figure 3. The Effect of surfactant formulation 0.5% and co-surfactant additive on IFT](image)

Observation of the emulsion formation (Figure 4) shows that the addition of APG and ethoxylate co-surfactant has no significant effect compared to anionic surfactants. IFT measurement also does not give better results with the addition of the co-surfactant. The use of ethoxylate surfactants is produce quite low of interfacial tension values and emulsions by 3%. The use of APG provides emulsion observations 2% but does not produce low IFT. It can be concluded that the addition of co-surfactant does not increase the effectiveness of the resulting emulsion breaker.

3.2.2 Co-Solvent
The use of co-solvent is expected to provide better results than co-surfactants. Co-solvent used is a mixture of toluene and xylene with several different mixing ratios. Fan et al. [4] explains that demulsification process with surfactants can be improved the effectiveness with the use of polymer and solvent mixtures. Type of aromatic solvents such as benzene and toluene can be used in the preparation of demulsifier process [6].

IFT measurements (Figure 5) on the emulsion breaker with the addition of co-solvent showed different results compared to the use of co-surfactants. IFT measurements were conducted to the whole of solution mixing of emulsion breaker. The results of IFT measurement show a value of 10^{-3} dyne/cm, which is lower than the use of anionic surfactant alone. The measurement results showed a tendency of
IFT increased along with increased concentrations of co-solvent in various ratios of toluene: xylene. The lowest IFT was produced at the co-solvent concentration of 0.1% with a ratio of toluene: xylene 1: 3. IFT value generated at 1.33x10^{-3} dyne / cm.

**Figure 5.** The effect of co-solvent concentration at different ratio of toluene: xylene on IFT

The results of IFT measurement showed that the addition of co-solvent gives lower IFT, especially on the use of co-solvent by a ratio of toluene: xylene 1:3 and 3:1. But if the three co-solvent ratio compared, the ratio of 1:1 has high IFT value compared to the two co-solvent ratio. The value generated by the ratio of 1:1 is quite different namely 10^{-2} dyne/cm, but the resulting value is still in the scale of 10^{-3} dyne/cm, which is still within the limits of applicable surfactant solution for injection process, namely ≤ 10^{-2} dyne/cm [7]. In addition, the use of co-solvent capable to lowering the IFT compared to surfactant alone. The decline of IFT occur due to the co-solvent is able to completely dissolved in the emulsion breaker that consisting of anionic surfactant and formation water.

Emulsion breaker formula with the addition of co-solvent is able to lower the IFT. This is because the co-solvent disrupts asphaltene aggregation that form films on the surface of emulsion droplet through interactions with asphaltene aggregate polar groups. When asphaltene aggregation disrupted, the emulsion stability will be disrupted because the film gradually thins and breaks. The film break causes the emulsion breaker adsorbed on the surface of oil and water that change the IFT. Adsorption of emulsion breaker on the surface of the water and oil will affect the free energy in the interface area that decreases IFT [8]. Interface free energy or interfacial tension is the minimum amount of work required to expand the area of the interface.

**Figure 6.** The effect of settling time on emulsion percentage at co-solvent addition with different solvent ratio
Observations (Figure 6) show that the emulsion percentage 0% can be produced within 10 minutes, especially in solvent concentrations of 0.1 and 0.3% of various solvent ratios. The use of solvent proved to be effective in removing the emulsion formed between oil and water. The longer settling time, the better separation of oil and water. Although the first minute observations will produce a fairly high percentage, but gradually there is perfect separation of water and oil and no emulsion produced until 100 minutes. This shows that temperature affects the destabilization of emulsion, the longer an emulsion system in contact with the reservoir temperature, the better effectiveness of the emulsion separation. Temperatures cause increased brown motion and mass transfer in the interface area of the two droplets of dispersed phase. This situation causes the momentum of the dispersed phase increases and causes coalescence [9]. Therefore, the longer the contact with the temperatures produces better separation.

The effectiveness of co-solvent addition to break the emulsion is due to the use of aromatic hydrocarbon solvents. As it was explained earlier, asphalthene as natural emulsifier is the cause of emulsions formation. According to earlier studies, it is known that asphalthene increasing to dissolved in line with the increase in aromatic compounds. The use of aromatic co-solvent can generate a good emulsion separation. Aromatic solvent mixture will be able to separate the emulsion formed by disturbing \( \pi-\pi \) bond and polar bond between asphalthene monomer [10]. The presence of surfactant in emulsion breaker will solved asphalthene monomer so that it will remain dissolved in the oil and does not form aggregates which produce the film. This is the cause of the use of emulsion breaker with the addition of co-solvent is more effective than just anionic surfactants and the addition of co-solvent.

Observations on the emulsion percentage showed that at various ratios and concentrations of co-solvent is able to eliminating the emulsion. While at IFT measurement results it is concluded that there are two co-solvent ratio that showed the lowest IFT value which are 1:3 and 3:1 at concentration of 0.1%. The best concentration based on Duncan test is 0.5% therefore, the concentration that will be choose as the best concentration is 0.1%. The concentration of 0.1% resulted in the separation of emulsions as well as a concentration of 0.5% and the fewer of co-solvent amount will reduce production cost. For the co-solvent ration that will be use as the best ratio is 1:3. Ratio 1:3 showed the lowest IFT value and ratio of toluene that had been using is very low, compared with the other ratio. Using of solvent with a low flash point began to reduce in the field. This is because the solvent with a low flash point is flammable, thus would endanger and disrupt oil production process. Increasing the temperature of the solvent with a low flash point will cause changes into vapor and eventually reach the point of the flame.

### 3.3 Performance Test

Performance test is conducted to determine the most effective of emulsion breaker according to IFT variance analysis and emulsion observations. The best emulsion breaker is obtained from surfactant concentration 0.5% with co-solvent concentration 0.1% at a ratio of toluene : xylene 1:3. Performance tests are consisting of thermal stability test, filtration ratio (filtration test) and core flood test.

#### 3.3.1 Thermal Stability Test

Thermal stability test on emulsion breaker formula was conducted to determine the changes on the formula produced at hot temperature or at reservoir temperature based on IFT value. Measurements to the fifth day produce IFT in the range of \( 10^{-3} \) dyne/cm (Figure 7). Although IFT value increased at the seventh day but the values is still \( \leq 10^{-3} \) dyne/cm. Measurement of thermal stability is closely related to the soaking time that will be applied in reinjection process of emulsion breakers into oil wells. Based on the results of thermal stability test, it can be concluded that surfactant formula is still able to work well in reservoir temperature until the seventh day.
3.3.2 Filtration Ratio
Filtration ratio measurement is intended to determine the suitability of emulsion breaker when applied. Filtration ratio aims to determine the indication of plugging from the emulsion breaker seen from the filtration ratio value that less than 1.2. The emulsion breaker solution was passed through a filter that has a pore size of 1.2 µm that representing pores of reservoir rocks. The filtration ratio value is determined by the calculation of the volume of emulsion breaker solution based on a certain time.

Filtration test showed that the filtration ratio of the emulsion breaker is 1.04 (≤ 1.2). The result showed that the emulsion breaker capable of passing through a filter. The solution that can pass through the filter and has filtration ratio value less than 1.2 indicate that there is no possibility of the injected solution could be the cause of plugging. Plugging in the oil field is undesirable because it affect the permeability and porosity of the native core.

3.3.3 Core Flood Test
Core flood test was conducted to determine the extent of oil recovery that can be produced through emulsion breaker injection when applied in oil field. The calculation of oil recovery value on emulsion breaker injection was done after soaking for 12 hours. Injection of emulsion breaker is able to give a recovery of 13% (Figure 8). This proves that surfactant injection was able to increase the oil recovery that produce 43.6% of total oil production in the reservoir.

![Figure 7. The Effect of Heating Time on emulsion breaker IFT](image)

![Figure 8. Incremental oil recovery with emulsion breaker](image)
4. Conclusions

Emulsion breaker formula was produced from the best surfactant concentration namely anionic surfactant 0.5%, addition of co-solvent 0.1% and ratio of toluene: xylene 1: 3. The addition of co-solvent additives into the emulsion breaker cause increase in the IFT value and the percentage of emulsion produced compared with the addition of co-solvent that able to reduce IFT value to $10^{-3}$ dyne/cm and produces perfect oil and water separation. Results of performance test (core flood test) using oil well fluid samples from the Semanggi Field and core Berea show that the resulting emulsion breaker capable to improve oil recovery to 13%.

Reference

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