Formulation of alternative demulsifiers with palm oil based surfactants for crude oil demulsification

Fajar Bagas Saputra¹, Haruhiro Fujita², and Erliza Hambali³

¹P.T. Great Giant Food, Indonesia
²Niigata University of International and Information Studies, Japan
³Surfactant and Bioenergy Research Center, IPB University, Indonesia

*Email: fajarbagassaputra@gmail.com

Abstract. Palm oil-based surfactants were used to formulate demulsifiers for crude oil demulsification as alternatives to petroleum-based surfactants. A light crude oil sample obtained from x field crude oil well contained 0.713% (w/w) asphaltene and 25.75% BS&W. The formulation of demulsifiers was carried out by the selection of a primary surfactant from Sodium Methyl Ester Sulfonate (SMES) and Diethanolamide (DEA), and the concentration of co-surfactant addition. The best formulation was SMES as a primary surfactant with the addition of a 10% DEA co-surfactant. The best solvent was the solution of toluene and xylene (1:1). The temperature treatment of 80 °C separated 100% water from crude oil emulsion and decreased BS&W to 5.45%.

Keywords: Alternative demulsifiers, Crude oil demulsification, Palm oil-based surfactants

1. Introduction

Crude oil emulsion is of water-in-oil type and stabilized by various natural surface active agents such as resins and asphaltenes. It is formed when two immiscible liquids (oil and water) are agitated together to disperse droplets of one liquid into another. The agitation is taken place by the flow of crude oil from the well to the surface line. The agitation of water and crude oil stabilizes the crude oil emulsion in which water remains dispersed for a long time [1].

The crude oil emulsion is one of the major obstacles in crude oil production. Water in the crude oil emulsion can contain gas hydrates and salts such as NaCl, MgCl₂, CaCl₂, and KCl which are responsible for corrosion of production equipment and pipelines. They also decrease the quality of petroleum distillates, especially by the reactions of heavy components such as boiler fuel, the raw material for catalytic cracking and others [2]. In addition, the crude oil emulsion increases transportation cost as it occupies extra spaces and increases the viscosity of the crude oil. Therefore, the demulsification of crude oil emulsion is one of the most important processes in all oil fields.

The demulsification is the basic process used to separate water from the crude oil emulsion. The demulsification can be classified into electrical, mechanical, and chemical methods. Chemical demulsification is the most common method in the industry due to its applicability. This method involves the use of chemical additives to enhance emulsion separation processes, of which surfactants are commonly used. Demulsifiers being used in the petroleum industry are usually petroleum-based or
polymer-based surfactants. The petroleum-based surfactant is less environmental-friendly, while the polymer-based surfactant costs higher as raw materials are not easily available.

The development of demulsifier by palm oil-based surfactants is of necessity considering the use of abundant biomass materials, hence zero carbon emission, as the Republic of Indonesia produced 35 million tons of CPO from a total plantation area of 12 million ha in 2017 [3]. In this study, a formula of a demulsifier was developed to break emulsion in crude oil using palm oil-based surfactants, i.e., diethanolamine (DEA) and sodium methyl ester sulphonate (SMES). The objectives of this study are to formulate a demulsifier by palm oil-based surfactants, applying a mixture of a primary surfactant and a co-surfactant, and to determine the effects of solvent and temperature on crude oil demulsification.

2. Materials and Methods

The materials used in this study were crude oil, formation water, anionic surfactant sodium methyl ester sulfonate (SMES) and nonionic diethanolamide (DEA) surfactants and other chemicals for analyses.

The physicochemical analysis of the crude oil fluid was carried out, to observe density, API gravity, specific gravity, viscosity, Basic Sediment and Water (BS&W) using the ASTM 6560 method and asphaltene contents.

Demulsification performance test by the fast water drop (FWD) and BS&W, to compare SMES and DEA as the primary surfactant. Then the co-surfactant concentrations at 10%, 20%, and 30% were tested for the performance.

The solvents, i.e., toluene, xylene, and a solution of toluene and xylene (1:1), and heating temperature variations of 50 °C, 60 °C, 70 °C, and 80 °C were also tested for the performance.

3. Results and Discussions

3.1. Physicochemical properties

The physicochemical properties of the crude oil are shown in Table 1.

| Parameter          | Results | Unit  |
|--------------------|---------|-------|
| Density            | 0.82059 | g/cm³ |
| API density        | 0.85334 | g/cm³ |
| API specific gravity | 0.85418 | o     |
| API gravity        | 34.16   | o     |
| Asphaltene content | 0.713   | %     |
| BS&W              | 27.73   | %     |

The density and API density were 0.82059 and 0.85334 g/cm³ respectively. The API specific gravity and API gravity were 0.85418° and 34.16° respectively. The oil with smaller specific gravity value contains a shorter chain of alkanes fraction so that the molecular density gets lower. The sample crude oil was classified as a light crude oil as the API Gravity value was higher than 31.1° [4].

The concentration of asphaltene was 0.713%. Asphaltene is a natural emulsifier in crude oil that affects oil and water emulsions stability. Asphaltene is the heaviest molecule and the most polar fraction of crude oil composing condensed aromatic rings with aliphatic side chains and various types of functional groups. With these attributes, the asphaltene acts as a natural emulsifier agent [5], as in Figure 1.
The basic value of sediment and water (BS&W) was 27.73%. The sediment is an impurity component of the mud-shaped oil. The higher the value of BS&W, the quality of oil decreases. The sediment in the oil should be decreased, hence, the oil demulsification process is conducted to decrease the value of BS&W. The standard value of BS&W of crude oil after the demulsification process is expected to be between 0.2-5% [7].

3.2. Formulation of Demulsifier

3.2.1 Primary surfactant selection

Surfactant is a compound that has an ability to reduce the surface tension of a media as it has a hydrophilic group at a polar part and a lipophilic group at nonpolar parts. Surfactants are generally used as emulsifying agents of a distinctly different mixture, as presented in Figure 2. Contrarily, surfactants perform as demulsifiers. Roodbari et. al. [8] proved that surfactants had both emulsification and demulsification functions in different cases and some surfactants for making oil in water emulsions could demulsify water in oil emulsions.

Figure 1 Mechanism of emulsion stabilization: asphaltenic thin film formation at the oil/water interface (after [5] and [6])

![Figure 1](image1.png)

Figure 2 Schematic display of demulsifier structure and its penetration into the layer around water droplet (after Roodbari et al. [8])

![Figure 2](image2.png)
In recent years, many studies were carried out on ionic and nonionic demulsifiers. Studies have shown that the presence of more hydrophilic parts in demulsifiers cause more separation of water from oil and it had a substantial effect on the amount of HLB number of surfactant [9]. Generally the nonpolar (lipophilic) has a long alkyl chain, while the polar (hydrophilic) contains hydroxyl groups [10]. The surfactants used in this study were sodium methyl ester sulfonate (SMES) and diethanolamide (DEA) from palm oil. The SMES surfactant is anionic one that is a negatively charged surfactant on its hydrophilic group or surface-active part. The formulation of the SMES surfactant starts with the formulation of MESA (methyl esters sulfonic acid) synthesis of methyl ester by the sulfonation followed by the neutralization using 50% NaOH to produce the SMES. DEA is a nonionic surfactant synthesized from methyl ester olein and diethanolamine by the amidation process. The effects of surfactants on demulsification are shown in Table 2.

| Surfactant | FWD (%) | BS&W (%) |
|------------|---------|----------|
| SMES       | 38.12   | 12.67    |
| DEA        | 6.88    | 25.73    |
| Control    | 3.75    | 26.31    |

The separation value of water at 15 minutes (FWD), the SMES surfactant showed 38.125% compared to the DEA surfactant of 6.875%. The SMES had better water separation capability than the DEA surfactant. BS&W values were decreased after the demulsification process. The SMES surfactant decreased BS&W to 12.67%, while DEA surfactant to 25.31%. The smaller value of BS&W shows the better quality of crude oil as the impurities on the oil decreases. SMES surfactant had better performance in solving crude oil emulsion as SMES might have had sulphonate groups which are appropriate hydrophilic parts. This group allows the surfactant more hydrogen bonds and has stronger hydrophilic parts.

3.2.2 Co-surfactant addition

In the industry, the use of more than one type of surfactant is very common to improve the demulsification performance. Every surfactant has different characteristics. Nonionic surfactants are often used as co-surfactants and mixed with other surfactants as they are generally lipophilic. The performance of nonionic surfactants is stronger when mixed with ionic surfactants and amphoteric surfactants in their applications. SMES was selected as the primary surfactant and DEA as a co-surfactant. The effects of co-surfactant addition on demulsification are shown in Table 3.

| Level of co-surfactant addition (%) | FWD (%) | BS&W (%) |
|------------------------------------|---------|----------|
| 0                                  | 38.12   | 12.67    |
| 10                                 | 55.00   | 11.92    |
| 20                                 | 49.75   | 12.40    |
| 30                                 | 10.00   | 19.43    |

Co-surfactant addition has an effect in increasing the performance of the demulsifier. The 10% and 20% co-surfactant additions increased the demulsifier performance on water separation in 15 minutes to 55% and 49.75% respectively. While the 30% addition, FWD declined to 10%. The same result was also shown on the value of BS&W. The 10% addition of 11.92% and 20% of 12.40% respectively. The 30% co-surfactant addition increased BS&W to 19.43%. The 10% DEA addition was selected for the co-surfactant addition.
The analysis of variance showed that the addition of co-surfactant significantly \((\alpha = 0.05)\) influenced the increase of water separation and the decrease in BS&W. The Duncan test showed that each level of co-surfactant addition was significantly different from other levels in the water separation response and the value of BS&W. The analysis showed that the 10% co-surfactant addition showed the best result of FWD 55% and of BS&W 11.92%. It was also demonstrated that the higher co-surfactant addition with the reverse demulsification performance. The demulsifier performance decreased when the addition level exceeded 20%. This may have associated, an increase in the nonionic surfactant addition that might have precluded interfacial activity. Muhpidah [11] observed that increasing the addition of nonionic co-surfactants to anionic surfactants would inhibit the performance of anionic surfactants in demulsification.

3.2.3 Solvent selection

The demulsification is a process to break the emulsion by disrupting the viscoelastic film layer in the droplet. The film layer acts in stabilizing the emulsion composed of aromatic groups and hydrogen interactions between the resin and asphaltene [12]. Therefore, in demulsifier formulation, the solvent is necessary to disrupt the interaction between the asphaltenes-resin.

In this study, xylene, toluene, and an equal mixture were applied. The selection of xylene and toluene was based on previous studies that this solution was able to disrupt the emulsion stability in crude oil. Atta (2013) [13] used xylene and toluene solutions for the solvents on polymer-based demulsifier formulations and it was proven that both solutions could decrease the interface tension to disturb the stability of crude oil emulsions. The effects of solvents on demulsification are shown in Table 4.

| Solvents                  | FWD (%) | BS&W (%) |
|---------------------------|---------|----------|
| Xylene                    | 10.30   | 22.00    |
| Toluene                   | 15.10   | 20.10    |
| Xylene:Toluene (1:1)      | 20.00   | 18.80    |

The result showed that the toluene destabilized the emulsion 40.25%, slightly higher than the xylene’s FWD 39.25%. The mixed solution of xylene and toluene (1:1) improved the separation at 59.83% as well as the lowest BS&W. Hence the mixed solution of xylene and toluene (1:1) was selected as a solvent for demulsifier formulation.

The results indicate the possible solvent disruption on crude oil emulsion stability. Toluene and xylene solvents might have interfered asphaltene-resin aggregation by interacting with aromatic groups. Toluene and xylene are classified as aromatic hydrocarbons. Toluene \((\text{C}_6\text{H}_5-\text{CH}_3)\) is a benzene-derived compound with one of its hydrogen atoms binding to a methyl group \((\text{CH}_3)\). Toluene is used to separate the asphaltene from crude oil. Toluene is able to dissolve the asphaltene up to 65.09% [14]. Xylene \((\text{C}_8\text{H}_{10})\) or dimethyl benzene is an aromatic compound in the form of 3 isomers: ortho-, meta- and para-xylene or 1,2-, 1,3-, and 1,4-dimethyl benzene. Xylene is also capable of dissolving asphaltene to 61.95% [14]. Asphaltene has varying degrees of solubility from certain types of solvents. Therefore, it is sometimes necessary to mix two types of solvents to increase the solubility efficiency of asphaltene. Lightfor et al. [15] confirmed that additional solvents can be used to improve the solubility efficiency of asphaltene.

| Solvents (0.4 v/v) | FWD (%) | BS&W (%) |
|--------------------|---------|----------|
| Xylene             | 39.25   | 15.83    |
| Toluene            | 40.25   | 10.00    |
| Xylene:Toluene (1:1)| 59.83   | 9.85     |
3.2.4 Effects of temperature

The effects of temperature on demulsification with demulsifier are shown in Table 5. Fernando [16] reported that the temperature had a significant influence on emulsion demulsification in crude oil. The increase of temperature leads to decrease oil density and viscosity, increased collision frequencies between emulsion droplets, and increased solubility of compounds contained in the emulsion system. The temperature rise played a role in weakening the resin solvent to asphaltene and weakening the interaction of Van der Waals aggregate asphaltene resin. The effects of temperature on demulsification with demulsifiers are shown in Table 6.

Table 6. Effects of temperature on demulsification with demulsifiers

| Temperature | FWD (%) | BS&W (%) |
|-------------|---------|----------|
| 50°C        | 59.83   | 9.85     |
| 60°C        | 80.90   | 6.60     |
| 70°C        | 95.40   | 5.80     |
| 80°C        | 100.00  | 5.45     |

The analysis of variance showed that the heating temperature had a significant effect ($\alpha = 0.05$) on increasing the water separation and decreasing BS&W value. Duncan test showed that each temperature level was significantly different from other temperature levels in the water-splitting response and BS&W values. The analysis showed that 80°C resulted in 100% water separation and the smallest value of BS&W, 5.45%.

4. Conclusions

A crude oil sample was classified as light crude oil. The crude oil contained 0.713% asphaltene and 27.73% basic sediment. The best palm oil-based demulsifier formulation was SMES as a primary surfactant with the addition of 10% DEA co-surfactant applying xylene : toluene (1:1). The formulation separated 100% water from crude oil emulsion and decreased BS&W to 5.45% at 80°C. Increasing the temperature of the demulsification process might have affected the emulsion stability so that the demulsification of crude oil emulsion increased.

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