Palm oil based surfactant products for petroleum industry

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Abstract. In petroleum production process, many problems causing reduced production are found. These include limited oil recovery, wax deposit, asphaltene deposit, sludge deposit, and emulsion problem. Petroleum-based surfactant has been used to overcome these problems. Therefore, innovation to solve these problems using surfactant containing natural materials deserves to be developed. Palm oil-based surfactant is one of the potential alternatives for this. Various types of derivative products of palm oil-based surfactant have been developed by SBRC IPB to be used in handling problems including surfactant flooding, well stimulation, asphaltene dissolver, well cleaning, and wax removal found in oil and gas industry.

1. Introduction
Many problems causing reduced productivity and environmental pollutions were found in petroleum production process. These problems include limited oil recovery, wax deposit, asphaltene deposit, sludge deposit, emulsion formation, and water and land pollution as a result of spilled oil residue. Efforts need to be done to overcome these problems as the demand for oil is increasing and there is no other source of energy can replace it yet. Pollution handling is an important thing to do as environmental pollution endangers living organisms in land and sea.

Chemical injection is used to overcome several problems in oil industry. The chemical used is usually petroleum-based surfactant. It is known that surfactant plays a role in reducing interfacial tension between fluid and fluid, fluid and rocks, and fluid and hydrocarbon to increase the permeability of formation in an effort to increase production rate. In addition, surfactant can break surface tension of oil emulsion bonded to the rocks (emulsion block), reduce the occurrence of water blocking, and alter the wettability of rocks from oil-wet to water-wet. The common surfactant used is petroleum-based surfactant. Therefore, innovation to solve these problems using surfactant containing agricultural materials deserves to be developed.
One of the innovations to be developed is oil palm-based surfactant. Total crude palm oil (CPO) production in Indonesia in 2015 was 31.3 million tons. In 2020, palm oil production is estimated to reach 40 million tons. With high CPO production in Indonesia, it will be important to further develop oil palm derivative products to increase the added value of palm oil and at the same time overcome problems in oil industry. This way, oil palm plays a role in the improvement of national oil productivity.

2. The Role of Surfactant for Oil and Gas Industry

Surfactant or surface active agent is a molecule which has hydrophilic and hydrophobic groups in one structure. Surfactant reduces interfacial tension between fluid and fluid, fluid and rocks, and fluid and hydrocarbon to increase the permeability of formation in an effort to increase production rate. In addition, surfactant can break surface tension of oil emulsion bonded to the rocks (emulsion block), reduce the occurrence of water blocking, and alter the wettability of rocks from oil-wet to water-wet. The common surfactant used is petroleum-based surfactant. The role of surfactant in the improvement of production rate is depicted in figure 1.

![Figure 1. Capillary number versus oil recovery [1]](image_url)

There are two dominant forces working in the pores of oil reservoir rocks, namely capillary \((\sigma \times \cos \theta)\) and viscous \((\nu \times \mu)\) forces. The ratio between these two forces is called Capillary Number as depicted in Figure 1 which shows the oil that can be pushed out (% oil recovered). Therefore, % oil recovered indicates the percentage of residual oil which can be taken out from the pores after water injection. In general, the Capillary Number found in primary production and Water Injection process lies in the range of \(10^{-7} – 10^{-5}\) (dimensionless). This means that there is no waterflood \(S_{or}\) (residual oil saturation) which can be pushed by normal water. Therefore, surfactant is used to reduce capillary forces and this means increasing capillary number effectively so that the process become operationally feasible and more economical.

Increasing Capillary Number can also be done by altering wettability (namely contact angle, \(\theta\)). If contact angle \(\theta\) can be altered to 90° (and this is Neutral wettability, not water-wet), then \(\cos(\theta) = \cos(90°) = 0\) and capillary forces becomes null (0) so that Capillary Number becomes infinite. As a result, residual oil after waterflood can be pushed perfectly up to 100%. It is expected that, in addition to its function of reducing the IFT of oil-water, surfactant can alter wettability to a netral direction.

If surfactant solution can form microemulsion with particle size smaller than the size of the smallest pores of porous rocks, then the surfactant solution will most probably be able to to push residual oil out as much as possible. Microemulsion can be formed when the IFT is very small \((\sigma < 10^{-2}\) dyne/cm)
and surfactant solution has a tendency to dissolve in oil. In a miscible displacement mechanism (IFT = 0, where the pushing fluid is soluble in the pushed fluid), surfactant is able to push 100% Sor (residual oil saturation) out from inside the pores.

Palm oil-based surfactant is expected to be able to substitute petroleum-based surfactant. Palm oil based-surfactant developed by SBRC IPB is biodegradable as it is made from palm oil which is abundant in Indonesia so that its sustainability is ensured. Palm oil-based surfactant is more resistant to Ca$^{2+}$ and Mg$^{2+}$ ions and salinity. It has an IFT value $\leq 10^{-3}$ dyne/cm and adsorption value $< 400$ µg/g core. It is stable at reservoir temperature for 3 months, produced at Phase III / II(-), and it has a Filtration Ratio $\leq 1.2$.

3. Palm Oil-based Surfactant for Various Purposes

Based on the its ionic charge of hydrophilic groups after it is dissociated in liquid medium, surfactant is classified into four types, namely (1) anionic; its hydrophilic group contains negative charge, (2) cationic; its hydrophilic group contains positive charge, (3) non ionic; its hydrophilic group contains almost no charge, and (4) amphoteric; molecules in its hydrophilic group contains positive or negative charge depending on the medium pH [2]. All types of surfactants can be synthesized from palm oil because of its physicochemical properties and fatty acid composition as shown in table 1 and 2 fit the requirements.

| Physical and chemical properties | Value |
|----------------------------------|-------|
| Triglyceride                     | 95%   |
| Free fatty acids                 | 2.5%  |
| Color (5 ¼ “ Lovibond Cell)      | Red orange |
| Water and filth content          | 0.15-3.0 % |
| Peroxide number                  | 1 – 5.0 (meq/kg) |
| Anisidine value                  | 2-6 (meq/kg) |
| $\beta$-carotene content         | 500-700 ppm |
| Phosphorus number                | 10-20 ppm |
| Iron (Fe) content                | 4-10 ppm |
| Tocopherol level                 | 600-1000 ppm |
| Diglyceride                      | 2-6%  |
| Acid number                      | 6.9 mg KOH/g minyak |
| Saponification number            | 224 – 249 mg KOH/g minyak |
| Iodine number (wijs)             | 44-54 mg iod/g minyak |
| Melting point                    | 21-24 °C |
| Refraction index (40 °C)         | 36.0-37.5 |

Some palm oil-based surfactants developed by SBRC IPB and had potential for applications in oil industry in Indonesia include glycerol ester, diethanolamide, alkyl polyglycoside, and methyl ester sulphonate. Various derivative products of palm oil-based surfactant, whether in their formulation process, surfactant ia used as a single component or there is another additive substance added in, are potential to be used as a substitute for petroleum-based surfactant. This surfactant can be used in many applications including chemical flooding, stimulation, asphaltene dissolver, wax dissolver, emulsion breaker, sludge breaker, well cleaning, oil spill dispersant, and enhanced bioremediation.
Table 2. Fatty acid composition of palm oil

| Fatty Acids       | PKO  | CPO  | RBDPO | PFAD | Olein | Stearin |
|-------------------|------|------|-------|------|-------|---------|
| Lauric (C12:0)    | 40–52| <1.2 | 0.12–0.28 | 0.1–0.3 | 0.1–0.5 | 0.1–0.6 |
| Myristic (C14:0)  | 14–18| 0.5–5.9 | 0.87–1.19 | 0.9–1.5 | 0.9–1.4 | 1.1–1.9 |
| Palmitic (C16:0)  | 7–9  | 32–59 | 42.46–48.54 | 42.9–51.0 | 37.9–41.7 | 47.2–73.8 |
| Palmitoleic(C16:1)| 0.1–1| <0.6 | 0.13–0.16 | - | 0.1–0.4 | 0.05–0.2 |
| Stearic (18:0)    | 1–3  | 1.5–8 | 4.10–4.75 | 4.1–4.9 | 4.0–4.8 | 4.4–5.6 |
| Oleic (18:1)      | 11–19| 27–52 | 35.23–41.67 | 32.8–39.8 | 40.7–43.9 | 15.6–37.0 |
| Linoleic (18:2)   | 0.5–2| 5.0–14 | 7.74–11.75 | 8.6–11.3 | 10.4–13.4 | 3.2–9.8 |
| Linolenic (C18:3) | -    | <1.5 | 0.06–0.24 | - | 0.1–0.6 | 0.1–0.6 |
| Arachidic (C20:0) | -    | -    | 0.27–0.44 | - | 0.2–0.5 | 0.1–0.6 |

3.1 Surfactant for chemical flooding

Chemical flooding is a method used to obtain more oil after the reduction of primary production process (natural) by using natural energy originating from the reservoir itself (natural reservoir drive) [7]. Chemical flooding is obtaining oil by injecting materials from outside the reservoir [8]. Surfactant to be used for chemical flooding should have the following properties: pH 7-8, IFT value ≤ 10^{-3} dyne/cm, adsorption value < 400 µg/g core. It should also be stable for > 3 months at thermal stability test (±10^{-3} dyne/cm), produced at Phase III / II(-), have a filtration ratio ≤ 1.2, and have incremental oil recovery in a coreflooding test of about 15.0-20.0 % IOIP.

![Figure 2. Formation of microemulsion phase at 60℃](image1)

![Figure 3. SBRC 100A 0.3% - polymer 0.1% is stable in thermal stability test at reservoir temperature of 60℃ until 12 months.](image2)
3.2. Surfactant for Stimulation
Stimulation is a process of oil well repair in order to increase formation permeability in an effort to increase production rate. This process causes dissolution of particles blocking porous space of rocks. Acidizing and surfactant injection are the stimulation methods commonly used in oil industry [9]. In surfactant stimulation process, reservoir rocks are soaked in surfactant to give time to surfactant to penetrate into reservoir rocks. Surfactant penetration is expected to alter rock wettability to water wet, reduce interfacial tension, reduce capillary force, and reduce water cut occurrence. This way, permeability and well productivity can be improved. In surfactant stimulation process, surfactant can make contact with high reservoir temperature for a long period of time [10]. SPRC IBP has developed surfactant for stimulating agent with the following properties: IFT value ≤ 10^{-3} dyne/cm, stable at reservoir temperature, stable at stability thermal test (IFT value ≤ 10^{-3} dyne/cm), and filtration ratio value <1.2.

3.3. Surfactant for Asphaltene Dissolver
The use of solvent in asphaltene deposit handling can only remove about 50% of asphaltene deposit. The addition of surfactant in deposit handling makes surfactant dispersed in asphaltene molecules by breaking down the bonds between asphaltene molecules. This, in turn, will inhibit the reformation of asphaltene deposit. Temperature, pressure, oil composition changes and injection of chemical substances in oil production process result in the disruption of balance and stability of asphaltene miscelles in oil. This disruption is initiated by the release of resin from asphaltene surface. Then there is an interaction among asphaltene molecules and a solid phase is formed through a precipitation process. Further, the solid phase moves up to the surface causing the formation of asphaltene deposition [11].

The asphaltene dissolver produced by SBRC IPB has asphaltene solubility level of 99.38% and it can alter the contact angle of rocks from 48.60° too 80.89°. It was shown from wetting characteristic test that this asphaltene dissolver has an ability to increase wettability on a metal surface. This is characterized by the small amount of deposit remain which is left on the metal surface and asphaltene removal which reaches 99.66%.

3.4. Surfactant for Well Cleaning
Well cleaning is surfactant developed as an agent to clean holes of perforation well, pipe lines, and oil production equipment from blocking oil remains so that oil production process can be optimum. Results of palm the performance test of oil-based surfactant showed as a well cleaning agent show that there are two phases formed and there is no macroemulsion phase is formed in the phase behavior test. This surfactant is also shown to have IFT value of 10^{-2} dyne/cm and it is stable at reservoir temperature in a thermal stability test.

3.5. Surfactant for Wax Dissolver
Wax is formed as a result of lowered temperature under oil pouring point. Wax deposit is formed around tubing and production pipe causing a decrease in oil production by 10-35%. Surfactant plays an important role in increasing oil production in highly depleted wells by reducing interfacial tension, altering wettability of rocks, and cleaning oil wells from organic sediment. The use of surfactant in a solvent is a way of handling wax chemically. Dissolving wax is more effective by using a solvent and surfactant than by using a solvent only. Wax dissolver developed from palm oil-based surfactant by SBRC IPB is able to reduce the viscosity of crude oil with high wax content from 149.05 cP to 14.96 cP at 40° C.

4. Conclusion
Various palm oil-based surfactants have been specifically developed at SBRC IPB for oil and gas industry needs. Surfactants can be specifically produced for either improved oil recovery (IOR) or
enhanced oil recovery (EOR), well stimulation, asphaltene deposit removal, well cleaning agent and wax removal agent.

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