Chemically induced demulsification of water in crude oil emulsion from East Kalimantan oil fields

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Abstract. The application of demulsifiers on dewatering of crude oil emulsions from East Kalimantan oil fields is reported in this work. Two types of experiment were conducted: the bottle test in which emulsion resolution was carried out after demulsification process within the time intervals of 0, 5, 10, 15, 20, 25, 30, 40, 50, 60, 120 and 180 min at temperature of 40 ℃ followed by the appearance of separated aqueous layer, and identification of variety of fractions or compounds in crude oils that promote and stabilize these emulsions. Demulsification was successfully obtained by adding PT Pertamina (Persero)’s commercial demulsifier series of Pertadem B-02 and Pertadem B-06. Pertadem B-02 is the best candidate for destabilizing water in oil emulsions. The optimal percentage demulsification efficiency (DE) achieved by Pertadem B-02 was 100% with just concentration of 18 ppm for field A and 97% for field B. Moreover, demulsification activities in the water in oil emulsions by Pertadem B-02 were faster compared to Pertadem B-06. Fractions identifications showed emulsifying agents in crude oil of Field A that promote very unstable emulsions compared to crude oil of Field B from East Kalimantan.

1. Introduction
Water in crude oil emulsions have significant practical importance during upstream and downstream operations and pose serious challenges on the economic values of petroleum industry [1]. Emulsified water in crude oils may contain chloride that generate corrosion problems to downstream refining equipments [2]. Thus, effective separations of emulsified water from feedstock oils of refineries is necessary to enhance the commercial value of the crude [3]. Certain fractions of crude oil have been reported their contribution on the formation of water in oil emulsions, including waxes, asphaltenes and resins that might be found in both the dissolved and particulate form [4]. Studies reported that crude oil emulsions are stabilized by naturally occurring surfactants or emulsifier which partially soluble in the oil and water phases and have a strong tendency to move and stabilize the interfacial layer of water droplets [5]. High concentrations of praticles and surfactants in crude oils promoted prevention of water droplet coalescence; producing stable emulsions [4].

A process aimed to separate the emulsion into two phases is called demulsification [6]. There are three primary methods for demulsification of highly stable crude oils: physical, chemical and biological in which the effectiveness of these methods can be measured by their ability to break the emulsion stability until the two phases separate [6,7]. Chemical demulsification is conducted by using chemical compounds in a small concentration (usually 10–1000 ppm) and is one of the very crucial techniques to minimize the formation of crude oil emulsion and to improve phase separation process [3,8]. Study on
the effect of the demulsifier’s chemical structure is needed to break these emulsions in fast and cost-effective separation.

The fundamental mean of chemical demulsification is that the adsorption kinetics and surface affinity of the demulsifiers gradually replace the naturally occurring emulsifiers within the water-oil interfacial film, and that might eventually destabilize the interfacial layer by some proposed mechanism: competitively adsorbing at the interfacial region, replacing natural emulsifiers of asphaltic aggregates, breaking up the asphaltic layer, along with lowering interfacial tension between the hydrocarbon and aqueous phase, leading to increasing the kinetics of water droplets coalescence [5,8].

The aim of the present study is to investigate the influence of two types of PT Pertamina (Persero)’s commercial demulsifier series of Pertadem B-02 and Pertadem B-06 on breaking the emulsion of crude oils from East Kalimantan oil fields. Two experiments were conducted: the bottle test in which emulsion resolution was carried out after demulsification process within the time intervals followed by the observation of separated aqueous layer, and identification of variety of fractions or compounds in crude oils that promote and stabilize these emulsions. Moreover, specific demulsifier formulations can be modified to the type of crude oil and the nature and fractions of emulsifying agents of asphaltenes and resins in crude oils.

2. Materials & methods

2.1. Materials
The crude oil sample was obtained from two oil fields located in East Kalimantan, Indonesia: field A and field B. Two homologous series of demulsifier of PT Pertamina (Persero)’s Pertadem B-02 and Pertadem B-06 were employed to perform demulsification test.

2.2. Demulsification experiments
To evaluate the ability of these chemicals to break the water in crude oil emulsions, certain amounts of Pertadem B-02 and Pertadem B-06 were added to the prepared water in crude oil emulsion and bottle test was conducted [9]. A 100-mL batch of each emulsion of crude oil from different fields was prepared by mixing the formation water (that comes with crude oil) (60 vol %) and crude oil (40 vol %) in a standard 100-mL uniform-shaped tube with scale. A small amount of Pertadem B-02 and Pertadem B-06 was added to the mixture of each batch of crude oils with final concentration of 18 ppm. Homogenization was performed by mixing the emulsion 150 times by hand after and before adding the demulsifier. The mixture of Pertadem series with emulsion was heated at 40 °C for 180 min in a thermostatic water bath. The samples were examined periodically in 0, 5, 10, 15, 20, 25, 30, 40, 50, 60, 120 and 180 min to record the amount of separated water.

2.3 Instrumentation
Identification of fractions in crude oils was evaluated using GC DHA (Agilent). The change of demulsifier’s weight that takes place during heating at constant rate were performed by thermogravimetric analysis (TA Instrument).

3. Results and discussion

3.1. Identification of fractions in crude oils
Figure 1 shows several fractions in petroleum from different oil fields from East Kalimantan. Crude oil from field A exhibits higher content of aromatics yet lower content of paraffins and olefins compared to crude oil from field B. Chemical characterization of crude oil is a very challenging work due to its essentially complex nature [10]. Saturated and aromatic hydrocarbons are the most useful compounds discovered in petroleum to generate fuels and other profitable products. Some compounds or fractions have been reported to play a role in the formation of water in oil emulsions of crude oils, including paraffinic waxes, asphaltenes and resins and might be found in both the dissolved and particulate form.
[4]. Paraffinic waxes might interact with asphaltenes and resins and form sub micrometer particles to stabilize the emulsions.

3.2. Identification of fractions in Pertadem series
Thermogravimetric analysis was employed in this work to evaluate components in demulsifier of Pertadem B-02 and Pertadem B-06 by monitoring the change of their weight that takes place during heating at constant rate of 20 °C/min (figure 2). The thermal decomposition of Pertadem B-02 started at 281.46 °C and finished at 582.25 °C, followed by major loss of its weight at temperature of 452.46 °C. Pertadem B-06 shows thermal decomposition that started at temperature of 182.00 °C and finished at 475.52 °C with major loss occurred at temperature of 386.8 °C. By comparing peaks between Pertadem B-02 and Pertadem B-06, it can be noticed that they differ in chemical constituents which play a role in destabilizing the emulsions.

Figure 1. Chemical fractions in petroleum from different oil fields.

Figure 2. TGA profiles of Pertadem B-02 and Pertadem B-06 at heating rate of 20 °C/min.
3.3 Demulsification performance of tested demulsifiers

Demulsifying performances of Pertadem B-02 and Pertadem B-06 at 40 °C in 180 min were quite different for two crude oils as demonstrates in figure 3(a–b). Pertadem B-02 with final concentration of 18 ppm performed a remarkable demulsification efficiency of 100% for crude oil from field A in 10 min settling time and 97% for crude oil from field B in 15 min settling time. Maximum demulsification efficiency of Pertadem B-06 was 95% for crude oil from field A in 180 min settling time and 83% for crude oil from field B, both in 180 min settling time. It suggested that chemical constituents in Pertadem B-02 and Pertadem B-06 that play a role in breaking the emulsion stability until the two phases separate are differ (figure 4a–b). The presence of paraffinic waxes in those oils may generate the emulsion to be relatively stable and cannot be separated easily [11].

![Graphs showing demulsification performance of Pertadem B-02 and Pertadem B-06](image)

**Figure 3.** Emulsion formation by East Kalimantan’s crude oils of: (a) field A and (b) field B with the addition of Pertadem B-02 and Pertadem B-06, respectively.

![Bottle test images](image)

**Figure 4.** Appearance of the bottle test that used in in this work for crude oils from field A (a) and field B (b) at 40 °C in 180 min.
4. Conclusions
We have demonstrated the application of two PT Pertamina (Persero)’s commercial demulsifier series on destabilizing water in crude oil emulsions from different oil fields. Experimental data revealed that Pertadem B-02 had better dan faster demulsifying activity than Pertadem B-06. Fractions identifications showed emulsifying agents in crude oil of field A that promote very unstable emulsions compared to crude oil of field B from East Kalimantan. It should be noticed that specific demulsifier formulations can be modified to the type of crude oils and the nature and fractions of emulsifying agents in crude oils.

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References
[1] Adewunmi A A and Kamal M S 2019 J. Mol. Liq. 279 411
[2] Czarnecki J 2009 Energy and Fuels 23 1253
[3] Peña A A, Hirasaki G J and Miller C A 2005 Ind. Eng. Chem. Res. 44 1139
[4] Lee R F 1999 Spill Sci. Technol. Bull. 5 117
[5] A Issaka S 2015 J. Pet. Environ. Biotechnol. 06
[6] Raya S A, Mohd Saaid I, Abbas Ahmed A and Abubakar Umar A 2020 J. Pet. Explor. Prod. Technol. 10 1711
[7] Zolfaghari R, Fakhru’l-Razi A, Abdullah L C, Elnashaie S S E H and Pendashteh A 2016 Sep. Purif. Technol. 170 377
[8] Grenoble Z and Trabelsi S 2018 Adv. Colloid Interface Sci. 260 32
[9] Hazrati N, Miran Beigi A A and Abdouss M 2018 Fuel 229 126
[10] Niyonsaba E, Manheim J M, Yerabolu R and Kenttämäa H I 2019 Anal. Chem. 91 156
[11] Zaki N, Schoriing P C and Rahimian I 2000 Petrol. Sci. Technol. 18 945