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Demulsification of crude oil emulsion via electrocoagulation method

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ABSTRACT

During oil production and processing emulsions were formed and seriously cause problem, both in terms of chemicals used and production losses. The traditional methods of breaking crude oil emulsions are disadvantageous from both economic and environmental perspectives. In this paper, the potentials of electrocoagulation technology in demulsification of crude oil emulsion were investigated. The crude oil obtained from Petronas Ponapean Melaka, Malaysia. For stability performance test, Span 80 was used as emulsifier, while for chemical demulsification performance test, Hexylamine was used. The electrocoagulation method was used for demulsification of W/O emulsion. For electrocoagulation demulsification, three factors namely; voltages 15-50 V, current density 1.04-3.94 mAcm⁻², and concentration of NaCl 0.5-2.5 g/L. The electrocoagulation demulsification showed that the best water separation efficiency was achieved at voltage 50 V, current density 3.94 mAcm⁻², and NaCl concentration 2.5 g/L, whereas the separation efficiency reached at 98%. Results have shown the potential of electrocoagulation method in separation of water-in-crude oil emulsions, W/O.

Keywords: Crude oil; demulsification; electrocoagulation; chemical; W/O emulsion

1.0 INTRODUCTION

Crude oil production from the fields there is a production of water with oil this is called an emulsion which either be controlled or avoided. This emulsion resulted in an increase in viscosity which can very affect the production of oil from sand phase up to flow line. Failure to separate the oil and water mixture efficiently and effectively could result in problems such as overloading of surface separation equipment, increased cost of pumping wet crude, and corrosion problems (Salam, Alade, Arinkoola, and Opawale, 2013).The two most common emulsion types are water droplet dispersed in the oil phase and termed as water-in-oil emulsion W/O and if the oil is the dispersed phase, it is termed oil-in-water O/W emulsion (Langevin, Poteau, Hénaut, and Argillier, 2004).Generally ,the presence of emulsifying agents which are naturally Demulsification, the separation of an emulsion into its component phases, is a two-step process. The first step is flocculation (aggregation, agglomeration, or coagulation). The second step is coalescence. Either of these steps can be the rate-determining step in emulsion breaking (Kalogirou, 2014). The produced emulsion must be completely separate before further processing (Nor Ilia Anisa, 2011).

In various sectors of industry, including petroleum refinery, natural gas processing and transmission, as well as oil and gas production, oil-water emulsion is generated. These emulsions cause a number of operational problems such as tripping of separation equipment in gas-oil separating plants, production of off-spec crude oil, and creating high pressure drops in flow lines. Emulsions have to be treated to remove the dispersed water and associated inorganic salts in order to meet crude specification for transportation, storage and export and to reduce corrosion and catalyst poisoning in downstream processing facilities. The conventional ways in demulsification crude oil emulsions has disadvantages from both environmental and economic perspectives (S. Kokal et al., 2002); (Peña, Hirasaki, and Miller, 2005).

2.0 MATERIAL AND METHODS

2.1 Material

In this study, crude oil sample was obtained from Petronas Refinery at Melacca, Malaysia. The crude oil type was light crude oil, for stabilization purposes, the light oil was blended with heavy crude oil with ratio of (50-50 vol. %). For emulsion's stabilization, Span 80 was used as stabilizer, while Hexylamine was used as demulsifier to break the W/O emulsions.

2.2 Electrocoagulation

The demulsification process of W/O emulsions was conducted by using electrocoagulation system. The electrocoagulation experiment is a monopolar batch reactor with two electrodes (all made of the same material aluminum because it is cheap and easy to produce) connected in parallel to a digital DC power supply (110 V, 10 A). The electrodes were disposed vertically in the cell at a distance from each to other. The volume of the treated emulsion was 500 ml. The runs were performed at room temperature (25–28 °C). The electrocoagulation system used in this study is shown in Figure 1.



Figure 1. Electrocoagulation system

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2.3 Emulsion Preparation

In the laboratory, the ratio of water-in-oil emulsion (50-50) vol. % was prepared. Emulsions were in 500 ml graduated beakers, with ranges by volume of water and oil phase. The prepared emulsion was checked whether (W/O or O/W) using test tube method and only W/O emulsion was selected for further steps. For emulsion preparation the stabilizing agent (surfactant) was used Span 80 with concentration 0.5 vol. %. To prepare W/O emulsions the emulsifier was dissolved into the continuous phase (crude oil) and vigorously sheared for 3 minutes. Then the dispersed phase (water) was added slowly to the oil phase while mixing with standard three blade propeller and sheared for 4 minutes with mixing speed of 1000 rpm at temperature of 28-30° C. Figure 2 shows the steps for preparing (W/O) emulsion.



Figure 2: Preparing (W /O) emulsion system

3.0 RESULTS AND DISCUSSION

The physical properties of crude oil was determined, these properties are: density, viscosity, API gravity, surface tension and interfacial tension.

3.1 Physical Characterization

The physical properties of crude oil was determined (Nadkarni, 2007). In this study, the crude oil used is light crude oil as it has API degree is 34. The density of the crude oil it was 0.8528 g/cm^3 . The crude oil viscosity is also one of the important parameters which deal with the rheological studies, the viscous oils can create many problems throughout the system, and may cause difficulties during pumping and transportation as well (Rand, 2003). It was found that the crude oil viscosity was 91.25 mPa.s at 25 °C.

The pour point is one of the flowing properties of the crude oil. The study of pour point is very important, especially during the transportation, whatever, the pour point is the lowest temperature at which the oil cans no longer stops the following and became semi-solid. Pour point of the crude oil increases by increasing the specific gravity. The pour point of crude oils varies from -60° C to $+30^{\circ}$ C. During preheating from $45-65^{\circ}$ C the temperature of the pour point decreases and this is due to the paraffinic crystal existed in crude oil (Taraneh, Rahmatollah, Hassan, and Alireza, 2008). In this research the crude oil has the pour point-11° C. The measurements of surface tension and interfacial tension were also conducted for the crude oil. The physical properties of the crude oil are shown in Table 1.

Properties	Measurement
Viscosity (cp) at 28 °C	91.25
Density (g/cm ³)	0.8528
API Gravity	34
Pour point (°C)	-11
Surface Tension (mN/m) at 25 °C	62.983
Interfacial Tension (mN/m) at 25 °C	5.00
Shear Rate (sec ⁻¹) Shear Stress (pa)	51 4.765

Table 1. Physical properties of crude oil

3.2 Characterization of the Emulsion

The rheological study of the emulsion has a great importance in understanding the formation and stability mechanism of an emulsion. Therefore, the effect of two important parameters such as viscosity and emulsion droplet size were investigate as shown in Table 2.

Table 2 Physicochemica	l properties of (W/O) crude oil emulsion
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Properties	Measurement
droplets size of (W/O) emulsion μm 1% of span80 (50-50 %) phase ratio	83.123
droplets size of (W/O) emulsion μm 2% of span80 (50-50 %)phase ratio	80.754
viscosity (cp) at 28 ° C	402.8
shear rate (1/sec)	23.8
shear stress (pa)	9.61

3.3 Viscosity of the Emulsion

The actual viscosity of the emulsion was investigating under the effect of shear stress, shear rate, stirring intensity (during the emulsion preparation). Viscosity of an emulsion is proportional to the viscosity of continuous phase (crude oil) and is defined as the relationship between shear stress and shear rate. Highly viscous oils regularly form more stable emulsions these oils cause emulsions difficult to treat, because they decrease the movement of droplets, delaying the coalescence (S. L. Kokal, 2005).

Effect of Shear Rate on the Viscosity of the Emulsion

Usually, viscosity is a function of shear rate. Figure 3; illustrate the effects of shear rate on the viscosity of W/O emulsions at phase ratio (50-50) %, prepared with emulsifier Span 80 at 0.5 vol. % concentration. As well as different stirring intensity (50, 100, 150 and 200) rmp were applied for the viscosity measurement.

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It is clear that in all types of the samples, the apparent viscosity showed a reduction was recorded from (81.8 to 43.2) cp with increasing the shear rate from (17 to 68) Sec⁻¹. This may be attributed to the breakup of flocculated particles caused by the force carried by the shear rate and hence reduced the viscosity. However, the emulsion prepared with Span 80 exhibited higher viscosity the reason is may be the more stability of the emulsions as analyzed through the microscopic images.(Fingas & Fieldhouse, 2014) stated that stable emulsions are more viscos comparing to the loss emulsions, i.e. means that the flow encounters less resistance at higher shear rates. This is due to the molecular chains found in the crude oil. As the shear rate increases, the chain type molecules disentangled, stretched, and reoriented parallel to the driving force, and hence reduced the crude oil viscosity (Ghannam & Esmail, 2006),



Figure 3. Effect of shear rate on viscosity of 50 - 50 % W/O emulsion with Span 80 prepared at 1000 rpm

Effect of Shear Rate on the Shear Stress

The effects of shear rate and shear stress on the viscosity of crude oil emulsions are the important factors to understand the flow behavior of the emulsions. Therefore, the measurement of viscosity and shear stress of all emulsions were investigated versus shear rate. Through these measurements, the details of Newtonian or Non-Newtonian flow behavior of the emulsion can be obtained. Figure 4, indicate the complete information about the flow behavior of prepared W/O emulsion formed with Span 80 different shear rates (17, 34, 51 and 68) 1/sec and applied stirring intensity (50, 100, 150 and 200). It can be observed that the viscosity and shear stress of the emulsion are dependent on the shear rate. The shear stress of the emulsion increased gradually and significantly with the shear rate which indicates crude oil exhibiting Non-Newtonian behaviors this is due to the relationship between the shear rate and the applied stress is linear (Ghannam & Esmail, 2005)



Figure 4. Effect of shear rate and shear stress on the viscosity of 50 - 50 % W/O emulsion stabilized with Span 80 prepared at 1000 rpm.

3.4 Droplet Size of the Emulsions

The droplet size of the emulsions is very important factor in studies of the emulsions. The droplet size has significant impact on the stability and viscosity of the emulsion. Importantly, there are some factors that can influence the property of the droplet size, for example; emulsifier type, emulsifier concentration, volume fraction water (dispersed phase), and stirring speed. The emulsifier type and emulsifier concentration are very effective on the droplet size of the emulsions (Windhab, Dressler, Feigl, Fischer, and Megias-Alguacil, 2005), the emulsifier concentration 1% and 2%. When increased the emulsifier concentration the droplets size decreased (83.123 and 80.754) μ m, that one, if the concentration of emulsifier is sufficiently high, then the coalescence of water droplets is stopped this is leading to stable emulsions.(Wang, Gong, and Angeli, 2011). Figure 6and 7 display the microscopy images of the droplet sizes.



Figure 5. Optical microscopy images of 50-50 % W/O emulsions stabilized with 1 vol. % emulsifier prepared at 1000 rpm.



Figure 6. Optical microscopy images of 50-50 % W/O emulsions stabilized with 2 vol. % emulsifier prepared at 1000 rpm.

3.5 Electrocoagulation Demulsification

For electrocoagulation operating conditions, the main effects of many factors; voltages 15-50 V, current density 1.04-3.94 mAcm⁻², and NaCl concentration 0.5-2.5 g/L on water separation efficiency.

Effects of Current Density

The current density is defined as the electric current per unit area an important operating factor manipulating the performance of electrochemical process which describes the coagulant dosage (Ün et al., 2006). To identify the current density effect, four voltages were applied. Figure 7 describes the effect of current density on the water separation efficiencies; it can be seen from the figure that the rate of water separation efficiency increases with applied current density. The water separation efficiency was 98% at 3.94mA cm⁻², 92 % at 2.84mA cm⁻², 88% at 1.95mA.cm⁻² and 80% at 1.04mA.cm⁻² after 23 minute reaction. At a high current density, increasing the generation of hydrogen gas formed at electrode surfaces. This leads to an increase in the number of gas bubbles inside the beaker. Subsequently, the attachment step between gas bubbles and oil drops is higher, and more oil drops are carried out by gas bubbles i.e. the initial high rate of oil separation may be recognized to the high frequency of collision between the neutralized oil drops (Un et al., 2009).



Figure 7. Variation of water separation efficiency with current densities

Effects of NaCl Concentration

The effect of sodium chloride concentration on the percentage of separation was illustrated in Figure 8. Increasing the sodium chloride concentration was effective on the separation efficiency. The results indicate that the percentage of water separation increased by increasing the amount of sodium chloride. When the concentration of NaCl in solution increases, solution conductivity was raised and decreases the size of hydrogen gas bubbles. Since the buoyancy of smaller bubbles is lower than larger bubbles, they rise slowly to the surface with high chances for collision with oil drops. This leads to an improvement in the percentage of separation.(Daneshvar et al., 2003). Clearly, electrocoagulation process with 2g/L NaCl and 2.5g/L NaCl, the separation efficiency was reached at 88% and 92% respectively.



Figure 8. Variation of water separation efficiency with NaCl concentration

4.0 CONCLUSIONS

Emulsion stabilization and destabilization was investigated in this paper. The stabilization of w/o emulsion is a serious challenge, which can cause serious problems in separators and refining processes. It was found that the density, viscosity, pour point, and API gravity of crude oil were 0.8528 g/cm^3 , 91.25 cp, $-11 \degree$ C, and 34 at room temperature, respectively. For w/o emulsion preparation and stabilizations, Span 80 was used with concentration of 0.5% (v/v) at w/o ratio of 50:50% (v/v). It was found that the w/o emulsions were more viscous and dense than the crude oil. The demulsification process was accomplished using electrocoagulation demulsification method and Hexylamine as a demulsifier. At the highest current density, the fastest treatment rate for w/o emulsion was obtained. Increasing concentration of NaCl as coagulant aid, increased water separation efficiency 92%, 88%, 80%, 76% and 70% with 2.5, 2, 1.5, 1, 0.5g/L respectively, therefore decreased energy consumption in the electrocoagulation system.

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