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SEPARATION SCIENCE AND TECHNOLOGY, 37(6), 1307–1320 (2002)

DEMULSIFICATION OF WATER-IN-CRUDE OIL EMULSIONS BY A CONTINUOUS ELECTROSTATIC DEHYDRATOR

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ABSTRACT

The demulsification rates of water-in-crude oil emulsion in high AC fields were investigated under various conditions by using a model dehydrator. A continuous electrostatic dehydrator was constructed using a glass vessel of 6.5 cm diameter and 10 cm height equipped with a copper electrode and a perforated plate. The separation rate of water from the simulated crude oil increased along with the applied field, frequency, demulsifier concentration, temperature, and contact time. As the applied field increased up to 2.5 kV/cm, the separation percentage increased up to 90%, and as the concentration of the demulsifier reached 100 ppm, 80% of the water were separated at 2.5 kV/cm. Also it was observed that the separation percentage increased as the temperature, frequency of field, and contact time. It is proposed that the breakup of droplets depends on the interfacial polarization

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and the proper deformation of water droplets in the field induced by the electrostatic charge.

Key Words: Demulsification; Water-in-oil emulsion; Continuous electrostatic dehydrator; Separation rate

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INTRODUCTION

Demulsification is an essential industrial process, mainly used for removing water and salts from crude oil. Water is dispersed as small droplets in crude oil and most of the salts are dissolved in water droplets in crude oil. Since this water is a salt carrier, the terms dehydration and desalting are used synonymously. If these impurities, such as water and salt included in the crude oil, were not removed, they would cause serious corrosion and fouling in the heat exchanger and distillation equipment. To be efficient, the water content should be less than 0.5–3.0% after demulsification, i.e., dehydration or desalting.

Among the many different methods of demulsification, (e.g., centrifugation technique, sedimentation technique, and thermal breaking method), the electrostatic demulsification method in a high-voltage field is one of the most effective and simplest demulsification methods (1). Electrostatic forces cause the coalescence of the dispersed water droplets and their growth to larger drops, which then fall readily due to electric forces or gravity. These forces increase dramatically as the distance between the dispersed water droplets becomes lesser.

An efficient demulsification process can be achieved with both DC and AC fields. In DC fields, the electrophoretic droplet motion enhances the probability of coalescence, whereas in AC fields, the greater motion in the bulk fluids is necessary to increase the coalescence (2). Therefore, the AC field is more suitable for the continuous demulsification process.

The following parameters are considered to have the effect on the demulsification kinetics: (operating conditions) voltage, frequency, temperature, degree of mixing, shape, and distance of two electrodes; (emulsion properties) density, viscosity, interfacial tension, water drop size, holdup, surfactant concentration in oil phase, electrolyte concentration in water phase (3). In this study, a continuous electrostatic dehydrator was constructed and the water-in-crude oil emulsions were demulsified continuously by the application of a high-voltage AC field. The rates of demulsification were investigated by varying some of the parameters.

The papers on demulsification were experimented mostly in batch condition (1,3) under electrostatic force or demulsifier separately and little research has been reported on continuous electrostatic demulsification (4).

In this work, we experimented in continuous condition that is similar to real process. Besides, applying the electrostatic force and demulsifier together, we could study the relative effect of the two conditions and found a large increase in separation efficiency due to the synergistic effect.

EXPERIMENTAL

Preparation of Water-in-Crude Oil Emulsion

The water-in-crude oil emulsion containing 20% water (% by volume) was prepared in the following way. Crude oil of 160 mL was placed in a beaker and stirred by an electronic stirrer (Heidolph RZR 2051, Germany) at 1000 rpm. Distilled water of 40 mL was added slowly to this crude oil. Stirring was continued for 10 min to form the complete 20% water-in-crude oil emulsion (% by volume). The emulsion gathered up to 1 L for continuous demulsification. It was stable for about one month under room temperature.

The size of the water droplets dispersed in the crude oil was investigated by an optical microscope and was in the range 15–60 μm.

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Measurements

The interfacial tension of crude oil/water interface was investigated by a KRUSS K8 tensiometer and viscosity was measured by an ARES fluid rheometer (Rheometric Scientific Inc., Piscataway, NJ).

Continuous Electrostatic Dehydrator

The demulsification apparatus, a continuous electrostatic dehydrator, used in this study is shown schematically in Fig. 1. The apparatus was made of glass with internal dimensions of 6.5 cm radius and 10 cm height. A copper electrode made of a perforated plate was installed at the bottom of the apparatus. The glass-insulated upper electrode was made of a glass cup with 5 cm as the external diameter to prevent short-circuiting. The cup was filled with sodium chloride aqueous solution into which a copper wire was immersed. The mineral oil was used to cover the surface of the solution to insulate it.

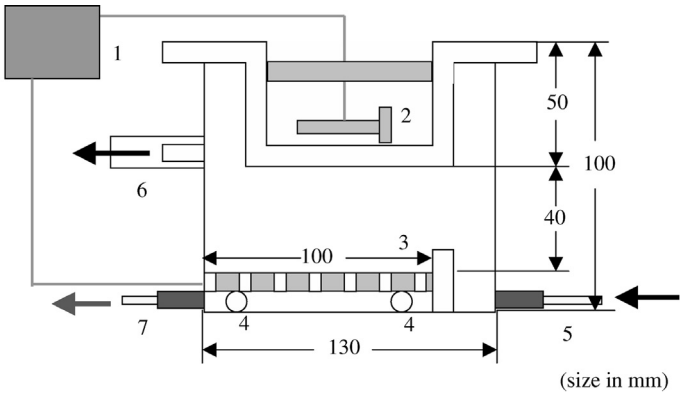

Figure 1. Experimental apparatus (Continuous Electrostatic Dehydrator) 1. AC high voltage amplifier, 2. Upper electrode, 3. Lower electrode, 4. Glass tubes, 5. W/O emulsion inlet, 6. W/O emulsion outlet (the demulsified emulsion), 7. Water outlet (size in mm).

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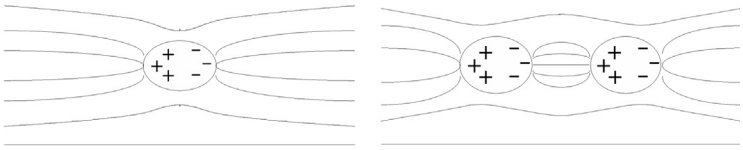
Continuous Demulsification

After the water-in-crude oil emulsion of 1 L was prepared, a chemical demulsifier (2W 151: Betzdearborn Korea Ltd., Seoul, Korea) was added and stirred for 5 min at 500 rpm. Then this emulsion was put into the water bath to get set to the desired temperature (20, 40, 60°C) aging the demulsifier for 15 min. This emulsion was fed through the water-in-oil (W/O) emulsion inlet into the apparatus by the pump (Masterflex, Cole-Parmer Instrument Co., Vernon Hills, IL, Model No. 07521-00). A high AC electrical voltage of 2–20 kV and frequency of 60–2000 Hz was applied between the two electrodes by a high-voltage amplifier (TREK 20/20B). The flow rate of the pump was adjusted for emulsion to have 3 min of contact time in the apparatus. The demulsified emulsion effused from the apparatus through the W/O emulsion outlet. The separated water effused out from the apparatus through the water outlet and the amount of separated water (WS%) was measured with a mass cylinder.

The demulsification rates were measured for various operating conditions (applied voltage, the amount of demulsifier, temperature, frequency, contact time-related with feed rate). All the results obtained are mean values of at least three measurements.

RESULTS AND DISCUSSION

An electrostatic demulsification process is based mainly on the coalescence and precipitation of water droplets. Although the electrostatic method has a



(a) Induced dipole (b) Dipole-dipole interaction

Figure 2. Induced dipole and dipole–dipole interaction: (a) induced dipole; (b) dipole–dipole interaction.

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relatively wide application, the mechanism of electrical coalescence is understood poorly because of the complexity of hydrodynamic and electrical phenomena of interfacial polarization. Generally, the coalescence of droplets consists of three steps: (1) motion and approach of droplets due to electrostatic force; (2) drainage of the film separating the droplets; (3) breakdown of the film and coalescence of the droplets. The electrical effect is related primarily to the first step, i.e., an increased rate of motion of the droplets in an electric field (5).

When the electric field is applied, the water droplets are polarized by the induced dipole. The AC fields induce an oscillating movement of the droplets and the water droplets deform into an ellipsoid, which have the effect of reducing the distance between the droplets. It can be seen from the distribution of the electrical field lines, that the density of the field lines increased between two droplets (Fig. 2). The gradient of the electrical potential of the two droplets is proportional to the attractive force, i.e., attractive force is proportional to gradient V. So the dense electrical field lines in Fig. 2 means that the gradient V and attractive force is large. As the distance between the droplets becomes lesser, they combine and become larger droplets. The combined droplets are liable to precipitate, and the precipitation rate of the droplets is proportional to the square of droplet diameter. We observed the diameter of the droplets by an optical microscope to be 15–60 μm but the distribution of the droplets hardly can be observed in dark media. However, the diameter of the stable water droplets in diesel oil W/O emulsion) was about 1–10 μm with a skewed normal distribution (6).

The Effect of Applied Field

Figure 3 shows the effect of the applied field strength on the water separation (WS%) up to 5 kV/cm of 60 Hz in 3 min contact and with the 300 ppm demulsifier concentration at 60°C. Here, we defined the WS% as the amount of water contents separated divided by the initial amount of water in crude oil. The

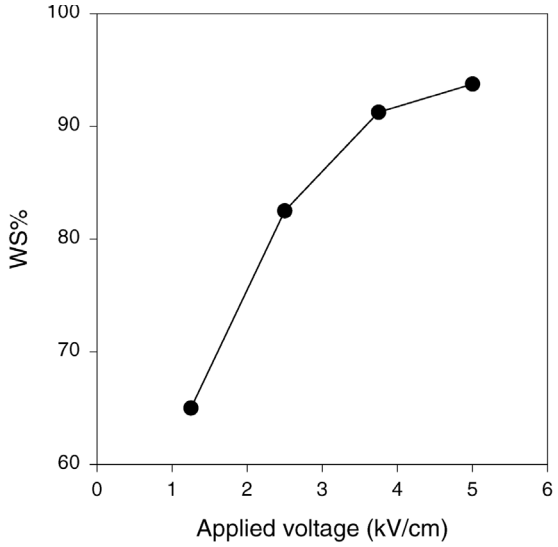

Figure 3. Effect of applied voltage. Other conditions—frequency: 60 Hz, demulsifier concentration: 300 ppm, temperature: 60°C, contact time: 3 min (feed rate: 142.5 mL/min).

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water separation increases with field strength up to 2.5 kV/cm, but after 2.5 kV/cm the WS% seems to be saturated near 90%.

The applied field could increase the removal rate of the droplets, and accelerate the hydrodynamic process along the electrostatic force. The droplets are elongated along the electrical field. Since the electrostatic attraction force could be calculated from the product of the charge density by field, the deformation and coalescence may occur by the induced dipole. However, the charge density at the edge of the deformed surface would not be proportional to the field strength. Below the threshold, the ionic components may just ponder the reorientation, and then, the charge density may increase proportionally with the field strength. Further, it is expected that the charge density become saturated because of the ionic concentration and space limitation. Therefore, the large increase in water separation at low field may be attributed to the induced dipole and the droplet elongation. However, at high field strength, the elongated droplets may break up into smaller droplets along the field. All of these observations indicated that the coalescence of droplets occur through a droplet chain structure along the field direction (7,8). When noninsulated electrodes are used, the formation of such a structure causes short-circuits, an excessive current flow. Taylor proved this through typical conduction-current profiles for the

electrostatic treatment of water-in-crude oil emulsions (2). A similar structure has been identified directly in oil-in-oil emulsion (9).

The Effect of Demulsifier Concentration

Figure 4 shows the effect of the demulsifier concentration (ppm) on the water separation (%). We observed no water separation without the demulsifier, and at 100 ppm the water separation increases with the demulsifier concentration up to 80%. When the two water droplets approach each other to form an oil film, the thickness of the film between the two droplets decreases. The drainage tends to increase the concentration of natural surfactant molecules (e.g., asphaltenes, resins, etc.) outside the film along the droplet surface and drive surfactant molecules from the inside to the outside of the film. Thus, the interfacial tension becomes higher inside the film than outside the film. Demulsifier molecules are adsorbed in the spaces left by the natural surfactant molecules. The adsorption of the demulsifier reverses the interfacial tension gradient and enhances the film drainage as depicted in Fig. 5. Ultimately a stage is reached when the film becomes very thin, and due to the proximity of the droplets, the van der Waals

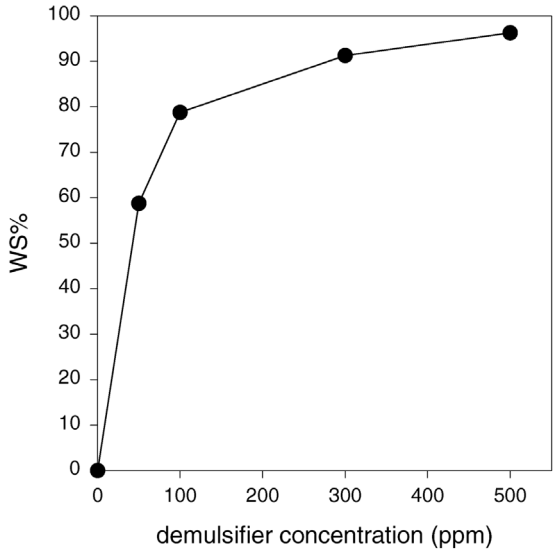

Figure 4. Effect of demulsifier concentration. Other conditions—applied voltage: 2.5 kV/cm, frequency: 60 Hz, temperature: 60°C, contact time: 3 min (feed rate: 142.5 mL/min).

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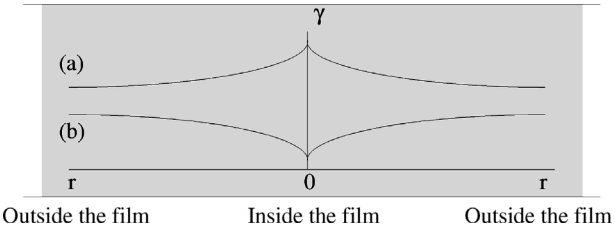

Figure 5. Interfacial tension profiles of the film between the droplets. γ: interfacial tension; (a): before demulsifier adsorption (only surfactants are present); (b): after demulsifier adsorption.

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forces of attraction dominate and the droplets coalesce (10). The interfacial tension of the crude oil/water interface with the demulsifier concentrations is shown in Fig. 6. As the concentration of the demulsifier increases, the interfacial tension of crude oil/water interface decreases. Thus, the increase in WS% with the increase in the demulsifier concentration can be expected. When the demulsifier was added without applying voltage, the WS% was 10–20% in 20–30 min, which is the operating time range with applied voltage (Fig. 7). It took 9 hr to reach 80% of the WS%.

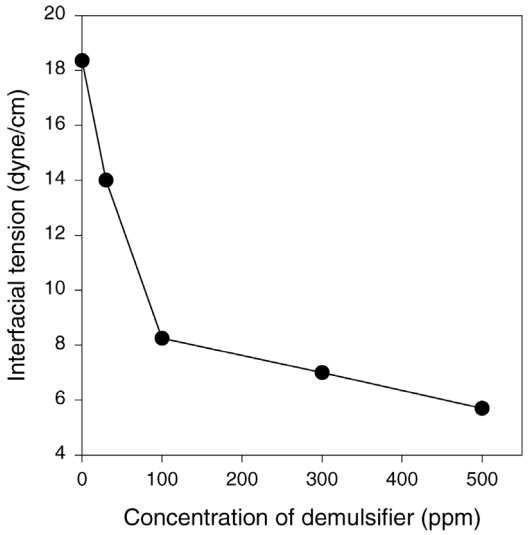

Figure 6. The interfacial tension of crude oil/water interface.

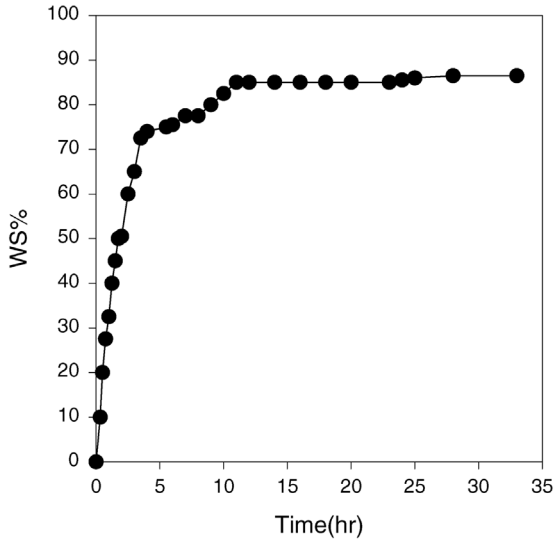

Figure 7. Only demulsifier without applied voltage. Other conditions—demulsifier concentration: 100 ppm, temperature: 60°C.

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The Effect of Temperature

Figure 8 shows the effect of temperature on the water separation (%). The WS% increases with temperature. When the crude oil is heated, the viscosity of the crude oil decreases; this promotes precipitation and reduces emulsion stability, and eventually the emulsion can be removed easily. As Fig. 9 shows, the viscosity of the crude oil decreases as the temperature increases.

With heating, two kinds of problem can occur. One is that the light components, which determine the price of crude oil, vaporize on heating and the price of treated crude oil falls. The other disadvantage is the decline of the separation efficiency due to the formed air bubbles. The air bubbles formed by heating can adsorb the surface-active components (11) and also adhere to the surface of water drops and decrease the apparent viscosity of the drops. These drops are not removed by sedimentation; they act as oil with low density, and come out from the electrostatic dehydrator without being removed. Thus, it is important to decide the appropriate temperature in the demulsification process to prevent these problems.

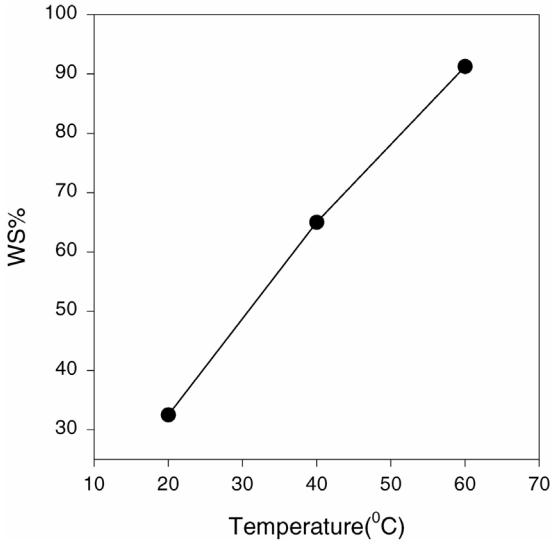

Figure 8. Effect of temperature. Other conditions—applied voltage: 2.5 kV/cm, frequency: 60 Hz, demulsifier concentration: 300 ppm, contact time: 3 min (feed rate: 142.5 mL/min).

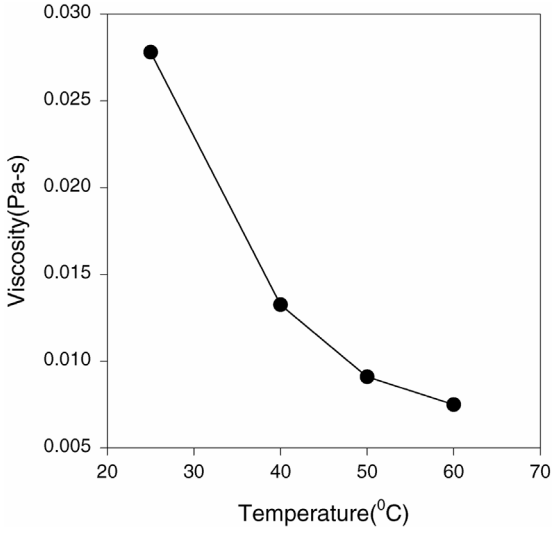

Figure 9. The viscosity change of the crude oil with temperature.

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The Effect of Frequency

The enhanced demulsification was observed with the increase in frequency and usually an optimum frequency was reported according to experiment conditions (5,12). The existence of an optimum frequency can be explained by the mechanism of the coalescence via chain formation (7,8). Figure 10 represents the effect of the frequency on the water separation (%). The WS% increases with frequency, but is saturated above 1000 Hz. In this range, no optimum frequency was observed. The oscillation of field may induce the forced relaxation of induced charge density and shape deformation, which are the results of mass flux by diffusion and flow. If the frequency exceeds the critical point, the enhanced flux could be diminished.

The Effect of Contact Time

Figure 11 shows the effect of contact time on the water separation (%). The contact time is defined as the volume of vessel under field divided by the flow rate of feed. The WS% increases with contact time, but apparently it is saturated after 3 min at 2.5 kV/cm, 60 Hz, 100 ppm, and 60°C. Under these conditions, 3 min may be

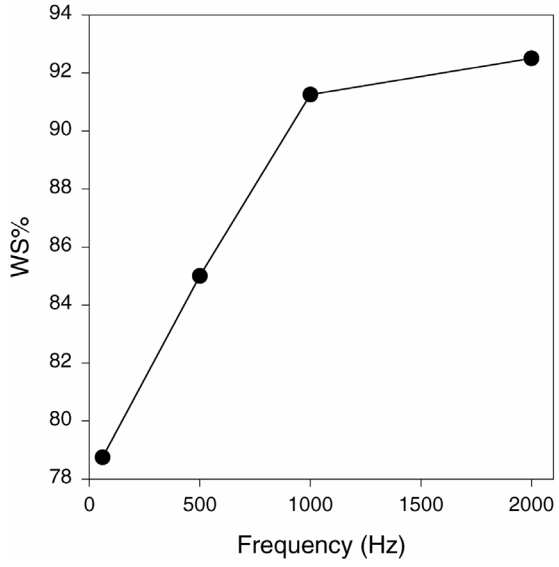

Figure 10. Effect of frequency. Other conditions—applied voltage: 2.5 kV/cm, demulsifier concentration: 100 ppm, temperature: 60°C, contact time: 3 min (feed rate: 142.5 mL/min).

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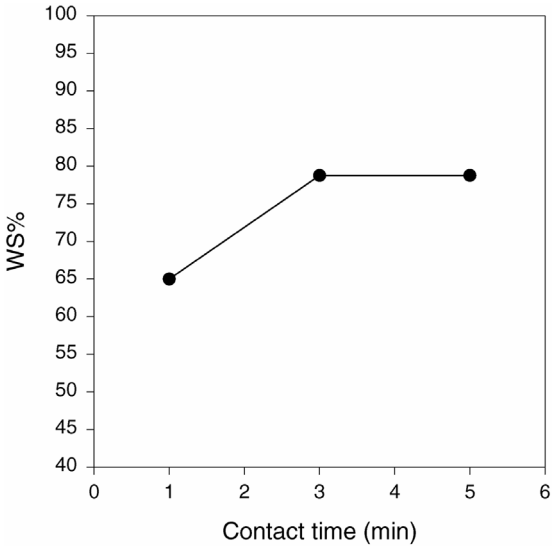

Figure 11. Effect of contact time. Other conditions—applied voltage: 2.5 kV/cm, frequency: 60 Hz, demulsifier concentration: 100 ppm, temperature: 60°C, contact time: 1, 3, 5 min (feed rate: 350, 142.5, 63 mL/min).

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enough to coalesce all the droplets, which undergo the induced deformation or oscillation by field. As the contact time increases, the small or less-charged droplets could get aligned and deformed along the electrical field after the big and highly charged droplets coalesced. Therefore, all the physical transformation may be accomplished by the rate process including the deformation, aligning, diffusion of charge, migration, coalescence, and scavenging.

CONCLUSIONS

The demulsification process in crude oil recovery has been simulated with the field strength and frequency, demulsifier, temperature, and contact time. A model emulsion of water-in-crude oil type containing 20% of water was prepared. The size of the water droplets was about 15–60 μm and was stable for about one month under room temperature.

Using a continuous electrostatic dehydrator, the demulsification rates of water-in-crude oil emulsion in high AC electric fields were investigated under various conditions.

The water separation efficiency, WS% increases with the applied field, because an electrostatic force between droplets increases due to the electrostatic law on the charged particles and because the droplets deform along the direction of field. The addition of demulsifier to emulsion increases the water separation to 80% at 100 ppm.

The WS% increase by temperature may be attributed mainly to the decrease in crude oil viscosity. No optimum frequency of WS% was observed in the range of our experiment and the WS% increased with contact time.

The residual water content of the demulsified water-in-crude oil emulsion was less than 3 wt% at 2.5 kV/cm, 60 Hz, 300 ppm demulsifier, and 60°C.

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