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Stability and Demulsification of Water-in-Crude Oil (w/o) Emulsions Via Microwave Heating

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Abstract: Formation of emulsions during oil production and processing is a costly problem, both in terms of chemicals used and production losses. Experimental data are presented to show the influences of Triton X-100, Low sulphur Wax Residue (LSWR), Sorbitan monooleate (Span 83) and Sodium Dedocyl Sulphate (SDDS) on the stability and microwave demulsification of emulsions. It was found that emulsion stability was related to some parameters such as, the surfactant concentrations, water-oil phase ratio (10-90%), temperature and agitation speed. For economic and operational reasons, it is necessary to separate the water completely from the crude oils before transporting or refining them. In this regard, the present study found that microwave radiation method can enhance the demulsification of water-in-oil (w/o) emulsions in a very short time compared to the conventional heating methods.

Key words: Microwave, demulsification, stability, w/o emulsions, heating, surfactants

INTRODUCTION

As crude oil is always produced with water, many problems occur during oil production because of the formation of emulsions (Schramnm, 1992). Emulsions are difficult to treat and 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 (Sunit, 2002). There are two forms of emulsions: water-in-oil (w/o) and oil-in-water (o/w). Most common emulsions in the oil field are water-in-crude oil (w/o) emulsions. Stability is an important characteristic of a water-in-oil emulsion. Characterization of an emulsion as stable or unstable is required before other properties can be considered, because properties change significantly for each type of emulsion.

For economic and operational reasons, it is necessary to separate the water completely from the crude oils before transporting or refining them. Minimizing water levels in the oils can reduce pipeline corrosion and maximize pipeline usage (Taylor, 1992; Harris, 1996). Effective separation of crude oil and water is an essential operation in order to ensure not only the quality of crude oil but also the quality of the separated water phase at the lowest cost (Dalmazzone *et al*., 2005). The concept of microwave demulsification of emulsions was first introduced by (Klaila, 1983; Wolf, 1986). Fang *et al*. (1995) presented demulsification of water-in-oil emulsions used microwave heating and separation method.

The objective of the present study is conducted to examine the influences of triton-X-100, Span 83, LSWR and SDDS on emulsion stabilization and microwave demulsification of water-in-crude oil emulsions. The findings showed that emulsion stability is related to surfactant concentrations, stirring time, temperature, water-oil phase ratio and agitation speed. The demulsification rate was significantly accelerated by microwave radiation.

MATERIALS AND METHODS

Two types of crude oil were used: Crude Oil A from Iran oilfield and crude oil B from Malaysia oilfield. Their respective compositions are given in Table 1. For emulsion preparations, a distilled water was used as the water phase (dispersed phase) and crude oil as oil phase (continuous phase) for both crude oil A and B. The commercially available Triton X-100, Low Sulphur Wax Residue (LSWR), Sodium Dodecyl-sulphate (SDDS) and sorbitan monooleate (Span 83) were used to emulsify the emulsion in this study. Emulsions were prepared in 900 mL graduated beaker, with ranges by volume of the water and oil phase. The emulsions were agitated vigorously using a standard three blade propeller at speed of 1600 rpm and temperature of 28°C for 7 min. The concentrations of water in samples were 10-90% by volume. The composition of W/O emulsion formulations and their corresponding stabilities are given in Table 2 which shows the surfactants used for the present study. In order to prepare

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Table 1: Density, viscosity, surface tension and interfacial tension of crude oils

	Crude oil A	Crude oil B
Density (g cm^{-3})	0.852	0.834
Viscosity (cp)	20.75	9.42
Surface tension (mN m^{-1}) at 28°C	28.20	26.20
Interfacial tension (mN m^{-1}) at 28°C	27.30	24.00

Table 2: Composition of W/O emulsion formulations and their corresponding stabilities

Emulsion	Stabilizer	Wt (%) stabilizer in ext. Phase (oil)	Emulsion type	Internal phase (%)
1	LSWR	0.50	w/o	50
2		0.75	w/o	55
3		2.00	w/o	60
4		5.00	w/o	70
5	Triton X-100	0.75	w/o	50
6		0.90	w/o	55
7		1.50	w/o	60
8		3.00	w/o	70
9	SDDS	1.00	w/o	65
10		1.50	w/o	70
11		3.00	w/o	75
12		3.50	w/o	80
13	Span 83	1.50	w/o	50
14		4.50	w/o	55
15		6.00	w/o	60
16		6.80	w/o	70

water-in-oil (w/o) emulsions, the agent-in-oil method was followed; the emulsifying agents were dissolved in the continuous phase (oil), then water was added gradually to the mixture. The volume of water settled to the bottom was read from the scale on the beaker with different times. The amount of water separation in percent was calculated as separation efficiency (e) from volume of water observed in the beaker as follows:

$$(\%\ \text{of water separation, e}) = \frac{(\text{Volume of water layer, mL})}{(\text{Original amount of water, mL})} * 100\% \quad (1)$$

The demulsification experiments were performed using Elba domestic microwave oven model: EMO 808SS, its rated power output is 900 watts and operation frequency of 2450 MHZ. A 900 mL graduated cylindrical glass was used as sample container. The diameter and height of emulsion sample container were 11.5 and 11 cm, respectively. Three thermocouples type (K-IEC-584-3) were connected to Pico-TC-08 data logging and connected to microwave oven as shown in Fig. 1. The data logging was connected to PC; with PicoLog R5.08.3 software. The thermocouples were inserted to different locations, top, middle and bottom of the emulsion sample to measure local temperatures.

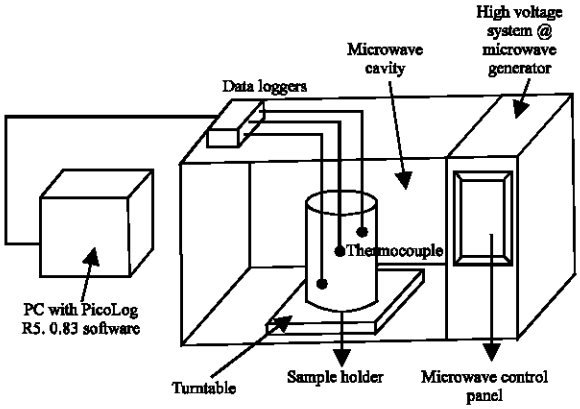

Fig. 1: Elba microwave oven

Microwave radiation: A number of studies were carried out on microwave heating (MW) of oil and water systems. Microwave heating because of its volumetric heating effects, offers a faster processing rate. The separation of emulsified water from crude oil has several stages, due to gravity settling, water droplet/droplet flocculation takes place as water droplets approach each other (Young *et al*., 1996). The purpose of heating water-in-oil emulsions with microwave radiation is to separate water from oil. When water-in-oil emulsion is heated with microwave radiation, two phenomena will occur; the first one is the increase of temperature, which causes reduction of viscosity and coalescence. The result is separation of water without addition of chemicals (Fang *et al*., 1988, 1989). According to Stoke's law, if oil is the continuous phase, the settling velocity of water droplets is given by:

$$v_w = \frac{(\rho_w - \rho_o)gD^2}{18\mu_o} \quad (2)$$

where D is the diameter of the droplets. The viscosity of oil very sensitive to temperature, as temperature increases, viscosity decreases much faster than the density difference, (ρ_w - ρ_o) does, the result when viscosity decreases, the droplets size increases. Therefore, microwave heating increases the velocity of water (v_w) and accelerates the separation of emulsion. The second phenomenon is coagulation. The higher temperature and lower viscosity make the coagulation process easier. The results are larger particle diameter D and rapid separation.

RESULTS AND DISCUSSION

The present study deals with the formation, production and stabilization of w/o emulsions, while in the second part discusses the emulsion breaking

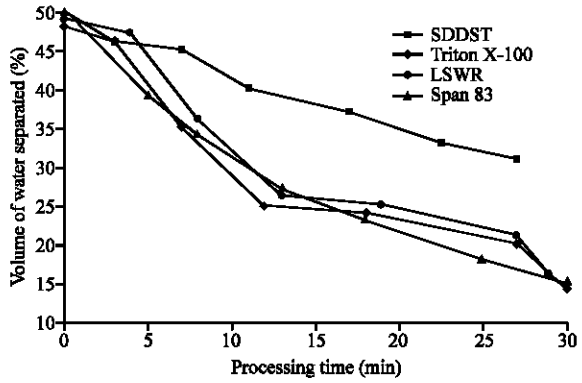

Fig. 2: Change of emulsion stability for crude oil A emulsions (50-50% w/o), as function of processing time and emulsifier applied

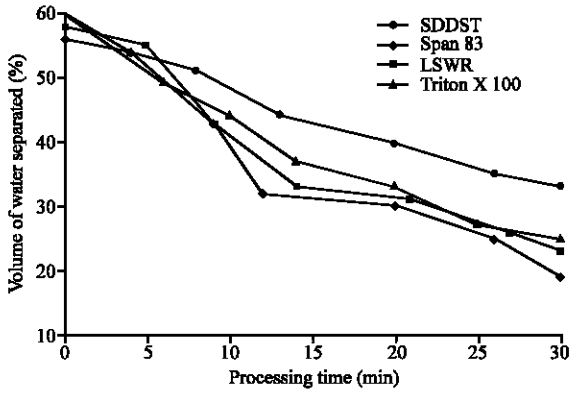

Fig. 3: Change of emulsion stability for crude oil B emulsions (50-50% w/o), as function of processing time and emulsifier applied

(demulsification) of w/o. According to Table 2, LSWR and Triton X-100 water-in-oil (w/o) emulsions were made with 50, 55, 60 and 70% (v/v) internal phase. For the 50 and 55 emulsion, a higher solids concentration was found (6 mg mL^{-1} oil versus 2 mg mL^{-1}) allowed easier emulsification and slowed the settling process. The 60 and 70% emulsions were appeared fairly stable with little settling. The LSWR and Triton X-100 stabilized emulsions exhibited only slight coalescence over three days. Some globule formation was observed and settling occurred. In contrast, the Span 83 emulsions were different from LSWR and Triton X-100 emulsions, even at similar dispersed phase volume fractions. Emulsions were made at 50 and 55% (v/v) internal phase with surfactant concentrations in the oil phase of 1.5 and 4.5% (w/w), at 60% (v/v) (3% w/w) and at 70% (v/v) (6.8% w/w). The different between surfactant concentrations for the 50 and 55% emulsions made by Span 83 appeared very significant on emulsions stability. High Span 83 concentrations increased emulsion stability; therefore, for high concentration of Span 83, the viscosity of w/o emulsion increased considerably and the emulsion droplets lost their shape.

The effect of the disperse phase on the stability of emulsion systems also examined with sodium dodecyl sulphate, (SDDS) as the emulsifying agent. In this regards, the SDDS emulsions were made with 65, 70, 75 and 80% (v/v) (1 to 3.5 w/w in oil) internal phase. An increase in the concentration of SDDS in oil did not cause an increase but decease of the demulsification rate. The decrease would be induced by the increase of the surface potential of water droplets arising from the increase of the density of SDDS anion on the surface, which overcame the decrease of the surface potential by the increase of ionic concentration in oil.

The emulsion stability for crude oils A and B were examined as function of processing time and emulsifier applied. Stability evaluated via the ratio of the total water separated. The evaluation was carried out with agitation speed at 1800 rpm at 30 min at 26.5°C. As demonstrated in Fig. 2 and 3 in most cases stability of emulsion increases with processing time.

It is worth noticing that all surfactants permit a very long time for separation of the water phase (emulsion more stable). However, the maximum amount of water separated from crude oil A was (50%) and crude B was (60%). From these observations, the classification in terms of decreasing stability efficiency is therefore the following; SDDS >Triton X-100 > LSWR > Span 83, respectively.

The effect of stirring time and phase ratio on emulsion stability was investigated again. A water-in-oil emulsion prepared with various volume ratios as shown in Fig. 4. At low phase ratio water/oil (10/90%) only low stability was obtained, the increment of the volume continued till (75/25%). It's interesting to observe that, increasing the phase ratio, surfactant availability increases accordingly leading to highly stable emulsion (75/10%). The variation in stability of the emulsions with phase ratio 75/10% it is very difficult to explain its behavior especially during the first 8 min of processing. When the volume of dispersed phase reached to (90/10%), the emulsion behavior completely has changed Fig. 4, the emulsion changed from w/o to o/w. from these measurements and observations, it can be deduced that the phase inversion point should be in the range of 68-72% water. The oil-in-water emulsion with a phase ratio of 90/10% is very instable emulsion. As the volume of the dispersed increases, the continuous phase must spread out farther to cover all of the droplets. This causes the

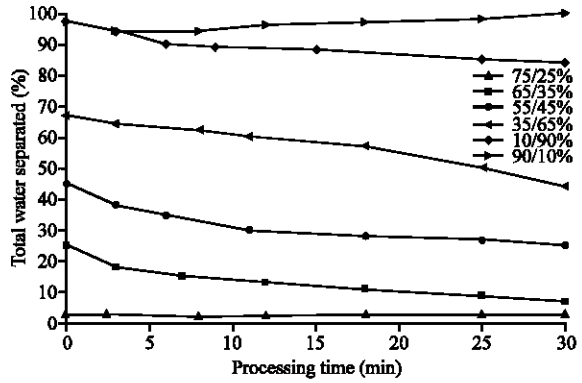

Fig. 4: Change of (w/o) emulsion stability for crude oil emulsions (stabilized with Span 83 surfactant) as function of processing time. Stability evaluated via the ratio of total water separated

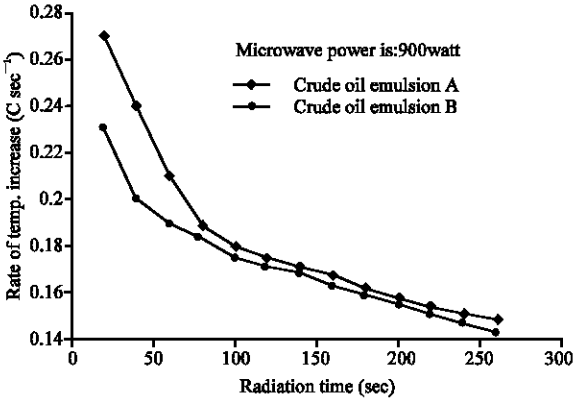

Fig. 5: Heating rate vs. microwave radiation time for crude oil emulsion (A and B)

likelihood of impacts to increase, thus decreasing the stability of the emulsion. This means that, the emulsion might not break as increase the volume of the dispersed phase. In fact this increment caused an emulsion to invert from one phase (w/o) to another (o/w).

Table 3 shows the experimental results of microwave radiation for crude oil emulsions A and B. it is obvious that, there were a correlation between the radiation time and the rate of temperature increase, as radiation time increases, the rate of temperature (dT dt^{-1}) decreases (Fig. 5). Also the rate of temperature increase (dT dt^{-1}) decreases at higher temperatures, this may attributed due to the small dielectric loss of water. The average rates of temperature increase for crude oil emulsion A and B were found as 0.171 and 0.182 C sec^{-1}, respectively, the same findings were reported by Fang *et al.* (1995). Since the purpose of heating water-in-oil emulsions with microwave is to separate water from oil, therefore, the separation efficiency of crude oil A and B emulsions calculated by using Eq. 1 were shown in Fig. 6 and 7, respectively.

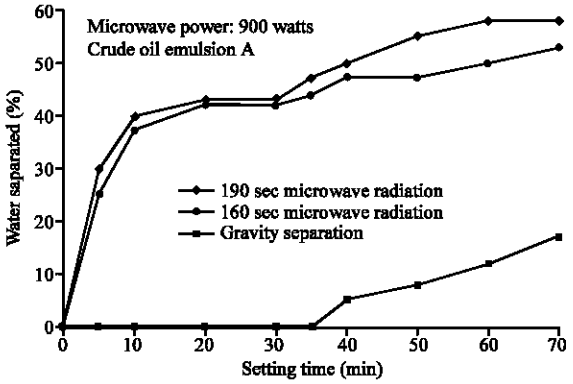

Fig. 6: Separation of water from crude oil emulsion A

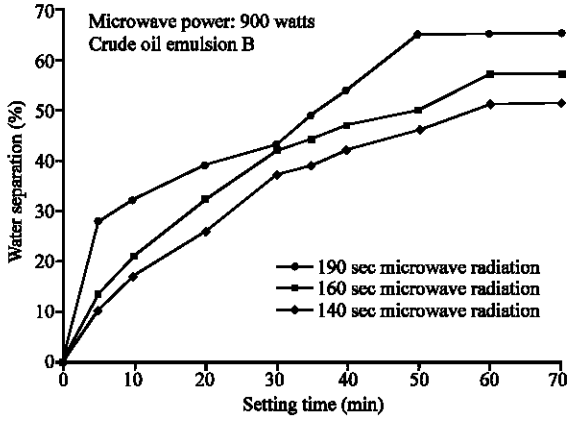

Fig. 7: Separation of water from crude oil emulsion B

Table 3: Experimental results of microwave radiation (crude oils A and B)

	Crude oil A		Crude oil B	
Time (sec)	Temp. increase $\Delta T, T_o = 26°C$	Rate of temp. increase (C/s)	Temp. increase $\Delta T, T_o = 26°C$	Rate of temp. increase (C/s)
20	4.60	0.230	5.40	0.270
40	8.00	0.200	9.60	0.240
60	11.34	0.189	12.60	0.210
80	14.64	0.183	15.04	0.188
100	17.40	0.174	17.90	0.179
120	20.40	0.170	20.88	0.174
140	23.52	0.168	23.80	0.170
160	25.99	0.162	26.72	0.167
180	28.44	0.158	28.98	0.161
200	30.80	0.154	31.40	0.157
220	33.00	0.150	33.66	0.153
240	35.04	0.146	36.00	0.150
260	36.92	0.142	38.48	0.148

Figure 6 shows that the separation in much faster with microwave heating than room temperature (gravity separation). At the end of 35 min of gravity settling, there is no separation of water layer was observed (Fig. 6). For crude oil A, at microwave radiation times 160 and 190 sec, the separation of water was found 54 and 59%, respectively. While for crude oil B, as shown in Fig. 7 at radiation times 140, 160 and 190 sec, water separation were found 50, 57 and 68%, respectively.

Table 3 shows with combination of Fig. 6 and 7 that microwave radiation can raise the temperature of emulsion, reduce viscosity and the result a separation of water from oil as mentioned by Eq. 2.

CONCLUSIONS

The water-in-crude oil emulsion has great importance in the oil industry. The formation, production and stabilization of water-in-crude oil (w/o) emulsions are investigated over a wide range of parameters. These parameters are surfactant concentrations, temperature, stirring time, water-oil phase ratio (10-90%) and agitation speed (800-1800 rpm). In terms emulsion breaking, the microwave demulsification was applied on water-in-oil emulsions. Results showed that microwave radiation is a dielectric heating technique with the unique characteristics of fast and volumetric heating. The microwave separation does not require chemical addition.

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