

*Full Length Research Paper*

# Demulsification of petroleum emulsions using microwave separation method

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**The formation of emulsions during oil production and processing is a costly problem, both in terms of chemicals used and production losses. For economic and operational reasons, it is necessary to separate the water completely from crude oils before transporting or refining them. Experimental data are presented to show the influences of Triton X-100, low-sulfur wax residue (LSWR), sorbitan monooleate (Span 83) and sodium dodecyl sulfate (SDS) on the stability and microwave demulsification of petroleum emulsions. It was found that emulsion stability was related to several parameters including the surfactant concentration, water-to-oil phase ratio (10 to 90%), temperature and agitation speed. Based on this study, a possible emulsion-minimization approach utilizing microwave irradiation is suggested, which could be implemented in refineries. Compared with conventional heating, the use of microwave heating can significantly enhance the demulsification rate, reaching over 90 v/v% for the emulsions studied in this work.**

**Key words:** Microwave, surfactant, demulsification, water-in-oil emulsion (w/o), separation.

## INTRODUCTION

As crude oil is always produced with entrained water, many problems occur during petroleum production due to the formation of emulsions (Schramm, 1992). Emulsions are difficult to treat and can cause a number of operational problems such as the tripping of separation equipment in gas-oil separating plants, the production of off-spec crude oil and the creation of high pressure drops in flow lines. There are two forms of emulsions: Water-in-oil (w/o) and oil-in-water (o/w). The most common emulsions encountered in the oil field are water-in-crude-oil (w/o) emulsions. Stability is an important characteristic of a water-in-oil emulsion. The characterization of an emulsion as stable or unstable is required before other properties can be considered, because these properties change significantly for each type of emulsion.

For economic and operational reasons, it is necessary to separate the water completely from crude oils before transporting or refining them. Minimizing water levels in these oils can reduce pipeline corrosion and maximize pipeline usage (Taylor, 1992; Solite and Abd El-Daiem, 2007; Hassan et al., 2006; Harris, 1996). Effective separation of crude oil and water is an essential operation 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). Wolf (1986) was the first person to introduce the concept of microwave demulsification of emulsions. Subsequent authors reported the demulsification of water-in-oil emulsions using a microwave-heating separation method (Fang and Lai, 1995).

A number of studies have been carried out on the microwave heating (MW) of oil-and-water systems. Microwave heating, because of its volumetric heating effects, offers a faster processing rate than traditional heating methods. The separation of emulsified water from

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**Table 1.** Physical properties of crude oils.

	Crude oil A	Crude oil B
Density (g/cm <sup>3</sup> )	0.852	0.834
Viscosity (cp)	20.75	9.42
Surface tension (mN/m) at 28 °C	28.20	26.20
Interfacial tension (mN/m) at 28 °C	27.30	24.00

**Table 2.** Compositions of w/o emulsion formulations and their corresponding stabilities.

Stabilizer	Weight% stabilizer in external phase (oil) in various % internal phase (water)			
	50	55	60	70
LSWR	0.50	0.75	2.00	5.00
Triton X-100	0.75	0.90	1.50	3.00
SDS	1.00	1.50	3.00	3.50
Span 83	4.50	6.00	1.50	6.80

crude oil occurs in several stages; due to gravity settling, water droplet/droplet flocculation takes place as water droplets approach each other (Fang et al., 1988). The purpose of heating water-in-oil emulsions with microwave radiation is to separate the water and oil. When a water-in-oil emulsion is heated with microwave radiation, two phenomena will occur. The first is the increase of temperature, which causes a reduction of viscosity and coalescence. The result is the separation of water without the addition of chemicals (Fang et al., 1989; Young et al., 1996). According to Stoke's law, if oil is the continuous phase, the settling velocity of water droplets is given by:

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

where D is the diameter of the droplets. The viscosity of oil is very sensitive to temperature; as temperature increases, oil viscosity decreases much faster than does the density difference,  $(\rho_w - \rho_o)$ , between water and oil. As a result, when viscosity is decreased, the water-droplet size increases. Therefore, microwave heating increases the velocity of water settling ( $v_w$ ) and accelerates the separation of the emulsion. The second phenomenon is coagulation. A higher temperature and a lower viscosity facilitate the coagulation process, resulting in a larger droplet diameter (D) and a more rapid separation.

The objective of this study was to examine the influences of Triton X-100, sorbitan monooleate (Span 83), low-sulfur wax residue (LSWR) and sodium dodecyl sulfate (SDS) on emulsion stabilization and microwave demulsification of water-in-crude-oil emulsions. Our findings showed that emulsion stability was related to surfactant concentration, stirring time, temperature, the water-to-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 an Iranian oilfield, and crude oil B, from a Malaysian oilfield. Their compositions are given in Table 1. For emulsion preparations, distilled water was used as the water phase (dispersed phase) and crude oil as the oil phase (continuous phase) for both crude oils A and B. The commercially available Triton X-100, low-sulfur wax residue (LSWR), sodium dodecyl sulfate (SDS) and sorbitan monooleate (Span 83) were used to emulsify the oil-and-water mixtures. Emulsions were prepared in a 900 ml graduated beaker over a range of volumetric ratios of the water and oil phases. The emulsions were agitated vigorously using a standard three-blade impeller at a speed of 1,600 rpm and a temperature of 28 °C for seven minutes. The concentrations of water in the samples were 10 to 90% by volume. The compositions of the w/o emulsion formulations and their corresponding stabilities are given in Table 2, which also shows the surfactants used in this study. To prepare water-in-oil (w/o) emulsions, the agent-in-oil method was followed; that is, the emulsifying agents were dissolved in the continuous phase (oil), then water was added gradually to the mixture. The volume of water settling to the bottom was read from the scale on the beaker at different times. The amount of water separation in percent was calculated as the separation efficiency (e) from the volume of water observed in the beaker as follows:

$$\text{Percentage water separation, } e = \frac{(\text{Volume of water layer, ml})}{(\text{Original volume of water, ml})} \times 100 \quad (1)$$

The demulsification experiments were performed using an Elba domestic microwave oven (model EMO 808SS), with a rated power output of 900 watts and an operating frequency of 2,450 MHz. A 900 ml graduated cylindrical glass vessel of 11.5 cm in diameter and 11 cm high was used as a sample container. Three thermocouples (type K-IEC-584-3) were connected to a Pico-TC-08 data logger and the microwave oven as shown in Figure 1. The

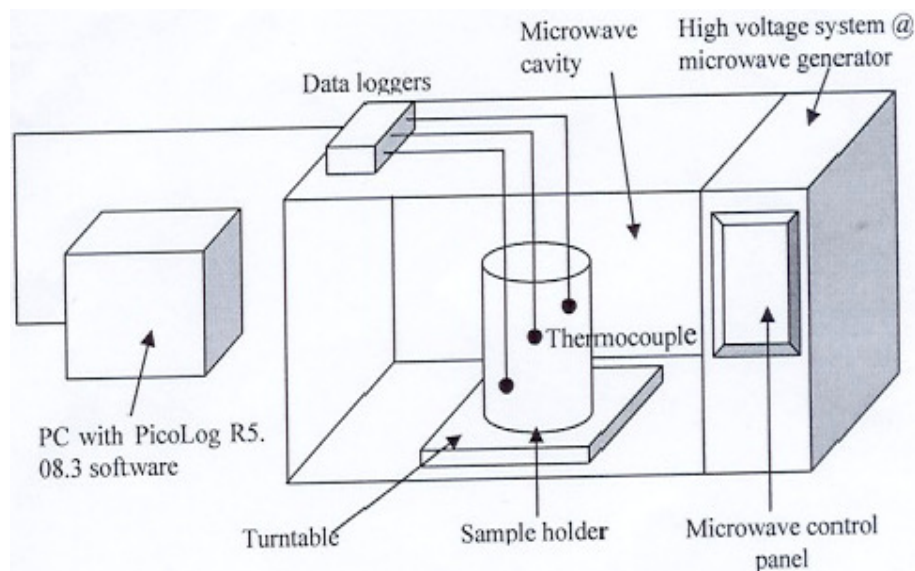


Figure 1. Testing setup in microwave oven.

data logger was connected to a PC with the PicoLog R5.08.3 software installed. The thermocouples were inserted at different locations (the top, middle and bottom of the emulsion sample) to measure local temperatures.

## RESULTS AND DISCUSSION

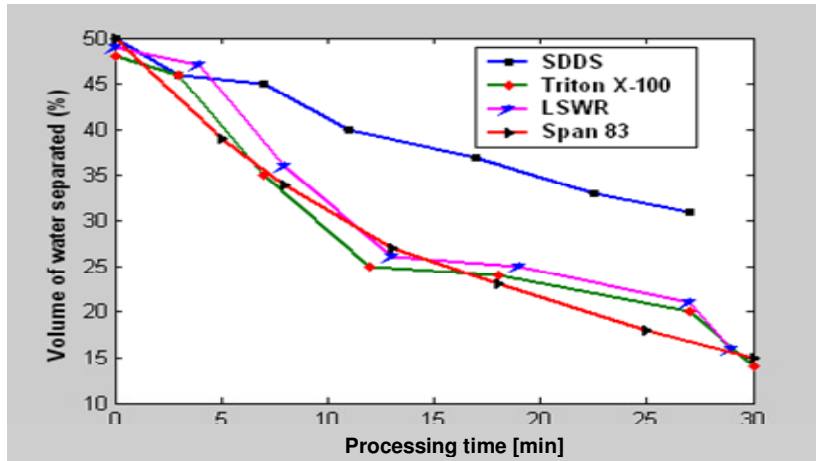
The first part of our experimental work studied the formation, production and stabilization of w/o emulsions and the second examined the breaking of these w/o emulsions (demulsification). As shown in Table 2, LSWR and Triton X-100 water-in-oil (w/o) emulsions were made with 50, 55, 60 and 70% (v/v) internal phase (water). For the 50 and 55% emulsions, a higher solids concentration was found (6 mg/ml oil versus 2 mg/ml), allowing easier emulsification and slowing the settling process. The 60 and 70% emulsions 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 the 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 difference between surfactant concentrations for the 50 and 55% emulsions made with Span 83 appeared very significant for emulsion stability. High Span 83 concentrations increased emulsion stability; therefore, for a high concentration of Span 83, the viscosity of the w/o emulsion increased considerably and the emulsion droplets lost their shape.

The effect of the dispersed phase on the stability of emulsion systems was also examined with sodium dodecyl sulfate (SDS) as the emulsifying agent. The SDS emulsions were made with 65, 70, 75 and 80% (v/v) (1 to 3.5 w/w in oil) internal phase.

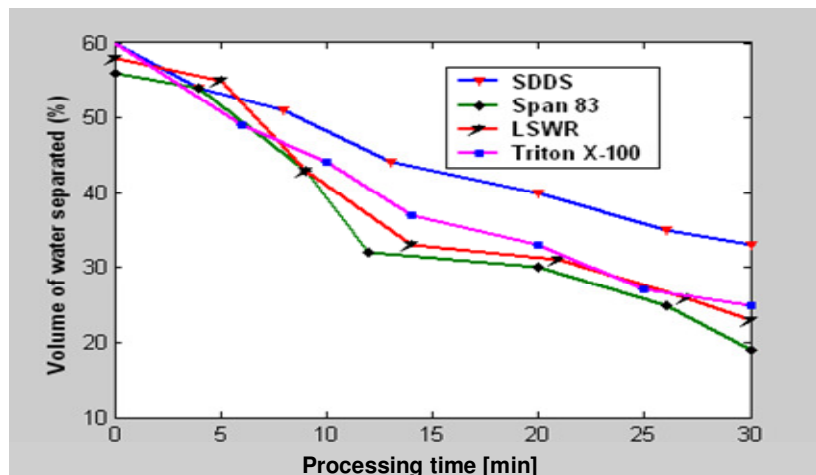
The emulsion stabilities for crude oils A and B were examined as functions of processing time and emulsifier. Stability was evaluated via the ratio of the total water separated. The evaluation was carried out with an agitation speed of 1,800 rpm for 30 min at 26.5°C. As demonstrated in Figures 2 and 3, in most cases, the stability of the emulsions increased with processing time.

It is worth noting that all surfactants yielded a very long time for the separation of the water phase, that is, relatively stable emulsions. However, the maximum amount of water separated from crude oil A was (50%) and that from crude oil B was (60%). From these observations, the classification in terms of decreasing stability efficiency is as follows: SDS > Triton X-100 > LSWR > Span 83.

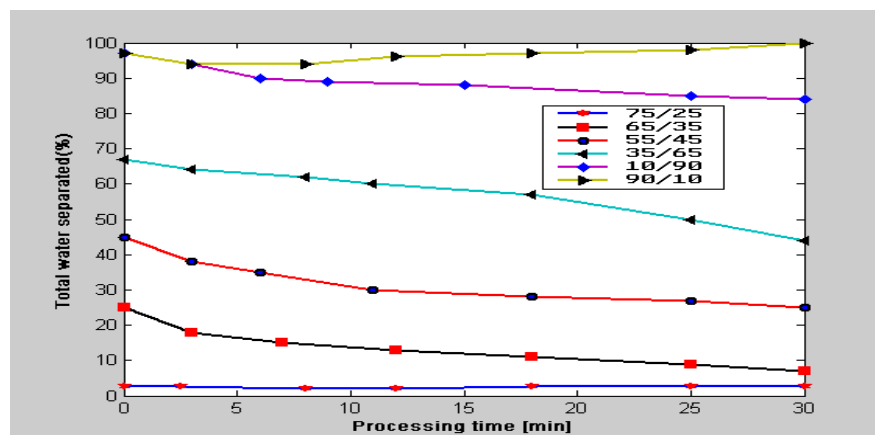
The effect of stirring time and phase ratio on emulsion stability was again investigated. Water-in-oil emulsions were prepared with various volume ratios, as shown in Figure 4. At a low water/oil phase ratio (10/90%), only low stability was obtained; the increment in stability continued as the phase volume ratio was increased up to 75/25%, leading to a highly stable emulsion. The variation in the stability of the emulsions with the phase ratio of 75/10% was unexpected, especially during the first eight minutes of processing. When the volume of the dispersed phase reached 90%, the emulsion behavior completely changed, as shown in Figure 4; the emulsion changed from w/o to o/w. From these observations, it can be deduced that the phase-inversion point was in the range



**Figure 2.** Change of emulsion stability for crude oil A emulsions (50 to 50% w/o) as functions of processing time and emulsifier applied.



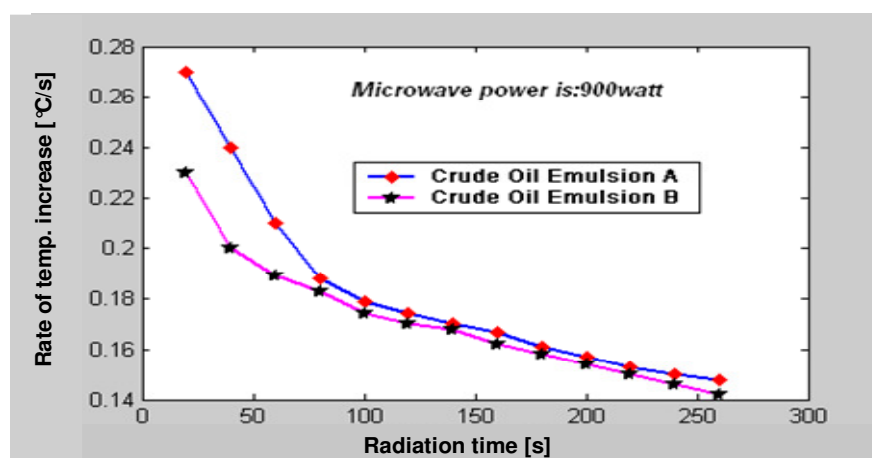
**Figure 3.** Change of emulsion stability for crude oil B emulsions (50 to 50% w/o) as functions of processing time and emulsifier applied.



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

**Table 3.** Experimental results of microwave irradiation of emulsions of crude oils A and B.

Time (s)	Crude oil A		Crude oil B	
	Temperature increase $\Delta T, T_0 = 26^\circ\text{C}$	Rate of temperature increase ( $^\circ\text{C/s}$ )	Temperature increase $\Delta T, T_0 = 26^\circ\text{C}$	Rate of temperature increase ( $^\circ\text{C/s}$ )
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 5.** Heating rate versus microwave irradiation time for crude oil A and B emulsions.

of 68 to 72% water. The oil-in-water emulsion with a phase ratio of 90/10% was a very instable emulsion. As the volume of the dispersed phase increases, the continuous phase must spread out farther to cover all of the droplets. This increases the likelihood of impacts, thus decreasing the stability of the emulsion. This means that the emulsion might not break as the volume of the dispersed phase is increased. In fact, this increment caused the emulsion to invert from one form (w/o) to another (o/w).

Following our study of the formation, production and stabilization of these emulsions, we then examined the inverse of emulsion stability, namely, demulsification or emulsion breaking. Table 3 shows the experimental results of the microwave irradiation of crude-oil emulsions A and B. Here, it is obvious that there was a correlation between the irradiation time and the rate of temperature

increase; as the irradiation time increased, the rate of temperature rise ( $dT/dt$ ) decreased. The rate of temperature increase ( $dT/dt$ ) also decreased at higher temperatures; this may attributed to the small dielectric loss of water. The average rates of temperature increase for crude-oil emulsions A and B were found to be 0.171 and 0.182 $^\circ\text{C/s}$ , respectively (Figure 5). Fang and Lai, (1995) reported the same findings. As the purpose of heating water-in-oil emulsions with microwaves was to separate water from oil, the separation efficiencies of crude oil A and B emulsions were therefore calculated using Equation 1, as shown in Figures 6 and 7, respectively.

As shown in Figure 6, the separation was much faster with microwave heating than at room temperature (gravity separation). Figure 6 shows that at the end of 35 min of gravity settling, there was no separation of water layer

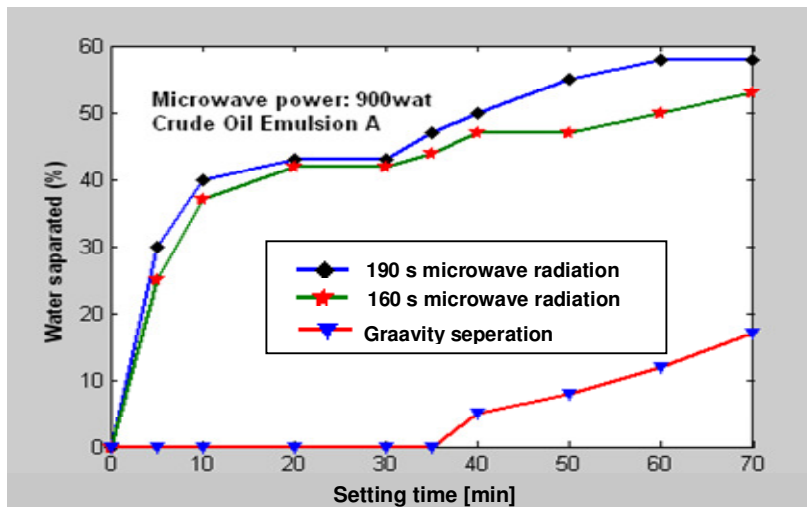


Figure 6. Separation of water from crude oil A emulsion.

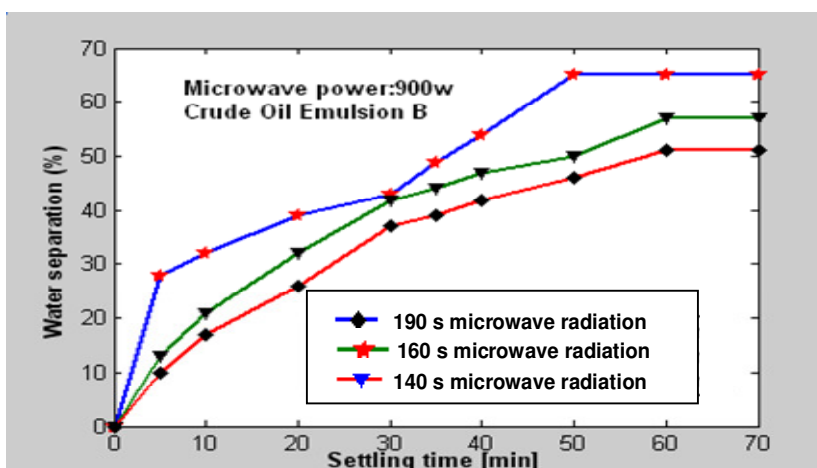


Figure 7. Separation of water from crude oil B emulsion.

observed. For crude oil A, at microwave irradiation times of 160 and 190 s, the water separations were 54 and 59%, respectively. For crude oil B, as shown in Figure 7, at irradiation times of 140, 160 and 190 s, water separations were 50, 57 and 68%, respectively.

The results shown in Table 3 and Figures 6 and 7 show that microwave irradiation can raise the temperature of the emulsion, reduce its viscosity, and result in the enhanced separation of water from oil, as predicted by Equation 2.

## Conclusions

Water-in-crude-oil emulsions are of great importance in the petroleum industry. The formation, production and stabilization of water-in-crude-oil (w/o) emulsions were

investigated over a wide range of parameters including surfactant type and concentration, temperature, stirring time, water-to-oil phase ratio (10 to 90%) and agitation speed (800 to 1,800 rpm). Microwave demulsification was applied on water-in-oil emulsions to evaluate its effects on emulsion breaking. The results showed that, microwave irradiation, a dielectric heating technique with the unique characteristics of fast and volumetric heating, speeds emulsion separation and do not require chemical addition.

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