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Demulsification of Water-in-Crude Oil (W/O) Emulsion by using Microwave Radiation

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Abstract: This study was conducted to examine a batch microwave process of 2450 MHz in demulsification of water-oil- (w/o) emulsions as well as the effect of triton X-100 and Low Sulfur Wax Residue (LSWR) from synthesized (w/o) emulsions stability and demulsification. Oil exploitation is always accompanied by the non-desired formation of emulsions caused by the presence of naturally occurring surface-active molecules such as asphaltenes and resins. Because their presence stabilizes the oil/water interface, it is necessary to break emulsions by adding other surface-active molecules. In this study, a microwave demulsification method was utilized in a 50-50% and 20-80% of water-in-oil emulsions with varied microwave exposure time. Results show that, temperature profiles of water-in-oil emulsions inside a cylindrical container were measured. The temperature rise at a given location was linear. The rate of temperature increase of emulsions decreased at higher temperature due to decreasing dielectric loss of water. Due to its fast, volumetric and selective heating, microwave heating can be used an alternative demulsification method for water-in-oil emulsions.

Key words: Demulsification, microwave heating, w/o emulsion, dielectric, crude oil

INTRODUCTION

A significant portion of the world crude oil is produced in the form of emulsion. Also during the lifting, transportation and processing of oil, emulsions and sludge's are created. Ninty percent of the oilfield emulsion produced is the type of water-in-oil (w/o) emulsions (Xia *et al*., 2004). Water/oil/solid emulsions are mixtures of ordinarily incompatible materials. Crude oil is composed of mostly hydrocarbons, both aliphatic and aromatic, as well as some molecules that naturally occurring surfactants in crude oil (asphaltenses and resins) have been identified as largely responsible for the stability of these emulsions. An emulsion may be tight (difficult to break) or loose (easy to break). Whether an emulsion is tight or loose depends on a number of factors such as the percentage of oil and water found in the emulsion, the amount of agitation, the types and amounts of emulsifying agents present, as well as the properties of oil and water (Ali and Alqam, 2000).

For economic purpose, pipeline considerations and for efficient refinery operations, the produced crude oil emulsions must dewatered and necessary to separate the water completely from the crude oils. The traditional methods of eliminating these emulsions include high heat and chemical utilizations, which force the emulsion to separate into water, hydrocarbon and solids. Usually these methods were expensive, chemical additives are carried into the wastewater streams, or follow the hydrocarbon into the refining process. The concept of microwave demulsification was first introduced by Klaila (1983) and Wolf (1986) in their patent applications. Chan and Chen (2002) and Fang and Lai (1995), Fang *et al.* (1989) reported demulsification of water-in-oil (w/o) emulsions by microwave radiation. The experimental results showed that the percentage of water separated from the emulsion by microwave radiation was higher than 80% under certain conditions. This study was conducted to examine a batch microwave process in demulsification of water-oil- (w/o) emulsions. Also, the study examined the effect of triton X-100 and Low Sulfur Wax Residue (LSWR) from synthesized (w/o) emulsions stability and demulsification. Results of the study showed that emulsion stability is depending on the concentration of the emulsifiers (Triton-X-100 or LSWR). The demulsification or coalescence rate was measured by dividing the volume of water separated to the total water content. The demulsification efficiency reaches 90% in a very short time under microwave radiation.

MATERIALS AND METHODS

This research was conducted in 2010 at University Malaysia Pahang's Laboratories. In this study, Elba domestic microwave oven model: EMO 808SS, its rated power output is 900 watts and its operation frequency is

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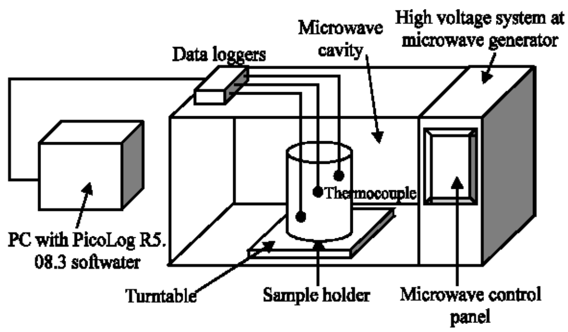

Fig. 1: Elba microwave oven

2450 MHz was used in heating water-in-oil emulsion samples. A 900 mL graduated cylindrical glass was used as sample container. The diameter and height of emulsion sample in the container were 11.5 and 11 cm, respectively.

Three thermocouples type (K-IEC-584-3) were connected to Pico-TC-08 data logging and then connected to microwave oven as shown in Fig. 1. The data logger 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.

Sample preparation and procedures: The crude oil samples were obtained from Petronas refinery at Malaka city, 50-50% and 20-80% water-in-oil emulsions were prepared. Emulsions were prepared in 900 mL graduated beakers, with ranges by volume of the water and oil phase. The microwave radiation was set to different power settings. The water phase is distilled water. The emulsions were agitated vigorously using a standard three blade propeller at speed of 1800 rpm and temperature 30°C for 8 min. The concentrations of water in samples were 20-50% by volume. The sample placed in a feed tank and used a pump to pull the samples to the Elba domestic microwave oven model: EMO 808SS for radiation. Three thermocouples were inserted in the settling tank of emulsion sample at different locations, top, middle and bottom. The emulsion samples were heated with microwave radiation for 20, 40, 60, 80, 100, 120, 140, 160, 180 and 200 sec. Temperature profiles of emulsions inside a cylindrical container during continuous microwave heating at 2450 MHz were recorded by Pico-TC-08 data logging. The surfactants used in this study were the commercially available Triton X-100; this Triton X-100 is a non-ionic water soluble molecule and Low Sulfur Wax Residue (LSWR). The emulsifying agents were used as manufactured without further dilution. In order to prepare water-in-oil emulsions, the agent-in-oil method was followed; that is, in this study, the emulsifying agent (Triton X-100) and LSWR 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:

$$\%\text{ of water separation (e)} = \frac{(\text{volume of water layer, mL})}{(\text{Original volume of water, mL})} \times 100 \tag{1}$$

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, also microwave has another unique feature other than how it interacts with matter, is its penetrating power. Microwave distributes energy within the bulk of most materials, rather than just on its surface. Any heat produced at the surface must then be conducted or convicted into the material. Microwave, because the wave length is relatively long and the method of interaction so mild, can penetrate deeply into a substance. Penetration energy deposition by microwave overcomes many surface-limiting characteristics of normal heating. The purpose of heating water-in-oil (w/o) emulsions with microwave radiation is to separate water from oil. Therefore, when water-in-oil emulsion is heated with microwave radiation, two phenomenons 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:

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

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_0) does, the result when viscosity decreases, the droplets size increases. Therefore, microwave heating increases the velocity of water (ν_w) and accelerates the separation of emulsion. The higher temperature and lower viscosity make the coagulation process easier. The results are larger particle diameter D and rapid separation. Since, microwave heats materials volumetrically, it is possible to calculate the volume rate of microwave heat generation from energy balance equation as:

Table 1: Experimental results of continuous microwave heating (50-50% w/o emulsions) (Microwave power is: 900 W)

Radiation time (sec)	$T_o = 25.6°C$ ΔT, (°C)	Rate of tem. dT/dt (C sec^{-1})	Rate of heat generation $q_{MW} = \frac{cal}{sec-cm^3}$	Dielectric constant $\varepsilon'_{r,50-50\%}$	Dielectric loss $\varepsilon''_{r,50-50\%}$	$\tan\delta = \frac{\varepsilon''_r}{\varepsilon'_r}$
20	10.00	0.500	0.284	33.530	3.779	0.113
40	12.00	0.300	0.170	33.221	3.572	0.108
60	14.40	0.240	0.136	32.849	3.352	0.102
80	18.72	0.234	0.133	32.180	3.017	0.094
100	22.40	0.224	0.127	31.610	2.780	0.088
120	25.68	0.214	0.122	31.102	2.597	0.083
140	29.40	0.210	0.119	30.526	2.417	0.079
160	32.16	0.201	0.114	30.098	2.299	0.076
180	35.50	0.197	0.112	29.581	2.170	0.073
200	38.50	0.193	0.110	29.117	2.066	0.071

Table 2: Experimental results of continuous microwave heating (20-80% w/o emulsions) (Microwave power is: 900W)

Radiation time (sec)	$T_o = 25.6°C$ ΔT, (°C)	Rate of tem. increase dT/dt (C sec^{-1})	Rate of heat generation $q_{MW} = \frac{cal}{sec-cm^3}$	Dielectric constant $\varepsilon'_{r,50-50\%}$	Dielectric loss $\varepsilon''_{r,50-50\%}$	$\tan\delta = \frac{\varepsilon''_r}{\varepsilon'_r}$
20	14.0	0.700	0.398	13.957	1.299	0.093
40	18.6	0.465	0.264	13.683	1.161	0.085
60	21.9	0.365	0.207	13.483	1.079	0.080
80	28.9	0.361	0.205	13.068	0.938	0.072
100	35.2	0.351	0.199	12.691	0.840	0.066
120	40.9	0.341	0.194	12.351	0.767	0.062
140	47.1	0.336	0.191	11.981	0.702	0.059
160	52.5	0.328	0.186	11.659	0.652	0.056
180	55.9	0.311	0.177	11.456	0.625	0.055
200	57.5	0.288	0.164	11.360	0.613	0.054

Table 3: Viscosity data for 50-50 % and 20-80 % w/o emulsions

Viscosity (cp)	Temperature (°C)	Shear rate (sec^{-1})	Shear stress (dyne cm^{-2})
50-50 % w/o			
340	28.5	32	25.0
206	40	35	27.4
180	50	39	30.5
147	60	46	33.0
130	70	52	40.0
90	80	60	45.0
20-80 % w/o			
100.56	28.5	29.67	20.2
88.73	40	32.61	22.3
55.59	50	35.60	25.7
30.57	60	38.40	28.9
19.24	70	43.70	30.8
12.13	80	46.60	36.0

$$g_{MW} = \frac{hA}{V}(T_m - T_a) + \frac{\varepsilon A\sigma}{V}\left[(T_m + 273.15)^4 - (T_a + 273.15)^4\right] + \rho C_p\left(\frac{dT}{dt}\right) \quad (3)$$

The above equation assumes that the rate of heat transfer from emulsified water droplets to the continuous phase (oil) is very rapid; therefore, water and oil practically have the same temperature. The right hand side of Eq. 3 comprises of three terms, convective heat transfer, radiative heat due to microwave and conductive heat in the sample respectively. From results of this study, the effect of radiative term is very small as well as convective term. Since, the sample container (glass) has low dielectric constant, therefore, its heat generated assumed to be negligible. For calculation of volume rate of heat generation in Eq. 3, the density (ρ) and (c_p) of the emulsions calculated from mixing rules as:

$$\rho_m = \rho_w\phi + \rho_o(1-\phi) \quad (4)$$

$$C_{pm} = C_{p,w}\phi + C_{p,o}(1-\phi) \quad (5)$$

The volume rates of microwave heat generation for 50-50% and 20-80% water-in-oil emulsions calculated from temperature measurements and Eq. 3 were summarized and shown in Table 1 and 2, respectively. While viscosity data shown in Table 3.

Dielectric constant and dielectric loss of water used in this work were given by Wolf (1986):

$$\varepsilon'_r = 85.215 - 0.33583T \quad (6)$$

$$\varepsilon'_r = 320.658T^{-1.0268} \quad (7)$$

Von-Hippel (1954) proposed equations for dielectric properties of various petroleum oils, in this regards, dielectric constant and loss tangent of crude oil for this study calculated from the equations below.

$$\varepsilon'_{r_o} = 2.24 - 0.000727T \quad (8)$$

$$\tan\delta_o = (0.527T + 4.82)*10^{-4} \quad (9)$$

Table 3 shows viscosity data for 50-50% and 20-80% water-in-oil emulsions, respectively.

RESULTS AND DISCUSSION

The results of coalescence between liquid droplets of 50-50% and 20-80% water-in-oil emulsions were shown in Fig. 2 and 3, respectively.

All experimental results showed that microwave radiation is very effective in separation of water-in-oil emulsions. Figure 2 and 3 illustrated that, microwave radiation can raise the temperature of emulsion, reduce the viscosity, increase the velocity and accelerate separation process as suggested by Eq. (2) and supported by Nour *et al*. (2006, 2007). It is found that triton X-100 and the LSWR stabilize water-in-oil emulsions, while in the absence of triton X-100 and LSWR, emulsions were not stable. The percent of coalesced or separated water is plotted against the time of sedimentation. It observed that, the 50-50% w/o was separated faster than 20-80% does, this may attributed due to high volume fraction for 50-50% (ϕ = 0.46) compared to 20-80% (ϕ = 0.18). The water separation in percent was calculated from volume measurements as described in Eq. 1. It found that the percentage of coalesced water droplets decreases with the concentration of the triton X-100 reached up to 0.8% and LSWR up to 2%.

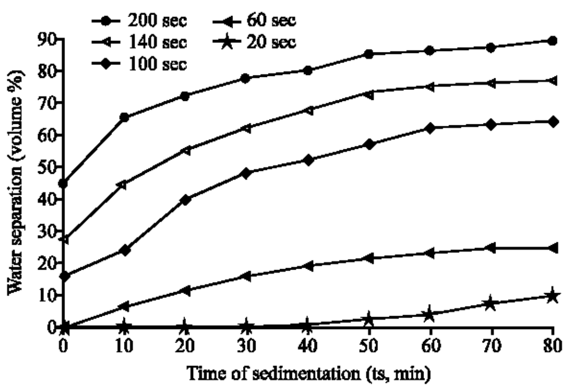

Fig. 2: Separation of water from 50-50% water-in-oil emulsion

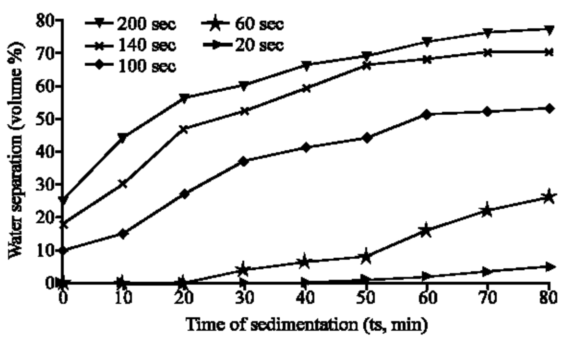

Fig. 3: Separation of water from 20-80% water-in-oil emulsion

The temperature increasing rates of irradiated samples, dielectric constant, dielectric loss, loss tangents and volume rates of heat generation for 50-50% and 20-80% w/o emulsions were shown in Table 1 and 2, respectively. The rate of temperature increase was calculated from temperature increase divided by radiation time. It is observed that, the rate of temperature increase (dT/dt) is inversely proportional to the increase in temperature ΔT; this was expected result since the dielectric loss of water is small. The rates of temperature increase for 50-50% and 20-80% w/o illustrated in Fig. 4. Equation 3 used to calculate the volume rate of heat generation, from the calculations; it found that the contributions of the heat loss by convective heat transfer and radiative heat loss were very small, while the contribution of heat accumulation in the emulsion is significant.

In application of Eq. 3 for calculation of volume rates of heat generation, the emulsion density (ρ_m) and heat capacity (cp_m) were calculated from mixture rules Eq. 4 and 5, respectively. It observed that, the dielectric properties of emulsions affected by temperature in this regards, Fig. 5 shows dielectric losses for 50-50% and 20-80% w/o emulsions, this supported by Nour *et al.* (2010). It is clear from the figure, dielectric loss for 20-80% w/o less than for 50-50% this may attributed to the high temperature of 20-80% compared with temperature of 50-50% w/o.

The shear rate, shear stress and viscosity of the emulsion samples were measured with Brookfield (DV-III) Rheometers given in Table 3. The viscosity, μ of an emulsion diminishes when the volume fraction of the dispersed phase ϕ is reduced.

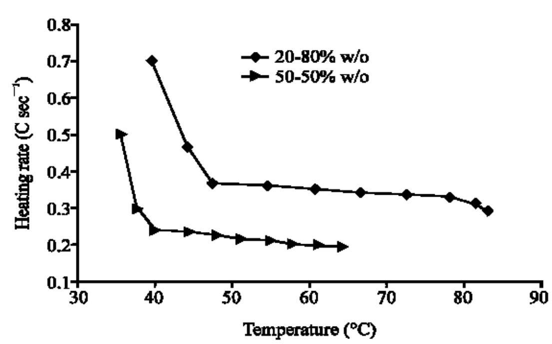

Fig. 4: Rates of temperature increase for 50-50% and 20-80% w/o

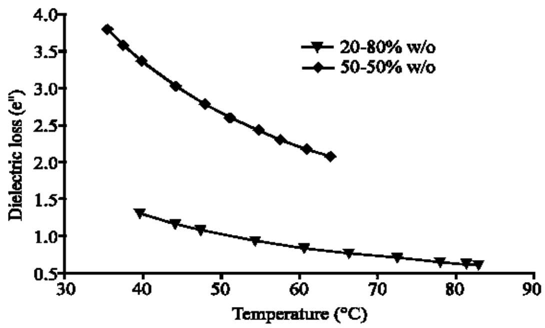

Fig. 5: Dielectric vs. temples for 50-50% and 20-80% w/o

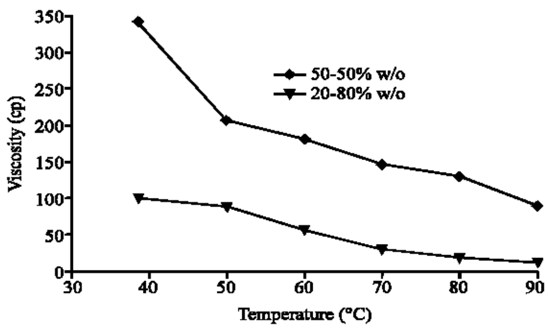

Fig. 6: Viscosity vs. temp. For 50-50% and 20-80% w/o

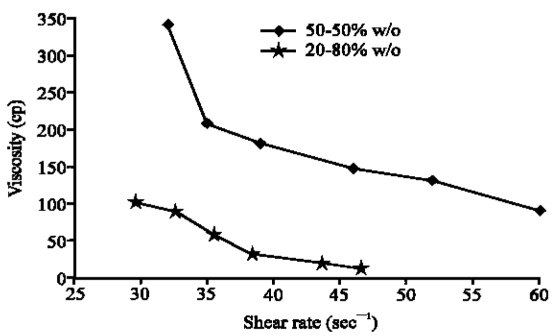

Fig. 7: Viscosity vs. Shear rate. For 50-50% and 20-80% w/o

Figure 6 shows the viscosity of w/o versus temperature, it's clear from the Fig. 6; emulsions were very sensitive to temperature. As temperature increases, the viscosity decreases fast.

The viscosities for 50-50% and 20-80% for w/o emulsions are shown in Fig. 7. Increases in the internal phase volume fraction lead to an increase in both the viscosity and the degree of shear thinning.

CONCLUSIONS

The microwave heating process was examined for water, oil and emulsion samples. Results of this study showed that, microwave radiation is a dielectric heating technique with the unique characteristics of fast, volumetric and effective heating is feasible and has the potential to be used an alternative way in the demulsification of water-in-oil emulsions. From temperature distribution profiles of irradiated emulsion, it appears water-in-oil emulsion has been heated quickly and uniformly by microwaves rather than by conventional heating. This new separation technology does not require chemical addition. Furthermore, microwave radiation appears to provide faster separation than the conventional heating methods.

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