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A Comparative Study on Emulsion Demulsification by Microwave Radiation and Conventional Heating

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Abstract: A heavy crude oil has been increasingly important sources of hydrocarbons in many parts of the world, in which transportation of this heavy crude oil to refinery can be a problem. During the lifting, transportation and processing of oil, frequently emulsions either water-in-oil or oil-in-water are created. Formation of these emulsions during oil production is a costly problem, both in terms of chemicals used and due to production losses. The traditional methods of eliminating these emulsions, utilize high heat and chemicals, which forces the emulsion to separate into water, hydrocarbon and solids. This study investigates comparatively on emulsion demulsification between the conventional and microwave heating. Two types of different crude oils were used as samples for the study. The oils are denoted as A and B. crude oils were synthesized in the laboratory. The water to oil ratio was varied from 30-50: 70-50. In company the two heating methods, the heating duration was varied from 5 to 60 min for conventional heating method, while for microwave heating, the duration was varied from 30 sec to 4 min. Microwave demulsification is primarily due to heating. However, the comparisons between the microwave heating and conventional heating show that they are different. The microwave induced molecular rotations also play a role. Molecular rotations can reduce zeta potential which suspends water droplets and solid particles in an emulsion.

Key words: Microwave, conventional, demulsification, heating, separation, emulsion

INTRODUCTION

In-water-in-oil emulsion, there are two forces in direct opposition. One force is the film of emulsifying agent that surrounds the water droplets. This force tends to prevent the droplets from merging together to form larger drops, even when the droplets collide. The other force is the opposite tendency of water droplets to join together to form larger drops. The larger drops yield to the force of gravity and settle out (Kruse, 1990). Therefore, the breaking of emulsions (demulsification) is necessary in many applications such as environmental technology, painting and petroleum industry. Methods currently available for demulsification can be broadly classified as chemical, electrical and mechanical. Chemical demulsification is the most widely applied method of treating water-in-oil (w/o) emulsions and involves the use of chemical additives to accelerate the emulsion breaking process. The breaking of petroleum emulsion is of considerable importance and necessity for several reasons. For economic and operational reasons, it is necessary to separate the water completely from the crude oil before transporting or refining them. Minimizing water

levels in the oils can reduce pipeline corrosion and maximize pipeline usage (Harris, 1996). In petroleum systems, asphaltenes and resinous substances comprise a major portion of the interfacially active component of the oil (Nordi *et al.*, 1991); (Sjoblom, *et al.*, 1992); (Urdahl *et al.*, 1992) and (Johansen, *et al.*, 1989). The concept of microwave demulsification of emulsions was first introduced by Klaila (1983) and Wolf (1986). Chih *et al.* (2002) and Fang *et al.* (1995) reported demulsification of water-in-oil used microwave heating and separation method.

The objective of this study is to compare the demulsification of water-in-crude oil (w/o) emulsions between the conventional and microwave heating methods. Results showed microwave heating is faster than the conventional heating.

MATERIALS AND METHODS

To accomplish the objective of this study, Elba domestic microwave oven model: EMO 808SS and conventional (hotplate) were used in heating emulsion samples. The microwave oven rated power output is

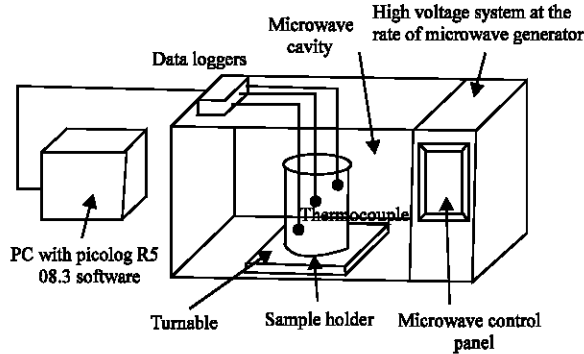


Fig. 1: Elba domestic microwave oven model: EMO 808SS

900 Watts at 2450 MHz, its power consumption is 1400 Watts (microwave) and 1000 Watts (heater), the oven cavity dimensions are: 215 mm(H)*350 mm(W)*330 mm(D). Fig. 1 shows the details of Elba domestic microwave used in this study.

MICROWAVE RADIATION

The objective of heating water-in-oil emulsions with microwave radiation, is to separate water from oil (Fang *et al.*, 1995). This radiation occur two phenomenons simultaneously. The first phenomenon is the increase of temperature, which leads to reduction of viscosity and coalescence, the result is separation of water from the oil without chemical addition (Fang *et al.*, 1989).

According to the force balance and Stoke's law, if oil is the continuous phase, the settling velocity of water droplets through oil is given by:

$$v_w = \frac{(\rho_w - \rho_o) * g * D^2}{18 * \mu_o} \quad (1)$$

Where:

- V_w = Settling velocity of water
- ρ_w = Density of emulsified water
- ρ_o = Density of oil
- g = Gravitational
- D^2 = Diameter of the droplets
- μ_o = Viscosity of continuous phase (oil)

In Eq. 1, the settling velocity is proportional to the density difference, square of droplet diameter and the reciprocal of oil viscosity. The viscosity of oil and water are very sensitive to temperature. As temperature increases, viscosity decreases much faster than the density difference, ($\rho_w - \rho_o$) does. Therefore, the heating, either by microwave or conventional heat, increases the velocity and consequently makes the separation of

emulsion faster. According to Osipow (1977), the rate of coalescence is given by:

$$\text{Rate} = A_1 e^{-B_1 / RT} \quad (2)$$

Where: A, B = Constants

R = Gas constant

T = Temperature of emulsion

The 2nd phenomenon is coagulation. The high temperature and lower viscosity make the coagulation process easier. The results are larger particle diameters, D and faster separation. In conventional thermal heating, energy is transferred to the material through convection, conduction and radiation of heat from the surfaces of the material (Chih *et al.*, 2002). In contrast, microwave energy is delivered directly to the material through molecular interaction with the electromagnetic field. Because microwaves can penetrate materials and deposit energy, heat can be generated throughout the volume of the material. The transfer of energy done not rely on diffusion of heat from the surfaces and it is possible to achieve rapid and uniform heating of thick materials (Thostenson *et al.*, 1999). In addition to volumetric heating, microwaves can be utilized for selective heating of materials. The molecular structure affects the ability of the microwaves to interact with materials and transfer energy. When materials in contact have different dielectric properties, microwaves will selectively couple with the higher loss material. In multiple phase materials, such as W/O emulsions, some phases may couple more readily with microwaves.

SAMPLE PREPARATION AND PROCEDURES

The crude oil samples were obtained from Petronas refinery at Malaka city, two types of crude oils was collected namely, crude oil (A and B), their respective compositions are given in Table 1. Different samples of water-in-oil emulsions were prepared used crude oils A, B and tab water. Emulsions were prepared in 500 mL graduated beakers, with ranges by volume of the water and oil phase. The water phase is tab water. The emulsions were agitated vigorously using a standard three blade propeller at speed of 1600 rpm and

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)	17.75	7.42
Surface tension (mN/m) at 28°C	26.20	23.20
Interfacial tension (mN/m) at 28°C	25.30	21.00

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

Emulsion	Stabilizer	Wt % ext. stabilizer in 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		4.00	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		4.00	w/o	70
9	Span 83	1.50	w/o	50
10		3.00	w/o	55
11		4.50	w/o	60
12		6.80	w/o	70

temperature 28°C for 5 min. The concentrations of water in samples were 30, 40 and 50% by volume. The demulsification experiments were performed using Elba domestic microwave oven Fig. 1, three thermocouples type (K-IEC-584-3) were connected to Pico-TC-08 data logger and then connected to microwave oven as shown in Fig 1. The container of emulsion sample was placed in the center of Elba domestic microwave oven model: EMO 808SS. Radiation time varied from 30, 60, 90, 120, 150, 180 and 210 sec. The thermocouples were inserted to different locations of the container, top, middle and bottom to measure local temperatures. The surfactants used in this study for emulsion formulation and stabilization were; low sulfur wax residue (LSWR), Triton X-100 and Span 83; the emulsifying agents were used as manufactured without further dilution. The composition of w/o emulsion and their corresponding stabilities are given in Table 2. In order to prepare water-in-oil emulsions, the agent-in-oil method was followed; that is, in this study, 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 water separation in percent was calculated as separation efficiency (e) from volume of water observed in the beaker as follows:

$$e = \frac{\text{Volume of separated water (mL)}}{\text{Original volume of water in the emulsion (mL)}} * 100\% \quad (3)$$

The prepared emulsion was used to check for W/O or O/W emulsions. All emulsions investigated were W/O emulsion (oil-continuous). Table 3 and 4 show the raw data of various water-in-oil emulsions heated with microwave radiation and conventional heating for crude oil A, while Table 5 and 6 illustrate the raw data for microwave radiation and conventional heating for crude oil B respectively.

Table 3: Various ratios of water-in-oil emulsions heated with microwave radiation (Crude oil A)

50-50% w/o			40-60% w/o			30-70% w/o		
Time (sec)	Temp (°C)	Heating rate (c/s)	Time (sec)	Temp (°C)	Heating rate (c/s)	Time (sec)	Temp (°C)	Heating rate (c/s)
30	27.3	0.91	30	29.3	0.98	30	30.6	1.02
60	32.6	0.54	60	35.1	0.59	60	37.5	0.63
90	34.3	0.38	90	39.6	0.44	90	44.2	0.49
120	43.7	0.36	120	49.3	0.41	120	50.9	0.42
150	54.9	0.37	150	56.9	0.38	150	57.9	0.39
180	63.5	0.35	180	64.6	0.36	180	66.6	0.37
210	64.7	0.31	210	66.8	0.32	210	74.1	0.35

Table 4: Experimental results of water-in-oil emulsion heated by conventional method (Crude oil A)

50-50% w/o			40-60% w/o			30-70% w/o		
Time (sec)	Temp (°C)	Heating Rate (c/s)	Time (sec)	Temp (°C)	Heating Rate (c/s)	Time (sec)	Temp (°C)	Heating Rate (c/s)
30	27.5	0.92	30	28.3	0.94	30	30.0	1.00
60	31.0	0.52	60	33.4	0.56	60	35.3	0.59
90	33.5	0.37	90	36.0	0.40	90	40.5	0.45
120	39.0	0.33	120	43.6	0.36	120	46.2	0.39
150	44.0	0.29	150	49.8	0.33	150	56.0	0.37
180	53.0	0.29	180	56.2	0.31	180	62.3	0.35
210	57.0	0.27	210	63.2	0.30	210	68.8	0.33

Table 5: various ratios of water-in-oil emulsions heated with microwave radiation (Crude oil B)

50-50% w/o			40-60% w/o			30-70% w/o		
Time (sec)	Temp (°C)	Heating rate (c/s)	Time (sec)	Temp (°C)	Heating rate (c/s)	Time (sec)	Temp (°C)	Heating rate (c/s)
30	28.3	0.94	30	30.2	1.00	30	32.3	1.08
60	35.0	0.58	60	38.8	0.65	60	40.3	0.67
90	42.9	0.48	90	49.2	0.55	90	55.8	0.62
120	51.8	0.43	120	60.5	0.50	120	68.7	0.57
150	61.9	0.41	150	71.6	0.48	150	79.8	0.53
180	70.6	0.39	180	82.0	0.46	180	88.0	0.49
210	79.6	0.38	210	82.9	0.39	210	97.0	0.46

Table 6: Experimental results of water-in-oil emulsion heated by conventional method (Crude oil B)

50-50% w/o			40-60% w/o			30-70% w/o		
Time (sec)	Temp (°C)	Heating rate (c/s)	Time (sec)	Temp (°C)	Heating rate (c/s)	Time (sec)	Temp (°C)	Heating rate (c/s)
30	26.5	0.88	30	28.9	0.96	30	30.3	1.01
60	33.4	0.56	60	36.2	0.60	60	37.0	0.62
90	38.5	0.43	90	47.1	0.52	90	50.3	0.56
120	46.8	0.39	120	55.0	0.46	120	62.4	0.52
150	57.9	0.39	150	63.0	0.42	150	75.5	0.50
180	66.4	0.37	180	72.0	0.40	180	82.0	0.46
210	74.0	0.35	210	78.0	0.37	210	89.4	0.43

RESULTS AND DISCUSSION

Results of this study is discussed in two parts, the first part studied the formation and stabilization of w/o emulsions, while the second part discusses the breaking

of emulsion (demulsification). All experimental runs showed that microwave radiation is effective in separating dispersed water from water-in-oil emulsions. Water can be separated from oil in water-in-oil emulsions by microwave radiation and conventional heating methods. As shown in Table 2, LSWR, Triton X-100 and Span 83 water-in-oil emulsions were made with 50, 55, 60 and 70% (v/v) internal phase. For 50 and 55 emulsion, a higher solids concentration was found (5 mg mL^{-1} oil versus 1.5 mg mL^{-1}) allowed easier emulsification and slowed the settling process. The 60% and 70% emulsions were appeared fairly stable with little settling. Emulsions stabilized with Triton X-100 and LSWR exhibited only slight coalescence over two days. In contrast, the Span 83 emulsions were found 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 3% (w/w), at 60% (v/v) (4.5% w/w) and at 70% (v/v) (6.8% w/w). The different between surfactant concentrations for Span 83, made the emulsion stability very significant. High Span 83 concentrations increased emulsion stability; therefore, for high concentrations of Span 83, the viscosity of w/o increased considerably and the emulsion droplets lost their shape. In terms of emulsion breaking, as shown in Fig. 2: the separation is much faster with microwave heating than room temperature (gravitational) and conventional heating separation. Fig. 2 shows that at the end of 35 min of gravity settling, there is no separation of water layer was observed. For conventional heating (hot plate), at 90 sec, the separation was 38%, while 90, 120, 150 and 180 sec of microwave irradiation showed 57, 73.4, 82 and 88.5% of separation, respectively.

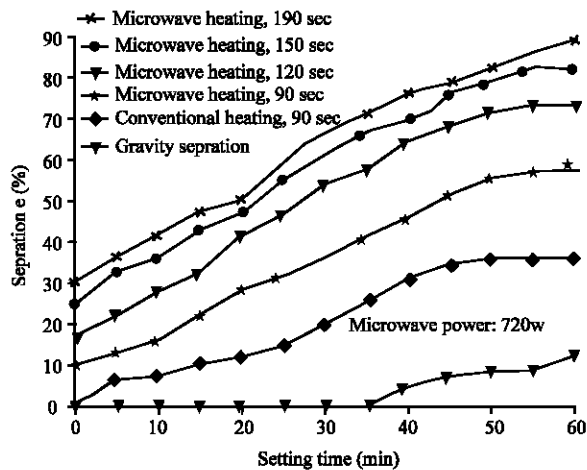


Fig.2: Separation of 50-50% w/o emulsion (Using microwave and conventional heating)

Results from Table 3 and Fig. 2 showed microwave radiation can raise the temperature of emulsion, reduce viscosity and the result a separation of water from oil as mentioned by Eq. 1 and 2.

As microwave is a nonionizing radiation that causes molecular motion by migration of ions and dipole rotations (Kingston, 1988), therefore, microwave induced molecular rotation of water molecules and causes in reduction of zeta potential, based on this, the comparison between the microwave heating and conventional heating of emulsions is of great interest. Fig. 3 shows the temperatures increases at 50-50%, 40-60% and 30-70% w/o emulsions for conventional and microwave irradiation. The temperatures of these samples (oil A) showed in Table 3 and 4, respectively.

Table 5 and 6 showed the results of the two methods for crude oil B. Fig. 4 shows the temperature increases for oil B, the figure illustrates the temperature is higher than that obtained from crude oil A for both

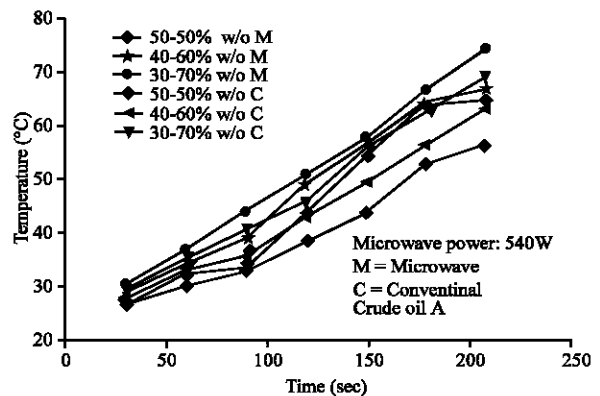


Fig. 3: Temperatures of 50-50%, 40-60% and 30-70% w/o (oil A) (Using microwave and conventional heating)

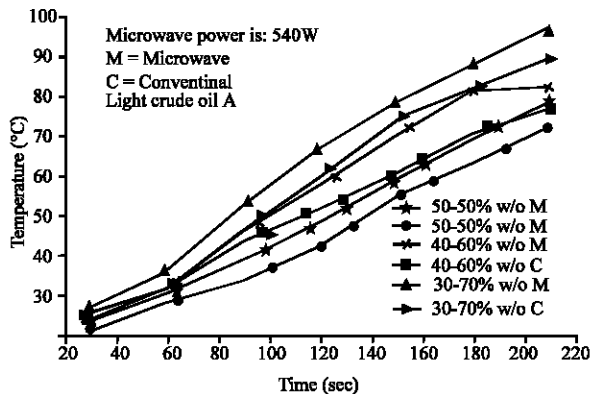


Fig. 4: Temperatures of 50-50%, 40-60% and 30-70% w/o (oil B) (Using microwave and conventional heating)

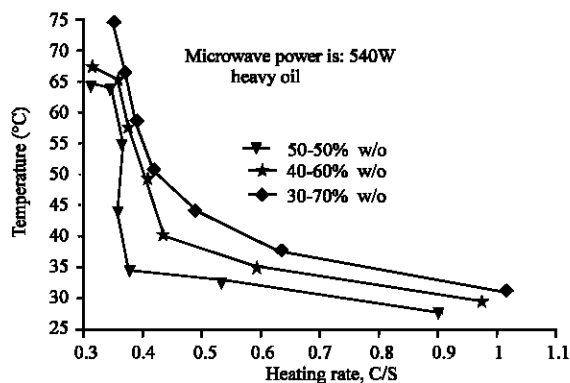


Fig. 5: Temperature vs. heating rate for oil A (microwave heating)

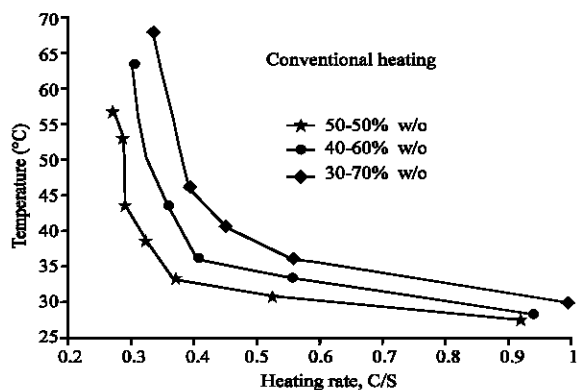


Fig. 6: Temperature vs. heating rate for oil A (conventional heating)

methods. The average heating rates of 50-50%, 40-60% and 30-70% water-oil emulsions for crude oil A obtained by microwave were 0.46, 0.50 and 0.52 respectively, while for conventional were 0.43, 0.46 and 0.48, respectively. For crude oil B, the rates were 0.52, 0.58 and 0.63 using microwave and 0.48, 0.53 and 0.59 for conventional heating. Fig. 5 shows a plot of temperature versus heating rate for oil A using microwave heating, while Fig. 6 showed the same data for conventional heating. It is obvious from the two figures the heating rates decreases at higher temperatures; this was expected to be the result because of decreasing dielectric loss of water and heat loss to the surrounding.

CONCLUSIONS

Based on results of this study, it can be concluded that, laboratory tests have been shown that microwave radiation can be an effective tool to separate emulsified water from oil mixtures. This new separation technology does not require chemical addition. Results also showed that, the temperature occurred by microwave always higher than that occurred by conventional heating (hotplate).

Microwave demulsification is based on heating. However, the comparisons between the microwave heating and the conventional heating show that they are different. Microwave has feature of penetrating power, it distributes energy within the bulk of most materials, rather than just on its surface. The microwave induced molecular rotations also play a role. Molecular rotations can reduce zeta potential which suspends water droplets and solid particles in an emulsion.

REFERENCES

Chih, C.C. and Y. C. Chan, 2002. Demulsification of W/O emulsions by microwave radiation. *Separation Sci. Technol.*, 37: 3407-3420.

Fang, C.S., P.M.C. Lai and B.K.L. Chang, 1989. Oil recovery and waste reduction by microwave radiation. *J. Environ. Progress*, 8: No.4.

Fang, C.S. and P.M.C. Lai., 1995. Microwave heating and separation of water-in-oil emulsions. *J. Microwave Power and Electromagnetic Energy*, 30: No.1.

Harris, J.R., 1996. *Hydrocarbon Process.* 75: 63-68.

Johansen, E.J., I.M. Skjarvo, T. Lund and J. Sjoblom., 1989. Water-in-crude oil emulsions from, the norwegian continental shelf, part I. Formation, characterization and stability correlation. *Colloids and surfaces*, 34: 353-370.

Kingston, H.M. and L.B. Jase, 1988. *Introduction to Microwave Sample Preparation. Theory and Practice.* American Chemical Society, Washington.

Klaila, W.J., 1983. Method and apparatus for controlling fluency of high viscosity hydrocarbon fluids. U.S. Patent, 4067.683.

Kruse, C.F., 1990. *Treating Oil field Emulsions.* 4th Edn., Petroleum extension Service and America Petroleum Institute, Austin, Texas.

Nordi, K.G., J. Sjoblom, J. Kizling and P. Stenius, 1991. Water-in-crude oil emulsions from the norwegian continental shelf, 4. Monolayer properties of the interfacially active crude oil fraction. *Colloids and surfaces*, 57: 83-98.

Osipow, L.I., 1977. *Surface Chemistry.* R.E. Krieger. Publisher Co. Melbourne, FL.

Sjoblom, J., L. Mingyuan, A.A. Christy and T. Gu, 1992. Water-in-crude oil emulsions from the norwegian continental shelf, 7. Interfacial pressure and emulsion stability. *Colloids and Surfaces*, 66: 55-62.

Thostenson, E.T. and T.W. Chou, 1999. *Microwave Processing: Fundamentals and Applications.* Elsevier Science Ltd.

Urdahl, O., T. Brekke and J. Sjoblom, 1992. ¹³C.n.m.r and multivariate statistical analysis of adsorbed surface-active crude oil fractions and the corresponding crude oils. *Fuel*, 71: 739-746.

Wolf, N.O., 1986. Use of Microwave radiation in separating emulsions and dispersions of hydrocarbons and water. U.S. Patent, 4582.629.