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Study on Demulsification of Water-in-Oil Emulsions Via Microwave Heating Technology

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Abstract: A batch microwave heating process of 2450 MHz was examined on crude oil emulsions. The mechanism of microwave heating is essentially that of dielectric heating. After exposing the emulsion to the microwave electromagnetic EM field, molecular rotation and ionic conduction due to the penetration of EM into the emulsion are responsible for the internal heating. In this study, microwave demulsification method was applied on a 50-50 and 20-80% water-in-oil emulsions with microwave exposure time varied from 20 to 180 sec Transient temperature profiles of water-in-oil emulsions inside a cylindrical container were measured. The temperature rise at a given location was almost horizontal (linear). The rate of temperature increase of emulsions decreased at higher temperature due to decreasing dielectric loss of water. Results of this work show that microwave radiation is a dielectric heating technique with the unique characteristic of fast, volumetric and selective heating is appropriate and has the potential to be used as an alternative way in the demulsification process. Microwave demulsification of water-in-oil emulsions does not require chemical additions.

Key words: Demulsification, batch process, microwave heating, w/o emulsion

INTRODUCTION

Electromagnetic radiation in the frequency range 300 MHz to 300 GHz are known as microwaves (Tanmay and Ayappa, 1997), microwave energy is a non-ionizing radiation that causes molecular motion by migration of ions and dipole rotations, but does not cause changes in molecular structure (Kingston and Tassie, 1988) and wavelengths ranging from a few cm to a few mm (Chatterjee *et al*., 1998). In the past 20 years, microwave (MW) energy has been widely applied in food and chemical processing for heating, thawing (melting), sintering of ceramics and many others (Ayappa *et al*., 1992; Basak and Ayappa, 1997; 2001). Faster cooking times and energy savings over conventional cooking methods are the primary benefits. Various oil-in-water (o/w) and water-in-oil (w/o) emulsions occur in industrial operations, such as petroleum refining, oil and gas production (Fang *et al*., 1995) and food processing industries, in this regards, efficient heating of emulsions is required for a faster processing based on industrial demand. Microwave heating, because of its volumetric heating effects, offers a faster processing rate. In conventional thermal processing, energy is transferred to the material through convection, conduction and radiation of heat from the surfaces of the material. In contrast, microwave energy is delivered directly to materials through molecular interaction with the electromagnetic field. In heat transfer, energy is transferred due to thermal gradients, but microwave heating is the transfer of electromagnetic energy to thermal energy and is energy conversion, rather than heat transfer (Thostenson and Chu, 1999). This difference in the way energy is delivered can result in many potential advantages to using microwaves for processing of materials. The transfer of energy does not rely on diffusion of heat from the surfaces and it is possible to achieve rapid and uniform heating of thick materials. In recent literature, many researchers reported non-thermal phenomena that have been broadly termed 'microwave effects'. Examples for microwave effect include enhanced reaction rates of thermosetting resins during microwave curing (Marand *et al*., 1992) and faster densification rates in ceramics sintering (Janney and Kimrey, 1991). As materials are processed, they often undergo physical and structural transformations that affect the dielectric properties. Thus, the ability of microwaves to generate heat varies during the process. Sharp transformations in the ability of microwaves to generate heat can cause difficulties with process modeling and control. Understanding the generation, propagation and interaction of microwaves with materials is critical. The

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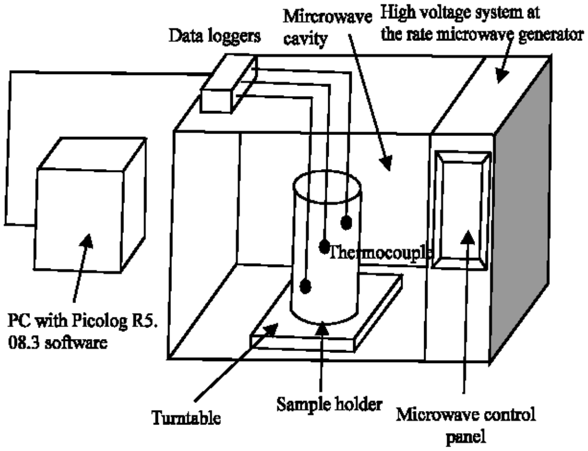

Fig. 1: Elba microwave oven

properties of the electromagnetic field, chemical composition of the material being processed, structural changes that occur during processing, size and shape of the object being heated and the physics of the microwave/materials interactions all complicate microwave processing. Therefore, in view of the above mentioned, the microwave heating technology was applied on water-in-oil emulsions with the following specific objectives: volume rate of heat generation, microwave power absorption at any location in the sample and temperature distribution in the sample.

MATERIALS AND METHODS

In this study, Elba domestic microwave oven model: EMO 808SS, its rated power output is 900 watts and its operation frequency is 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 Pico Log 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, two types of crude oil were collected namely, heavy oil and light crude oil. 50-50 and 20-80% water-in-oil emulsions were prepared using the same volumes of oil and water. Emulsions were prepared in 900 mL graduated beakers, with ranges by volume of the water and oil phase. The microwave radiation was set to its highest power setting. The water phase is tab water. The emulsions were agitated vigorously using a standard three blade propeller at speed of 1600 rpm and temperature 28°C for 7 min. The concentrations of water in samples were 20-50% by volume. The container of emulsion sample was placed in the center of Elba domestic microwave oven model: EMO 808SS. Three thermocouples were inserted in the 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 batch microwave heating at 2450 MHz were recorded by Pico-TC-08 data logging. The surfactant used in this study was the commercially available Triton X-100; this Triton X-100 is a non-ionic water soluble molecule. The emulsifying agent was 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) was 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:

$$(\text{\% of water separation, e}) = \frac{\begin{array}{c}(\text{Volumeof}\\ \text{water layer, mL})\end{array}}{\begin{array}{c}(\text{Original amount}\\ \text{of water, mL})\end{array}} * 100\% \qquad (1)$$

The prepared emulsion was used to check for w/o or o/w emulsions. All emulsions investigated were water-in-oil (w/o) emulsion (oil-continuous).

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:

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

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 (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.

Microwave power generation: Using microwaves as a source of heat in the processing (heating, melting, drying and thawing) of materials is one of the advantageous because it results in faster, more uniform heating than conventional heating does. This study, focus on generation of microwaves in the oven, temperature distribution, microwave power absorption as well as separation of emulsified water from crude oil. The variables affecting microwave power absorption by an element are dielectric constant and dielectric loss, location and microwave power incident at the load. For a sample in cylinder container, the local microwave power flux calculated as:

$$P_0 = \frac{453.2 + 59.8\ln(m)}{A} \tag{3}$$

Where, m is mass (g) of the sample, A is sample's container area. The microwave power absorption density at any location within the sample is one of the interesting terms, in this regards, the electric field attenuates (decay) exponentially in x and y directions within the sample due to dissipation as heat and can be expressed as Swami (1982).

$$P_z = P_0 e^{-2\alpha z} \tag{4}$$

Where, P_z is microwave power transmitted. The attenuation factor can be calculated from the electromagnetic field theory given by Von Hippel (1954) as:

$$\alpha_E = \frac{2\pi f}{c}\left[\frac{\varepsilon_r'}{2}\left(\sqrt{1+\tan^2\delta} - 1\right)\right]^{1/2} \tag{5}$$

The above equation will be used for calculation of the volume rate of heat generation by microwave radiation as:

$$q_{MWz} = \frac{2\alpha_E}{4.184} P_z \tag{6}$$

If the dielectric properties are assumed to be independent of temperature at Frequency 2450 MHz, the wavelength λ_m and penetration depth D_p within a sample for a radiation of the above frequency (2450 MHz) are related to dielectric constant ε′r and dielectric loss ε″r as follows:

$$\lambda_m = \frac{c}{f}\left[\frac{\varepsilon_r'\left(\sqrt{1+\left(\frac{\varepsilon_r'}{\varepsilon_r'}\right)^2} + 1\right)}{2}\right]^{-1/2} \tag{7}$$

and

$$D_p = \frac{c}{2\pi f}\left[\frac{\varepsilon_r'\left(\sqrt{1+\left(\frac{\varepsilon_r''}{\varepsilon_r'}\right)^2} - 1\right)}{2}\right]^{-1/2} \tag{8}$$

Since microwave heats materials volumetrically, it is possible to calculate the volume rate of microwave heat generation from energy balance equation as:

$$g_{MW} = \frac{hA}{V}\left(T_m - T_a\right) + \frac{\varepsilon A \sigma}{V}\left[\begin{array}{l}\left(T_m + 273.15\right)^4 \\ -\left(T_a + 273.15\right)^4\end{array}\right] + \rho C_p\left(\frac{dT}{dt}\right) \tag{9}$$

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 (Fang and Lai, 1995). The right hand side of Eq. 9 comprises of three terms, convective heat transfer, radiative heat due to microwave and conductive heat in the sample,

Table 1: Experimental results of microwave heating (water and crude oil)

Radiation time (sec)	Temp. increase ΔT, C $t_o = 25.6$C	Rate of temp. increase, dT/dt, C/s	Volume rate of heat generation q_{MW}, cal/s cm^3
Water			
20	8.4	0.420	0.419
40	14.0	0.350	0.349
60	18.4	0.307	0.306
80	22.9	0.286	0.285
100	26.5	0.265	0.264
120	30.0	0.250	0.250
140	33.7	0.241	0.241
160	39.1	0.244	0.244
180	44.2	0.246	0.246
Oil			
20	6.8	0.340	0.138
40	10.5	0.263	0.107
60	15.1	0.252	0.102
80	20.2	0.253	0.103
100	24.8	0.248	0.101
120	28.7	0.239	0.097
140	33.0	0.236	0.096
160	36.5	0.228	0.093
180	42.2	0.234	0.095

Table 2: Experimental results of microwave heating for emulsions

Radiation time (sec)	Temp. increase ΔT, C $t_o = 25.6$C	Rate of temp. increase, dT/dt, C/s	Volume rate of heat generation q_{MW}, cal/s cm^3
50-50% w/o			
20	11.1	0.555	0.321
40	14.8	0.370	0.214
60	23.8	0.397	0.229
80	26.6	0.333	0.192
100	34.5	0.345	0.199
120	37.1	0.309	0.179
140	40.2	0.287	0.166
160	46.7	0.292	0.169
180	49.1	0.273	0.158
20-80% w/o			
20	15.9	0.795	0.460
40	19.5	0.488	0.282
60	29.8	0.497	0.287
80	33.2	0.415	0.240
100	41.1	0.411	0.238
120	43.6	0.363	0.210
140	46.2	0.330	0.191
160	51.4	0.321	0.186
180	55.7	0.309	0.179

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. 9, the density (ρ) and (C_p) of the emulsions calculated from mixing rules as:

$$\rho_m = \rho_w \phi + \rho_o (1-\phi) \qquad (10)$$

$$C_{pm} = C_{p,w} \phi + C_{p,o} (1-\phi) \qquad (11)$$

The volume rate of microwave heat generation of the water and crude oil calculated from temperature measurements and Eq. 9 are shown in Table 1 while heat generation values for emulsion samples shown in Table 2.

RESULTS AND DISCUSSION

In this study, a batch microwave heating technology was successfully applied and examined on water, oil and emulsion samples. For temperature distributions, a three temperature readings were placed at the top, middle and bottom of the cylindrical sample container. Figure 2 and 3 depict temperature distribution of 50-50 and 20-80% water-in-oil emulsions respectively, for microwave irradiation time varies from 20, 40, 60, 80, 100, 120, 140, 160 and 180 sec. Figure 2 and 3 show the motion and distribution of temperature of water-in-oil emulsions in horizontal direction were slow and emulsions were heated uniformly through the microwaves. This was expected result since the sample container was covered with aluminum foil at the top and bottom and microwaves enter only on the side surface of samples. Also these results shown the temperature rise at a given location was linear, this may attribute due to the small dielectric loss of oil. The same findings were reported by Fang *et al.* (1995).

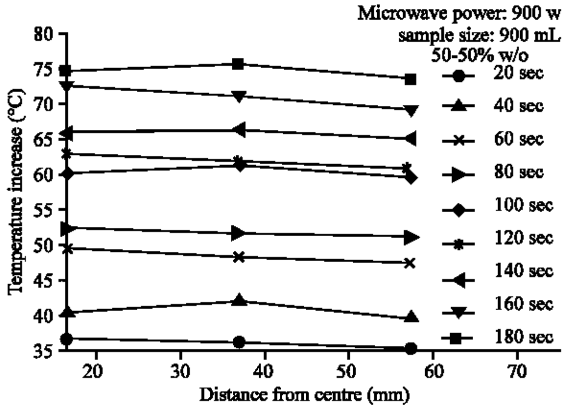

Fig. 2: Temperature distributions of 50-50% w/o emulsions

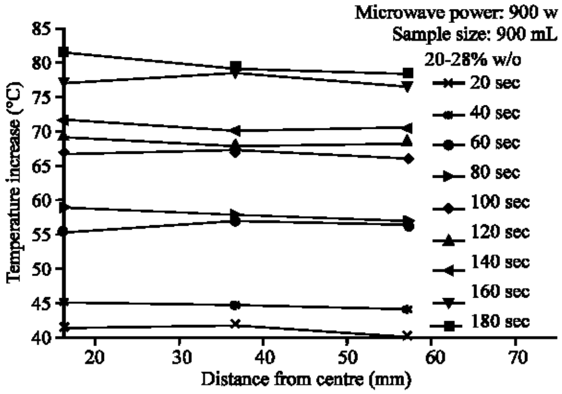

Fig. 3: Temperature distributions of 20-80% w/o emulsions

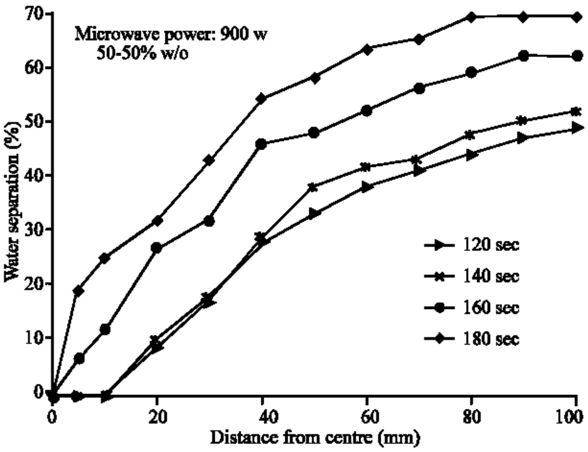

Fig. 4: Separation of water from 50-50% w/o emulsions

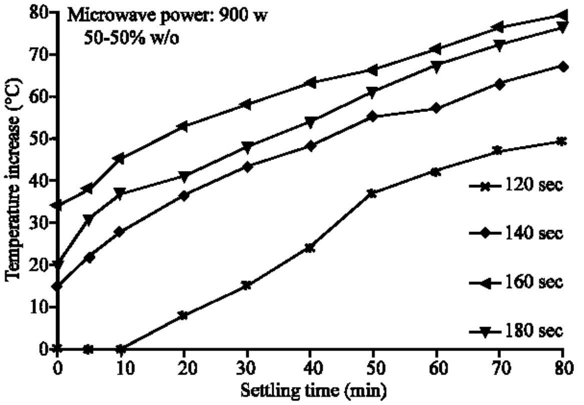

Fig. 5: Separation of water from 20-80% w/o emulsions

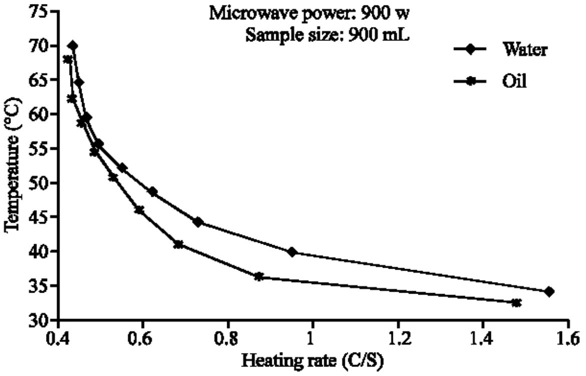

Fig. 6: Rates of temperature increase for water and oil

Table 3: Volume rates of heat generation of water and crude oil by microwave radiation

Radiation time (sec)	Temp. increase ΔT, C $t_o = 25.6C$	Rate of temp. increase, dT/dt, C/s	Volume rate of heat generation q_{MW}, cal/s cm^3	
			Experimental values	Calculated values
Water				
20	8.40	0.420	0.419	0.411
40	14.00	0.350	0.349	0.320
60	18.40	0.307	0.306	0.273
80	22.90	0.286	0.285	0.230
100	26.50	0.265	0.264	0.226
120	30.00	0.250	0.250	0.214
140	33.70	0.241	0.241	0.212
160	39.10	0.244	0.244	0.231
180	44.20	0.246	0.246	0.196
Oil				
20	6.80	0.340	0.138	0.146
40	10.50	0.263	0.107	0.114
60	15.10	0.252	0.102	0.132
80	20.20	0.253	0.103	0.143
100	24.80	0.248	0.101	0.140
120	28.70	0.239	0.097	0.161
140	33.00	0.236	0.096	0.158
160	36.50	0.228	0.093	0.144
180	43.20	0.240	0.097	0.127

Table 4: Volume rates of heat generation of emulsions by microwave radiation

Radiation time (sec)	Temp. increase ΔT, C $t_o = 25.6C$	Rate of temp. increase, dT/dt, C/s	Volume rate of heat generation q_{MW}, cal/s cm^3	
			Experimental values	Calculated values
50-50% w/o				
20	11.1	0.555	0.231	0.224
40	14.8	0.370	0.214	0.136
60	23.8	0.397	0.229	0.216
80	26.6	0.333	0.192	0.158
100	34.5	0.345	0.199	0.165
120	37.1	0.309	0.179	0.162
140	40.2	0.287	0.166	0.159
160	46.7	0.292	0.169	0.161
180	49.1	0.273	0.158	0.148
20-80% w/o				
20	15.9	0.795	0.460	0.363
40	19.5	0.488	0.282	0.223
60	29.8	0.497	0.287	0.252
80	33.2	0.415	0.240	0.231
100	41.1	0.411	0.238	0.224
120	43.6	0.363	0.210	0.198
140	46.2	0.330	0.191	0.167
160	51.4	0.321	0.186	0.142
180	55.7	0.309	0.179	0.137

The temperature increase rates of irradiated samples and their volume rates of heat generation were shown in Table 1 and 2 respectively. These samples comprise water, crude oil, 50-50 and 20-80% water-in-oil emulsions. The temperatures of emulsions were obtained from the average values of three location temperature readings. The rate of temperature increase was calculated from temperature increase divided by radiation time. The average rates of temperature increase of 50-50 and 20-80% water-in-oil emulsions are 0.351 and 0.437 C/sec, respectively. It observed that, the rates of temperature were decreases at temperature increases; this was the expected results since the dielectric loss of water is small.

The energy balance Eq. 9 was used to calculate the volume rates of heat generation; this Equation included three terms, convective heat transfer, irradiative heat

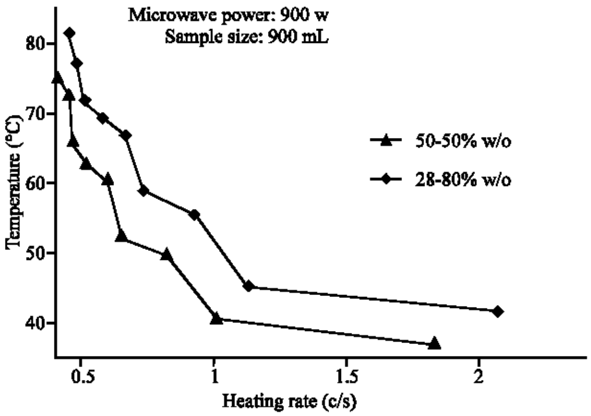

Fig. 7: Rates of temperature increase for 50-50 and 20-80% w/o

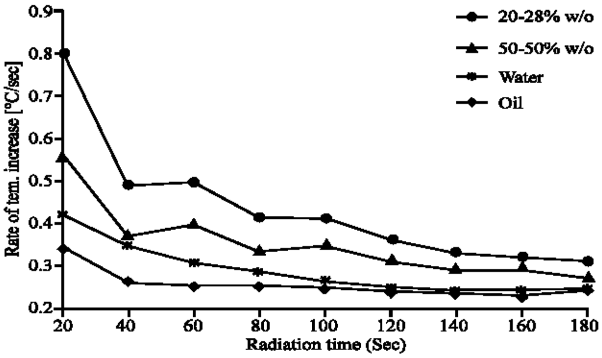

Fig. 8: Rate of temperature increase vs. radiation time for water, oil and emulsions

transfer due to microwave and conduction heat transfer respectively. From calculations of this study, the contributions of convective and irradiation terms are very small. Since the sample container is a glass cylinder (transparent to microwave and has very low dielectric constant), its heat loss assumed to be zero. The volume rates of microwave heat generation of water and crude oil calculated from the temperature measurements and Eq. 9 are shown in Table 1, while for 50-50 and 20-80% water-in-oil emulsions are shown in Table 2. In application of Eq. 9 for determination of volume rates of heat generation, the emulsion density (ρ_m) and heat capacity ($C_{p,m}$) calculated from Eq. 10 and 11, respectively. The calculated volume rates of heat generation of water and oil from Eq. 3 through Eq. 11 were shown in Table 3. While for emulsions were shown in Table 4. It observed that, for water and emulsions, the experimental results greater than the calculated, while for oil the reverse, the calculated results greater than the experimental, this attributed due to shortage of oil properties and used literature values.

Since the purpose of heating water-in-oil emulsions with microwave is to separate water from oil, therefore, the separation efficiency of 50-50 and 20-80% water-in-oil emulsions calculated by using Eq. 1 were shown in Fig. 4 and 5, respectively. The same trend was reported by Fang *et al.* (1988), Fang *et al.* (1989) and Chan *et al.* (2002).

All experimental results showed that microwave radiation is very effective in separation of water-in-oil emulsions. Figure 4 and 5 shows that, microwave radiation can raise the temperature of emulsion, reduce the viscosity and accelerate separation process as suggested by Eq. 2. The rates of temperature increase were decrease at higher temperatures, Fig. 6 shows the phenomenon for water and oil, while Fig. 7 shown the same phenomenon for 50-50 and 20-80% water-in-oil emulsions, respectively.

The wavelength (λ_m) and penetration depth (D_p) were found 1.39 and 3.427 cm respectively. Figure 8 shows the heating rate of temperature increase for water, oil and emulsions versus the radiation time.

CONCLUSIONS

The batch 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.

Notation:

V_w : Settling velocity of water droplet (cm/sec)
ρ_w : Density of dispersed phase (g/cm^3)
ρ_0 : Density of continuous phase (g/cm^3)
g : Gravity
D : Droplet diameter (cm)
p_0 : Microwave surface power (W)
A : Sample container area (cm^2)
m : Mass of sample (g)
p_z : Microwave power transmitted (W)
α_E : Electromagnetic attenuation factor (cm^{-1})
f : Frequency of incident microwaves
δ : Loss tangent
q_{MW} : Volume rate of heat generation (W/cm^3)

λ_m : Wavelength (cm)
D_m : Penetration depth (cm)
$\varepsilon''r$: Dielectric loss
$\varepsilon'r$: Dielectric constant
c : Speed of light (cm/sec)
h : Convective heat transfer coefficient (cal/s cm^2 °C)
v : Volume of water separated (cm^3)
T_m : Temperature of emulsion (mixture) °C
T_a : Temperature of ambient °C
σ : Stefan-Boltzmann constant
ϕ : Volume fraction of emulsified water
ε : Emissivity of surface
cp_{m0} : Heat capacity of emulsion (mixture) (cal/g°C)
ρ_m : Density of emulsion (mixture) (g/cm^3)

REFERENCES

Ayappa, K.G., H.T. Davis, E.A. Davis and J. Gordan, 1992. Two dimensional finite element analysis of microwave heating. AIChE J., 50: 2659-2662.

Basak, T. and K.G. Ayappa, 1997. Analysis of microwave thawing of slabs with effective heat capacity method. AIChE J., 43: 1662.

Basak, T. and K.G. Ayappa, 2001. Influence of internal convection during microwave thawing of cylinders. AIChE J., 47: 835.

Chan, C.S. and Y.C. Chan, 2002. Demulsification of w/o emulsions by microwave radiation. Technology, 37: 3408-3409.

Chatterjee, A., T. Basak and K.G. Ayappa, 1998. Analysis of microwave sintering of ceramics. AIChE J., 44: 2302.

Fang, C.S., B.K.L. Chang and P.M.C. Lai, 1988. Microwave demulsification. Chem. Eng. Comm., 73: 227-233.

Fang, C.S., B.K.L. Chang and P.M.C. Lai, 1989. Oil recovery and waste reduction by microwave radiation. Environmental Progress, 8: 235-238.

Fang, C.S. and C. Lai, 1995. Microwave heating and separation of water-in-oil emulsions. J. Microwave Power and Electromagnetic Energy, 30: 46-57.

Janney, M.A. and H.D. Kimrey, 1991. Diffusion-contrlled Processes in Microwave-Fired Oxide Ceramics. In: Snyder Jr. W.B., W.H. Sutton, M.F. Iskander, D.L. Johnson (Eds.). Microwave Processing of Materials II, Materials Research Society Proceedings, 189 Pittsburgh: Materials Res. Soc., pp: 215-227.

Kingston, H.M. and L.B. Tassie, 1988. Introduction to Microwave Sample Preparation: Theory and Practice. American Chemical Scociety, Washington.

Marand, M., H.R. Baker and J.D. Graybeal, 1992. Comparison of reaction mechanisms of epoxy resins undergoing thermal and microwave cure from *in situ* measurements of microwave dielectric properties and infrared spectroscopy. Macromolecules, 25: 2243-2252.

Swami, S., 1982. Microwave heating characteristic of simulated high moisture foof. MS Thesis, University of Massachusetts, Amherst, MA, USA.

Tanmay, B. and K.G. Ayappa, 1997. Analysis of microwave thawing of slabs with effective heat capacity method. AIChE J., 43: 1662-1666.

Thostenson, E.T. and T.W. Chu, 1999. Microwave Processing: Fundamentals and Applications. Elsevier Science Ltd. Part A 30, pp: 1055.

Von Hippel, A.R., 1954. Dielectric Materials and Applications. MIT Press, Cambridge. MA.

Young, H.K., A.D. Nikolov, D.T Wasan and C.S. Shetty, 1996. Demulsification of water-In-crude oil emulsions: Effect of film tension, elasticity, diffusion and interfacial activity of demulsifier. Individual components and thin blends. Mercel Dekker, Inc., 17: 33-34.