

[ED08] Microwave assisted demulsification of water-in-crude oil emulsions

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Introduction

Emulsions are of considerable practical significance both in processing industry and in the consumer sector. In the petroleum industry emulsions phenomena are particularly aware because it can lead to upstream and downstream production upset. A recent report stated that about 80% of exploited crude oil exists in an emulsion state, all over the world (Xia *et al.*, 2004). Emulsions are distribution or dispersion of one liquid, in the form of droplets, in another substantially immiscible liquid (Schramm, 1992). The liquid which exists as discrete particles is known as the internal or dispersed phase, the other liquid is known as the dispersing medium or external or continuous phase. Emulsification process allows these two immiscible components to be compounded into a single macrophase mixture together with an emulsifying agent. There are two basic types of emulsion in the petroleum industry, the oil-in water (o/w) type and the water-in-oil (w/o) type. The most common type of emulsion encountered in petroleum production is the later type. Naturally occurring surfactants in crude oils have been identified as largely responsible for the stability of these emulsions. The surfactants that exist naturally, such as asphaltenes and resins, apparently promote the stability of the emulsions by forming highly viscous or rigid films at the oil-water interface. The stability of emulsions is dependent on the capability of the emulsions to break-up into two phases. The stable emulsion required more time to complete the separation. It may take a few weeks, months or years.

Demulsification of stable w/o emulsions is necessary to speed up the break-up of phase separation of water and oil. A lot of techniques and methods have been used to resolve the emulsion phenomenon. Some of the approach includes mechanical, chemical, thermal and electrical that is generally used or applied world wide in the petroleum industry. The concept of microwave demulsification was

first introduced by Klaika, (1978) and Wolf, (1986) in their patent applications. Klaika conducted several other field tests after his patent was authorized and the results were encouraging. Later Fang *et al.*, (1988) presented a demulsification model for 1:1 and 3:7 water-in-oil systems under microwave radiation. The experiment results showed that the percentage of water separated from the emulsions was higher than 80% under certain conditions.

In microwave irradiation, energy is supplied by an electromagnetic field directly to the material (Thostenson and Chou, 1999). This results in rapid heating throughout the material thickness with reduced thermal gradients. The microwave energy is volumetric heating, which can reduce processing time and save energy. When microwave is supplied, it attacks the polar molecules which are in this case molecules of water. Therefore, molecules get energy and vibration occur (Johnk, 1975). The vibration will lower the interfacial tension or film around water molecules in the emulsions. This will result in film rupture and increase the degree of water molecules coalescence. The break-down of emulsions is a three step process. In the first step called flocculation, the dispersed droplets of internal phase flocculate into some large group but drops still exist without coalescence. In the next step called coalescence, the drops in group coalesce into a large drop with the result of the decrease of drop numbers. In the sink step, large internal drops sink by gravity to the interface between oil and water and coagulate into water phase resulting in the break-down of emulsion.

Materials and methods

Sample preparation

Crude oil from Middle East was used as oil phase. Distilled water mixed with 10g/ L of salt was prepared as brine. Low Sulfur Wax Residue (LSWR) was used as emulsifying

agent. Water base demulsifying agent was used as chemical solution for chemical demulsification and lastly, domestic microwave oven with frequency of 2450 Mhz and 900 watt was used as the microwave heating chamber.

Two models of simulated w/o emulsions were prepared, one consists of 50% brine and 50% crude oil, and the latter consists of 20% brine and 80% crude oil. Both of the samples were homogenized using handheld homogenizer at a speed of 2400 rpm for 3 minutes. 1% of LSWR was added to each emulsion as emulsifier. The stability of both emulsions was observed and recorded for duration of 2 days. Some physicochemical analyses were done in order to study the behavior of the emulsions.

Chemical Demulsification

In chemical demulsification, a specified amount of water based demulsifying agents was added into the emulsion. The mixed sample of emulsions and demulsifying agent was agitated for about 1 minute to ensure the sample was completely homogenized. For each sample prepared, the concentration of demulsifying agent added was varied in the range of 1000, 1500, 2000 and 2500 ppm. The samples were then put into the test tube and observed for separation process.

Microwave Demulsification

The prepared sample was placed in the microwave and irradiated for period of 5, 10, 15 and 20 seconds, respectively. The experiment was repeated with the combination of microwave and water based demulsifying agent with concentration of 2500 ppm.

Results and Discussion

Stability test study

From the experiment, it was found that no separation occurred for both emulsions (50:50 and 20:80 ratios) that were prepared from mixture of brine, crude oil and 1% LSWR. Hence, it can be concluded that the samples form very stable emulsions. Preliminary experiment showed that without the addition of LSWR, the emulsion formed was not stable (phase separation occurred within two days). In this case LSWR plays the important role as surfactants in the emulsions, beside the naturally asphaltene present in the crude oil.

The surfactant is adsorbed onto the oil-water interface, and forms viscoelastic films. The high stability of the water in oil emulsions is due to their low compressibility values for such films, since coalescence requires compression of the interface (Xia *et al.*, 2004). From Table 1 it can be seen that the interfacial tension of emulsions is been lowered by the addition of LSWR. These contribute to the high stability of emulsions as discussed.

TABLE 1 Physical properties of emulsions

Emulsions type	Surface Tension (m/Nm)	Interfacial Tension (dyne/cm)	Dynamic Viscosity (cp)
50/50 Emulsions w/out LSWR	28	54	26.4
50/50 emulsions with 1% LSWR	30	33	36.2
20/80 emulsions w/out LSWR	24	48	15
20/80 emulsions with 1% LSWR	26	30	13.5

Effect of chemical demulsifiers

The effects of chemical demulsifiers on demulsification of emulsions are shown in Figure 1 and Figure 2.

From Figure 1, generally it shows that by increasing the concentration of demulsifier, the percentage of water separated was also increased. In the first 200 minutes, the separation occurred rapidly until at one stage it remained constant and no significant changes were observed. From Figure 2, it shows that separation only occurred with concentration of 2500 ppm of demulsifier. Concentration of demulsifying agent lower than 2500 ppm showed no feasible separation. The use of chemicals demulsifier aims to create a low interfacial film elasticity, higher film diffusivity and low dynamic film tension in order to improve the coalescence of the droplets (Kim *et al.*, 1996). The water based demulsifier consists of hydrophilic and hydrophobic tail. The hydrophilic tail is attracted to the water molecules, whereas the hydrophobic otherwise. When the demulsifier is mixed with the emulsions, the hydrophilic

tail attacks water molecules, neutralizes the surfactant encapsulated water molecules and resulting in increasing the interfacial tension of emulsions. The films can easily rupture and enhance the coalescence of water droplets.

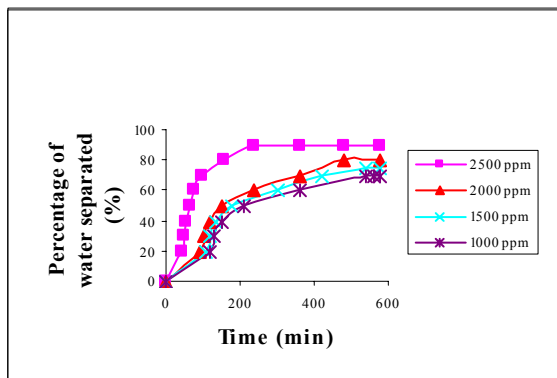


FIGURE 1 Effects of different concentration of water based demulsifier on 50/50 water in crude oil emulsions

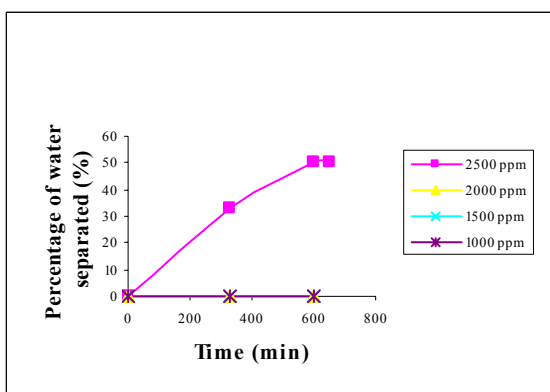


FIGURE 2 Effect of different concentration of water based demulsifier on 20/80 water in crude oil emulsions

Effect of microwave radiation

The effect of microwave radiation was studied with and without the addition of demulsifying agent. When the simulated emulsion was irradiated with the microwave energy without adding any demulsifying agent, it shows no separation occurs within 2 days of gravity setting. The maximum exposure time used was 20 seconds. Hence, the combination technique involving microwave radiation and chemical demulsifier was then examined. The results of this study are shown in Figure 3 and Figure 4.

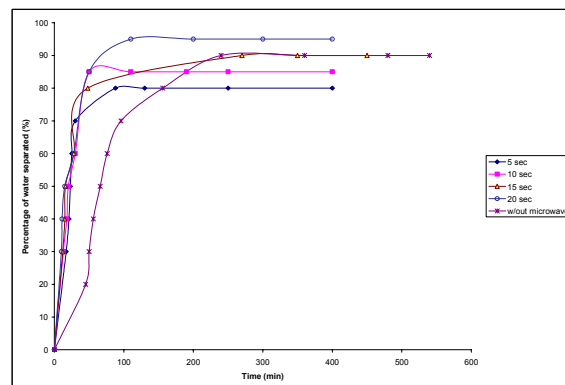


FIGURE 3 Effect of different exposure time of microwave radiation on the 50/50 water in crude oil emulsions with 2500 ppm water based demulsifier.

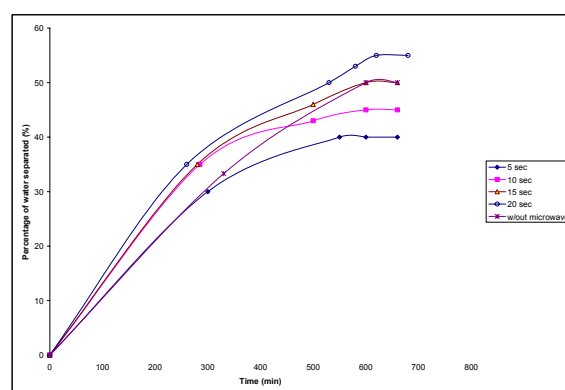


FIGURE 4 Effect of different exposure time of microwave radiation on the 20/80 water in crude oil emulsions with 2500 ppm water based demulsifier.

Figure 3 shows that microwave irradiation has a tremendous effect in accelerating the separation process of 50/50 water in crude oil emulsions. Generally, the initial rate of separation was increased by 2 folds when the mixture was subjected to microwave irradiation, irrespective of the exposure time. It was also observed that the microwave exposure shortened the time to reach equilibrium separation. The degree of equilibrium separation increased with increasing exposure time. In comparison to the un-irradiated sample, lower equilibrium water separation was achieved when the exposure time was less than 15 seconds. An increase of 7% in the percentage of equilibrium water separation was observed at exposure time of 20 seconds. Similar trend but with lower degree of microwave impactation was observed in Figure 4, for the 20/80 water in crude oil emulsions.

In the course of microwave application, the microwave energy will interact with polar

molecules, in this case, water molecules. When microwave is applied to the molecules, the dipoles try to follow the field by both directionally orienting with the field as well as moving in the direction of the applied field. Because the field changes from millions to many billions of times per second, the dipolar is wrenched back and forth with the electric field oscillations. The swinging motion of the dipoles tends to move the rest of the molecules. This induces motion and accumulates stress, which lead to disruption in the close association of the water molecules, weakening or destroying their ability to preserve the water-oil interface. The microwave also transfers the electromagnetic energy to thermal energy inside the water molecules and causes a temperature gradient across the water-oil interfacial and subsequent reduction in the stability of the films that separate the water droplets (Fang and Lai, 1995). Thus, the rate of separation was increased.

The duration of microwave exposure determined the amount of energy absorbed by the water droplets in the emulsion. This, in turn, influenced the degree of temperature increased of the emulsion. The increased in temperature reduced the viscosity of the emulsion. The large water droplets were readily settled downward to the water layer, while the small droplets would coalesce to form large droplets and settled.

From the results, it can be concluded that the microwave exposure time of less than 15 seconds is not sufficient for large crops of small droplets to coalesce and settle. The settling of large droplets, on the other hand, reduced the amount of water droplets in the emulsion, whence, encouraged the dispersion of small droplets in the emulsion. This phenomenon triggered the end of the phase separation, which is reflected by the fast accomplishment of the equilibrium water separation.

Conclusion

From the study that was carried out, it can be concluded that the integrated method between microwave and chemical demulsifier shows a potential technique in accelerating the separation of stable water in crude oil emulsions. The degree of improvement was dependent on the microwave exposure time,

the concentration of the demulsifying agent, and the water:oil ratio of the emulsion.

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References

- Fang, C.S., Chang, B.K.L., Lai, P.M.C. and Klaila, W.J. (1988). Microwave Demulsification. *Chem. Eng. Comm.* Vol. 73: 227-239.
- Fang, C.S. and Lai, P.M.C. (1995). Microwave Heating and Separation of Water-in-Oil Emulsions. *Journal of Microwave Power and Electromagnetic Energy.* 30. 1: 46-57
- Johnk, C.T. (1975). Engineering Electromagnetics Fields and Waves. 3rd ed. New York: John Wiley.
- Kim, Y.H., Nilkolov, A.D., Wasan, D.T., Diaz-Arauzo, H. and Shetty, C.S. (1996). Demulsification of Water-in-Crude Oil Emulsions: Effects of Film Tension, Elasticity, Diffusivity and Interfacial Activity of Demulsifier Individual Components and Their Blends. *Dispersion Science and Technology.* 17(1): 33-53.
- Klaika, W.J. (1978). U.S. Patent 4,067,683
- Schramm, L.L. (1992). Emulsions Fundamentals and Applications in the Petroleum Industry. American Chemical Society. Washington, DC.
- Thostenson, E.T. and Chou, T.W. (1999). Microwave Processing: Fundamentals and Applications. *Composites Part A.* 30: 1055-1071.
- Wolf, N.O. (1986). U.S. Patent 4,582,629
- Xia, L., Lu, S. and Cao, G. (2004). Stability and Demulsification of Emulsions Stabilized by Asphaltene or Resins. *Journal of Colloid and Interface Science.* 271: 504-506.