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# Study on Demulsification of Crude Oil Emulsions by Microwave Chemical Method

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**Abstract:** The demulsifying and separating experiments of crude oil emulsion were performed by using the heating method, the thermal chemical method, the microwave radiating method, and the microwave chemical method separately. The water content of this emulsion was 78 v/v%, and the type was water-in-oil (w/o). The influence tendencies of the key factors on demulsification effect were explored by changing the heating temperature, the demulsifier amount used and the microwave radiating time in this paper. With the microwave chemical experiments on the self-made emulsions of different water content, the demulsification rate and separation efficiency were explored. The type of these emulsions were oil-in-water (o/w), water-in-oil (w/o) and the multiple type, related to the water content scopes which were less than 30 v/v%, more than 70 v/v% and between them, respectively. The separation effect by the microwave chemical method for the high water content crude oil emulsion was better than that of emulsion with lower water content. For the crude oil used in this experiment, the result could be obtained that the separation efficiency was about 95 v/v% under the conditions of 50 ppm of demulsifier, 10 seconds radiation time, and 1 minute settling time for the microwave chemical method.

**Keywords:** Oil-water emulsion, demulsification, thermal chemical method, microwave chemical method

## INTRODUCTION

A lot of water is poured into oil wells to enhance the extracting efficiency in many oil fields. The oil and water, together with some surfactants which might

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be added in or natural, can form a stabilized emulsion (1–3). The crude oil containing water is harmful to the transportation, refinery, and quality of the products so that demulsification is one of the key steps in various sectors of the oil industry, including crude oil transportation, petroleum refinery, as well as oil production. Demulsification is a process of the oil and water separation from emulsions.

Two principal approaches of demulsification are chemical and physical methods. The chemical method is the addition of a proper demulsifier to the emulsion and typical physical treatment techniques include heating, electrical, ultrasonic, or a mechanical method such as centrifugation. The heating along with the addition of the demulsifier (thermal chemical method) and electrical techniques are most popular methods, but they have many disadvantages: power-wasting, a large addition of the demulsifier, bad water quality, and environmental pollution. Microwave has drawn much more attention as a clean and efficient energy in recent years. Many papers (4–9) have reported the advantages of this new technology after it was first tested by Klaila and Wolf (10, 11). However, the reports about the practical application of microwave demulsification are very limited up to now.

Microwave is an electromagnetic wave which has a frequency range from 300 MHz to 300 GHz. When an oil-water emulsion is treated with microwave radiation, two kinds of effects take place simultaneously (12–14). The principal effect is the heating effect, which can increase the temperature of the emulsions and consequently lead to reduction of viscosity and coalescence.

If oil is the continuous phase, the settling velocity of water droplets through oil can be given by Stoke's law as follows:

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

Where

$v_w$ is the velocity of water droplets, $\mathrm{m \cdot s^{-1}}$;
$\rho_w$, $\rho_o$ represent the density of water and oil respectively, $\mathrm{kg \cdot m^{-3}}$;
$D$ is the diameter of water droplets, m;
$g$ is the local gravity acceleration, $9.8\ \mathrm{m \cdot s^{-2}}$
$\mu_o$ is the viscosity of oil, $\mathrm{Pa \cdot s}$.

While water is the continuous phase, the rising velocity of oil droplets through water can be given by a similar equation. As temperature increases, the viscosity $\mu_{\mathrm{o}}$ which is very sensitive to temperature decreases much faster than the density difference $(\rho_w - \rho_O)$ does. So the heating can increase the separation velocity of the emulsions.

The heating mode by microwave is much different from the conventional thermal heating as the former relies on the molecular interaction with the electromagnetic field, rather than the convection, conduction, and radiation of heat from the surface of the materials. As a result, heat can be generated throughout the material, and consequently make the thick materials heated rapidly and uniformly. In addition to this heating, microwave can be utilized for the selective heating of materials because it is much easier to be applied to the higher loss materials. On the other hand, in w/o emulsions the inner phase is water, which can absorb more energy than oil and expand under microwave radiation, consequently press the interfacial film to be thinner.

According to the conclusions of Klaila (10), Wolf (11) and Fang et al. (4), molecular rotations that were induced by microwave radiation could destroy the electric double layers at the interface between oil and water molecules, followed by the reduction of the zeta potential which suspends water droplets in an emulsion. Without the support of zeta potential, water (oil) molecules can move up and down freely, and enable the droplets to collide with each other and cause the coalescence. This function is considered to play a role in addition to the primary heating effect in the acceleration of microwave demulsification. Fu and Wu (15) measured the Zeta potential of the oil droplets in water in their study. But according to the conclusion of Tsuneki Ichikawa (16–18), the high frequency microwave may not change the zeta potential, for lack of enough time for the absorbed ions to rearrange under microwave radiation. So the demulsification mechanism of microwave radiation is not quite clear now.

However the quality of oil which has been separated from emulsions only by microwave radiation is hard to meet the requirement of transportation or refining, because its water content is not low enough. This may be the first problem which obstructs the practical application of this new technology in China. In this study, crude oil emulsions and preparations of different water content were separated with the combined use of a demulsifier and microwave radiation (microwave chemical method). Based on the experiments, influencing factors on the separation efficiency and the applicability of microwave radiation were explored, and a proper technical process which could further reduce the water content of oil was proposed.



## EXPERIMENTAL

### Sample Preparation

The crude oil emulsions and demulsifier used in experiments were obtained from Dagang oil field (China), and these emulsions included two kinds: 1# (which had high water content) and 2# (which scarcely had any water). The demulsifier is a kind of block polyether. The thermal chemical treatment and microwave chemical method were adopted to study the demulsifications on the crude oil emulsions, 1#. The microwave chemical demulsification were explored on the self-made emulsions with the following water content: 10, 30, 50, 60, 70, and 90% by volume. For all the self-made emulsions the preparation procedure was the same: the volume of crude oil emulsions, 2#, and water, which were measured with the pipette, were mixed in a 300 mL graduated beaker and agitated vigorously with a stirring paddle at a very high speed for exactly 60 minutes. The concentration of all samples had been labelled with % for (v/v) percentage. These self-made emulsions were demulsified by the microwave chemical method, and before that, the types of the emulsions were measured. For all experiments, the procedures were repeated three times and the results were a mean value.

### Procedures of Demulsification Experiments

The demulsification experiments by the thermal chemical treatment were performed with a water-bath, at seven chosen temperatures(25°C∼85°C, and the temperature step was 10°C). The demulsifiers (0∼600 ppm, and the increment was 25 ppm) were added into the emulsions at each chosen temperature. Then the oil and water layers were observed. The volume of water depositing to the bottom could be read from the scale on the special graduated cylinder every 1 minute. While demulsified with microwave chemical method, each sample (10 mL) was placed in the same position in the microwave oven (700W, 2450 MHz) for irradiation for some seconds, and followed by the gravity separation (without the radiation of microwave). During the time of gravity separation, the volume of water depositing to the bottom was read in the same way mentioned above.

The separation efficiency ($S$) can be calculated from the following equation:

$$S, \% = \frac{\text{Vs, mL}}{\text{Vo, mL}} \times 100\% \tag{2}$$

Where

S is the separation efficiency, %;
Vs represents the volume of separated water, mL;
Vo represents the original volume of water, mL.

## RESULTS AND DISCUSSION

### Quality of Water-Oil Emulsions

No water was separated from the crude oil emulsion samples within three days (simple sedimentation) at room-temperature. The results indicate that the samples explored in the experiments are very stable. The water content of the crude oil emulsions, 1#, was 78%, measured by the distillation technology (19).

The type of water-oil emulsion is mainly influenced by water content. However, the maximum packing percent is also related to the size distribution of the droplets. In this paper the emulsion types of samples are explored by the dilution method. The type of the emulsion, 1#, was water-in-oil (w/o). For the self-made emulsion samples, the types included: o/w, w/o and the multiple type, related to the water content scopes which were less than 30%, more than 70% and between them, respectively.

## Demulsification Experiments on the Crude Oil Emulsion, 1#

Figure 1 shows the effects of microwave radiation time on demulsification (without demulsifier). The microwave radiation is effective in elevating the separation efficiency and speeding up the separation of water from water-oil emulsions. The separation efficiency and velocity can be enhanced with the increase of the microwave radiation time. The optimal separation efficiency was about 69.2%under the conditions of 12 seconds of the microwave radiation time, and 9 minutes of the sedimentation time.

Figures 2 and 3 give the composite effects of microwave radiation time and addition of the demulsifier on demulsification. The results indicate that increasing microwave radiation time and joining a suitable demulsifier are

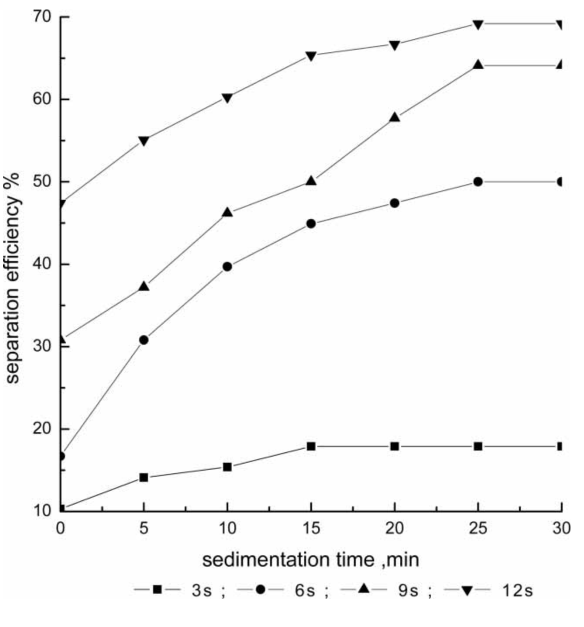


*Figure 1.* Effect of microwave radiation time.

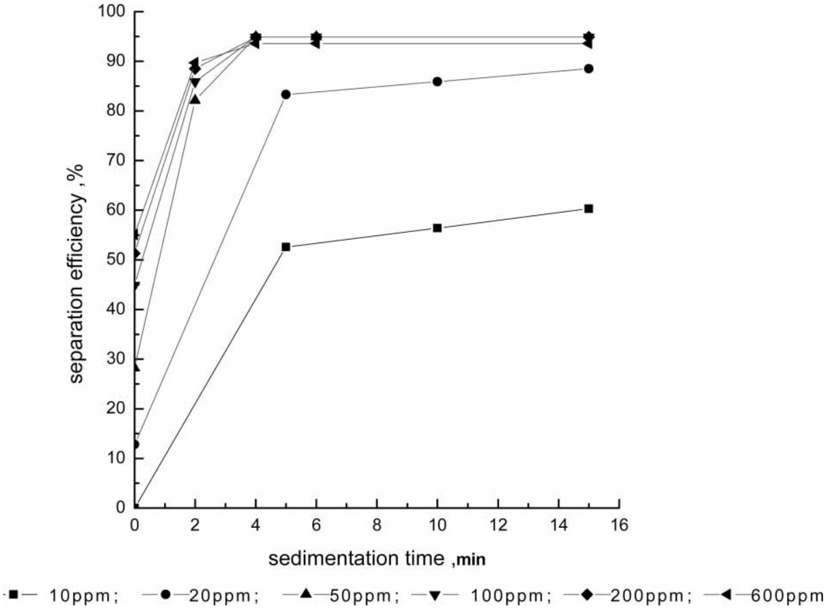


*Figure 2.* Effect of use level of demulsifier when the microwave radiation time is 5 seconds.

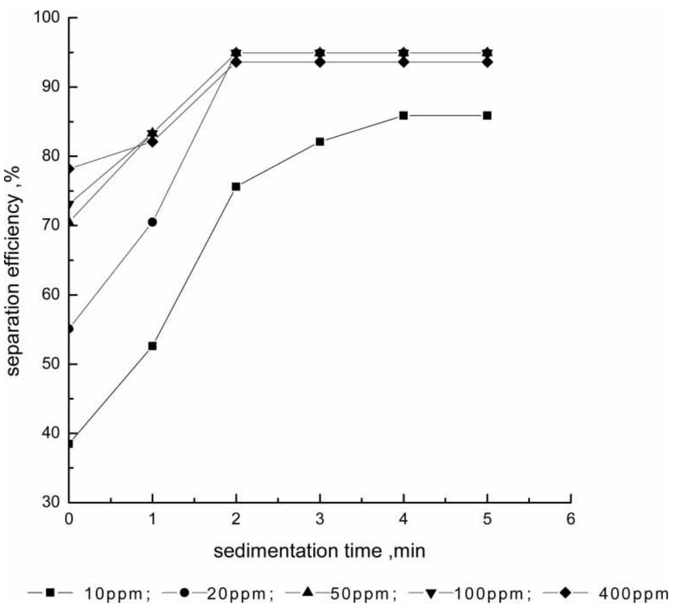


*Figure 3.* Effect of use level of demulsifier when the microwave radiation time is 10 seconds.

advantageous to the crude oil demulsification and separation efficiency, but the amount of demulsifier used has a best value when the radiation time is fixed; otherwise the efficiency of demulsification can be reduced. When the use level of the demulsifier achieves the optimum value, its adsorption concentration approaches balance, and then the boundary tension cease to descend, consequently the separation efficiency and demulsification effects attain the best status. The overused demulsifier can result in the elevating of demulsifier concentration at interface and the forming of micelle because of the molecular aggregates, and thus can increase the boundary tension and reduce the separation efficiency.

The results shown in Fig. 2 also demonstrate that, with 5 seconds of the microwave radiation time, initial separation efficiency and velocity can reach the minimum and the maximum value when the use level of the demulsifier is 10 ppm and 600 ppm, respectively. Separation velocity enhanced with the demulsifier use level increase. The final separation efficiency was 94.9% and almost the same when the demulsifier addition scope was 50 ppm–200 ppm, but fell slightly when the demulsifier amount was 600 ppm.

The separation efficiency could attain the same value, 94.9%, when the microwave radiation time was 5 seconds with 50 ppm of the demulsifier added or the microwave radiation time was 10 seconds with 20 ppm of the demulsifier added. When the use level of the demulsifier was 50 ppm, the separation efficiency could reach 94.9% after 5 seconds or 10 seconds of microwave radiating, but the sediment time needed was 4 minutes and 1 minute respectively. With the increase of microwave radiation time, the necessary amount of demulsifier and sedimentation time can be reduced for the purpose of reaching the optimal separation efficiency.

A series of demulsification experiments by the thermal chemical treatment were performed. The chosen experiment temperature changed from 25°C to 85°C by 10°C of the temperature step. At each chosen temperature, the use level of demulsifiers changed from 0 ppm to 600 ppm 85°C by 25 ppm of the increment. Out of the consideration for the need of actual application which required the higher separation efficiency, low use level of demulsifiers and shorter operation cycle, a group of data were chosen, and compared with the results got from the microwave chemical experiments. The correlative parameters are shown in Figure 4. The best separation efficiency was almost the same for the thermal chemical method and the microwave chemical method, but less amount of demulsifier and shorter time were needed for the microwave chemical method than the thermal chemical method. For the crude oil emulsions, 1#, used in this experiment, the result could be obtained that the separation efficiency was about 96% under the conditions of 100 ppm of demulsifier, 65°C heating temperature, and 9 minutes of heating time for the thermal chemical method; but for the microwave chemical method, the separation efficiency was about 95% with 50 ppm demulsifier, 10 seconds radiation time, and 1 minute settling time used.

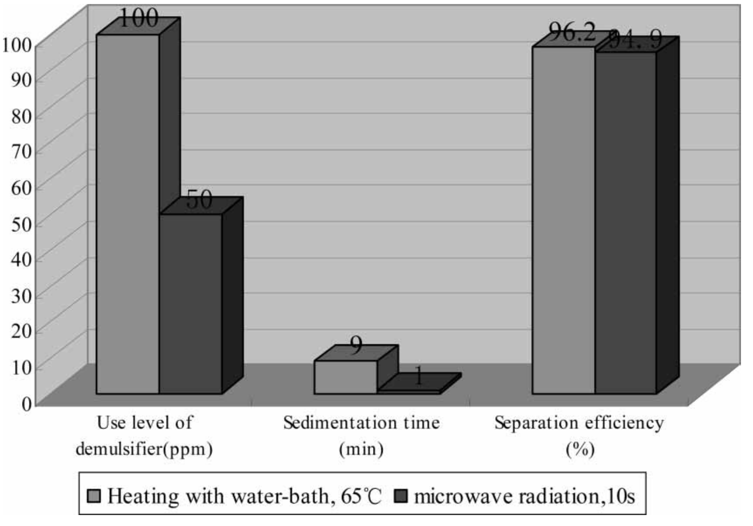


*Figure 4.* Comparison of the optimal conditions in operating between thermal chemical and microwave chemical method (the volume of sample is 10 mL).

## Influence of Water Content on the Demulsification Effect with Microwave Chemical Method Used

The optimal separation efficiency could be achieved respectively against different water content emulsions, through changing the demulsifier amount used and the microwave radiation time. But the results were not the same, as shown in Figs. 5 and 6. The experimental result shows that, the demulsification effect for the high water content crude oil emulsion is better than that of emulsion with a lower water content when demulsified with the microwave chemical method. Along with the water content descent, the separation efficiency and velocity are reduced, and the microwave radiation time and sedimentation time needed in demusification are increased, as well as the use level of the demulsifier. This phenomenon occurred mainly because of the selective heating of microwave on materials. The ability of microwave to interact with materials and transfer energy can change evidently with the molecular structure. When materials in contact have different dielectric properties, microwaves will selectively couple with the higher loss material (8). In crude oil emulsions, the water phase would couple more readily with microwaves. The dielectric properties and the loss factor would decline with the descent of the water content, and consequently bring down emulsions' absorption ability of microwave. Meanwhile, the demulsification by microwave radiation method on w/o type emulsions was better than o/w type emulsions. This might also be a result of the selective heating of microwave. When w/o emulsions are radiated by microwave, the inner

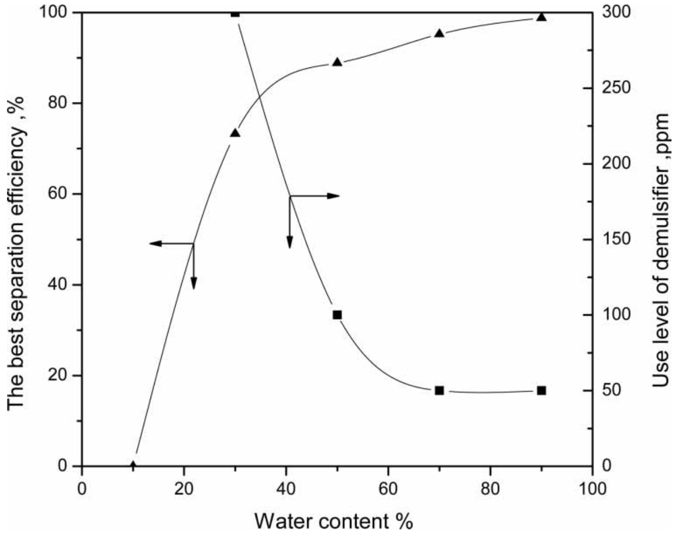


***Figure 5.*** Effect of water content on the best separation efficiency and the optimum use level of demulsifier.



phase of water can absorb more energy than oil, so the volume of the water phase expands and the oil membrane is almost unchanged, consequently the interfacial film is pressed to be thinner and easier to burst. So the demulsification effects of the microwave chemical method can be influenced greatly by water content, and it only suits the emulsions whose water content is relatively higher.

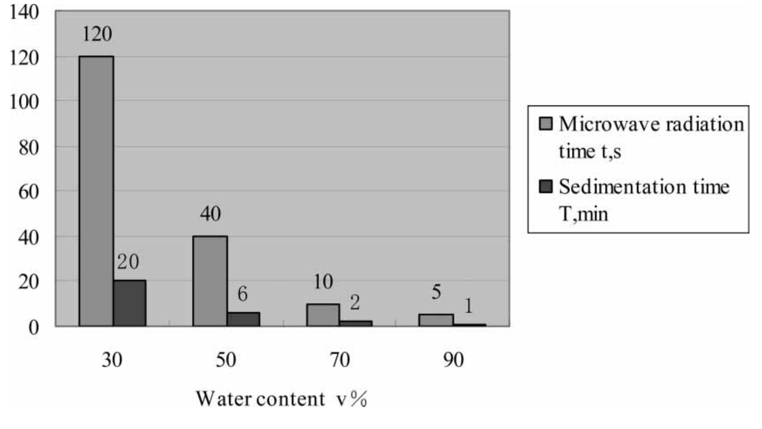


***Figure 6.*** Effect of water content on the least microwave radiation time and sedimentation time.

Now the separation technology adopted in many Chinese oil fields includes two steps: gravity sedimentation in a large tank, and thermal chemical separation. The long operation cycle and the large area occupied by the large tank are the terrible problems. Based on the results of the experiments which use different methods to demulsify the crude oil emulsion, a new separation process with two steps of demulsification is proposed. For the crude emulsions with relatively higher water content, it can be demulsified with the microwave chemical method firstly. Then after some time of sedimentation, the upper crude oil emulsion layer can be drawn out with an injector and treated with the heating method. For the crude oil emulsion, 1# with the water content of 78%, the water content of the upper layer was about 18% after the first process; and it became less than 0.3% through the second time treatment.



## CONCLUSION

The results of this work show that the microwave chemical method, which combines the demulsification function of demulsifier and microwave radiation, is an alternative technology to separate water from crude oil emulsions. The best separation efficiency and velocity by the microwave chemical method is greatly higher than the only microwave radiation. For the crude oil emulsion, 1# with the water content of 78%, less amount of the demulsifier and shorter sedimentation time are needed for the microwave chemical method than the thermal chemical method, though the best separation efficiency is almost the same for these two methods. The microwave chemical method is more appropriate for the demulsification on the high water content crude oil emulsion than that of emulsion with lower water content. The microwave chemical method and heating method can be used one after another for the crude oil emulsions with high water content: with the microwave chemical method used firstly, and then the heating method carried on upper crude oil emulsion layer formed in the previous process. If this technology is applied, it will be meaningful in protecting the environment and cutting down the operation cycle.

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