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Demulsification of Gas Oil/Water Emulsion via High-Intensity Ultrasonic Standing Wave

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GRAPHICAL ABSTRACT

High-intensity ultrasonic standing wave field was established in a horizontal direction and its effect on “gas oil” in “water” emulsion separation rate was studied. Also, effects of four parameters on emulsion instability behavior were investigated: ultrasound irradiation time (5–30 min), emulsion position in ultrasound field (17–37 cm), ultrasound input intensity (20, 45, and 75%) and dispersed phase concentration (0.5, 2, and 10%). Emulsion light absorbance, droplet diameter and distribution were measured to analyze separation efficiency. The optimum states were 10% oil in water emulsion treated at 17 cm distance from ultrasound source under 30 minutes irradiation time and 20% sound intensity.

Keywords Emulsion, flocculation, gas oil, ultrasound

1. INTRODUCTION

One of the most used fuels in the world is “gas oil” that is burnt as a motive force in diesel internal combustion engines and also domestic and industrial torches. Leakage or mixing of gas oil with water may cause stable oil in water emulsion that cannot easily be removed. Water pollution from oil sources is a major problem in today’s world. These emulsions are kinetically stable and do not change for a prolonged period, sometimes for decades. These systems exist in the metastable state, that is, the potential barrier preventing aggregation of the particles is sufficiently high. So, emulsion separation science must be discussed in detail. To understand the reasons for the relative stability of emulsions, it is necessary to determine mechanisms of destabilization. The major instability processes that emulsions undergo are: flocculation, coalescence, creaming, Ostwald ripening, and breaking. Also, penetration of o/w emulsion into soil has intensified the environmental case.

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Emulsion separation techniques have been used are thermal, electrical, chemical, flotation, membrane, and centrifuge. However, stable emulsions usually cannot be easily broken to their initial phases. Also, most of these conventional methods cannot efficiently remove the micron or submicron sized oil droplets. If oil droplet diameter in emulsion was below 1 μm or in nano range then the conventional separation methods cannot be effective and other new processes must be used. Ultrasound may be a new and good representative method. In this novel technology, under ultrasound force, oil droplets are accumulated in a special zone, depending on acoustic mismatch (F). Then these particles flocculate there and emulsion separation is taken place. All studies on emulsion breakage with ultrasound are utilized, low intensity ultrasonic field but nothing has been reported on the use of high-intensity ultrasonic standing wave-fields for liquid/liquid emulsion separation.

In this work, high-intensity horizontal direction ultrasonic standing wave field for gas oil in water emulsion separation was conducted. Emulsion light absorbance was measured to analyze flocculation rate. Also, droplet diameter and distribution were calculated for efficient separation. Furthermore, effects of four parameters on emulsion instability behavior were considered: ultrasound irradiation time, emulsion position in ultrasound field, ultrasound input intensity, and dispersed phase concentration.

2. MATERIALS AND METHODS

2.1. Sample Preparation

Model oil in water emulsion was prepared using Iran gas oil (density at 15°C: 0.82–0.86 Kg/L) and distilled water. Three cubic centimeters of gas oil was added into the 147 cc distilled water through digital mixers (oil volume fraction was 2%). The mixture was stirred for 10 minutes by Ultra-Turrax (T25 model, manufactured by IKA Lab) at 19000 rpm. One hundred fifty cubic centimeters of mixture was prepared in each run. The above process produced oil in water emulsion with average droplet sizes of 1.9 μm and homogenous volume distribution with narrow peak. Also, 0.5 and 10% oil in water emulsions were prepared respectively with average droplet sizes of 1.79 and 15.39 μm. For the later, 0.2% Span80 (HLB number = 15, purchased from Merck Lab) was added as emulsifier to the emulsion, too.

Prepared emulsion was poured into a small plexy-glass rectangular cell with outer dimensions of 2 × 6 × 6 cm and overall capacity of 50 cc. Then the cell was placed in experimental set-up (acoustic chamber).

2.2. Experimental Setup

The main part of the ultrasound system was a rectangular sonicator chamber. It was stainless steel with 48.5 cm length, 9 cm height, and 8 cm width. The chamber was manufactured with a double wall. So water could flow through a pump and keep the temperature constant during experiments. The chamber was filled with 2000 cm³ of water. Transducer (VCX 750 Sonics, 20 kHz) horn was fixed at the left horizontal wall of the chamber from the adjusted hole that was made there as shown in Figure 1. So the ultrasound standing wave field was established in the system by sound resonance between two chamber walls. Sample cells could be placed in different distances from ultrasound source in acoustic chamber and were irradiated with the transducer for the predetermined time and intensity.

2.3. Demulsification Procedures

The transparent cells with 50 cc of prepared emulsions (0.5, 2, and 10% oil in water emulsions) were placed in a standing wave field at different distance from sound source. The three distances were 17, 25, and 37 cm from the transducer horn. For every point, samples were irradiated with the transducer horn for 5, 15 and 30 minutes with the frequency of 20 kHz and three different intensities of almost 20%, 45%, and 75%. So, eighty one states should have been run. Temperature remained steady in 25°C through water flow in outer wall of chamber. After each run, treated emulsion was brought out to measure experiment revenue. Then, plexy-glass cell was washed with water-soap solution, dried with hot air and then used again. Experiments were repeated three times and average results were reported.

2.4. Measurements

The experiments were characterized, quantitatively, in term of light absorbance, value of treated emulsions. A UV-visible spectrophotometer (Shimadzu UV-160) analyzed the emulsion solution light absorbance in 200–800 nm range and gave its value at 305 nm according
to input program. The initial absorbance of spectrophotometer was set 2 at 305 nm. Emulsion solution for spectrophotometer analysis was prepared by mixing 0.5 cc of treated emulsion with 4.5 cc of distilled water. Also Souter diameter \(d_{32}\) and droplet volume fraction distribution of treated emulsions were calculated with a Laser Particle analyzer (Fritsch Analysette 22, Germany).

Emulsion instability was checked through visual observation using an optical microscope (Carl Zeiss, Jena) with 400 times magnification. Pictures were taken with digital microscope eye-piece camera (Dino-Lite) to study the emulsion separation behavior qualitatively. Also creaming rate as cream layer height to total emulsion height (in 14 cc falcon tube) was calculated immediately after ultrasound treating.

### 2.5. Statistical Data Analyze

Design and analysis of experiments were done by Minitab version 14 software. Analysis of variance was applied for analysis of data generated by the fractional factorial design. Alpha level for determining statistical significance was set at 0.05.

### 3. RESULTS

Plots that consider main effects of ultrasound irradiation time, emulsion position in ultrasound field, ultrasound input intensity and dispersed phase concentration on treated emulsion absorbance value were shown in Figures 2A–2D. It was clear that experimental parameter changes had influenced on emulsion separation rate but its degree and procedures was differed. Analysis of variance results of experimental absorbance output data for above four levels are shown in Table 1.

![FIG. 2. Simple effect of A) irradiation time, B) emulsion distance; C) ultrasound intensity, D) oil concentration on average amount of emulsion absorbance value.](image)

**TABLE 1**

<table>
<thead>
<tr>
<th>Factor</th>
<th>(F) value</th>
<th>(P) value</th>
<th>(F/P) value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emulsion position</td>
<td>31.20</td>
<td>0.004</td>
<td>7800</td>
</tr>
<tr>
<td>Irradiation time</td>
<td>23.66</td>
<td>0.006</td>
<td>3943.3</td>
</tr>
<tr>
<td>Intensity</td>
<td>21.83</td>
<td>0.007</td>
<td>3118.57</td>
</tr>
<tr>
<td>Disperse phase concentration</td>
<td>7.18</td>
<td>0.047</td>
<td>152.7</td>
</tr>
</tbody>
</table>

![FIG. 3. Microscope picture A) 2% o/w initial emulsion; B) treated emulsion with 20% intensity, 5 minutes, 17 cm distance; C) with 20% intensity, 15 minutes, 17 cm; D) with 20% intensity, 30 minutes, 17 cm; E) with 45% intensity, 30 minutes, 17 cm; F) with 75% intensity, 30 minutes, 17 cm.](image)

Microscope pictures of emulsion that was treated at 17 cm distance (as a sample distance) from sound source is displayed in Figure 3. Also droplet volume distribution graphs for all emulsion samples in experiments are drawn in Figure 4.

### 4. DISCUSSION

#### 4.1. Effect of Irradiation Time

As shown in Figure 2A, increasing emulsion exposed time to ultrasonic standing wave field made its light absorbance became less. Increasing irradiation time from 5 to 15 minutes caused mean light absorbance to change 0.1679 units and for 15 to 30 minutes was 0.1673 more. From ANOVA analysis, irradiation time had simple effect on emulsion separation rate \(\left( P < 0.05 \right)\).

It could be explained that increasing irradiation time caused enough time for all imposed force on emulsion droplet in acoustic chamber to act as effective force and push oil particle to high pressure zones. If oil droplets had been flocculated and then coalescenced with the help
of ultrasound standing wave field, then emulsion droplets diameter became larger and separation efficiency improved. As much as emulsion droplet diameter increased, light could pass easier. Therefore light absorbance decreased more compared to the initial ones.

Negative inclines in Figure 2A indicate that the increased in exposed time caused coarser oil droplet were formed in o/w emulsion because fine oil droplets obtained enough energy for going to anti node zones and also had excess time to establish oil bulk at that area. Therefore, light could pass easily and the amount of light absorbance decreased. In other words, increase in irradiation time affected the parameter on oil/water emulsion separation. But some researchers reported if irradiation time was being continued, after a special limit, then emulsion light absorbance decrease was stopped or increased.[6–7]

Microscopic pictures of emulsion behavior in ultrasonic standing wave fields were confirmed above result (Figure 3). Figures 3B–3d show 2% oil in water initial emulsion behavior at 17 cm distance from sound source with 20% ultrasound intensity for different irradiation time. Initial emulsion was stable and consisted of fine droplets (Figure 3A). During 5 minute irradiation, under ultrasound force, oil droplets approached each other and two different types of interaction patterns arised, affecting the flocculation process and colloid interactions. First, permanent aggregate formation probability of pair of colliding particles would increase the effect on collision efficiency and flocculation occurred very slowly (Figure 3B). The other aspect of colloid interaction was their effect on the strength of aggregates, which was less well understood.[8] So, flocculation was occurred only because droplets collided with each other and adhered when brought together by collision. “Rapid” coagulation (the repulsive interaction between particles predominates in the system) happened with increasing irradiation time to 15 minutes and oil flocs formation accelerated (Figure 3C). After 30 minutes, emulsion reached to highest instability mode (Figure 3D) and oil droplets were separated. As it can be seen in Figure 3, droplet deformation could be neglected for small droplets emulsion (less than 5 to 10 μm) as reported before.[9–11]

Whenever an emulsion was destabilized, a breakdown due to droplet creaming occurred simultaneously. Although in emulsion systems, flocculation would be significant for smaller droplets and creaming for larger ones. But, it was extremely important to have quantitative relationships that could predict the state of an emulsion. In the emulsion system, studied in these experiments under ultrasound field both creaming and flocculating were occurring and the creaming rate was determined for different states. For example, creaming rate for 2% oil in water emulsion irradiated for 5 minutes with 20% ultrasound intensity at 17 cm distance from sound source was 41.67%, its value for 15 minutes irradiation time was 52.08% and for 30 minutes was 72.3%. These types of analysis had the potential of greatly simplifying the process of predicting the instability of a given emulsion.

4.2. Effect of Emulsion Position in Ultrasound Field

Emulsion position in the acoustic chamber influenced on light absorbance value and thus on emulsion stability (Figure 2B). Emulsion light absorbance grew with an increase in sample distance from sound probe. Going forward in the acoustic chamber from 17 to 25 cm increased the mean light absorbance 0.057 units and from 25 to 37 cm was 0.3. The line slope was larger for the second parts. Furthermore, separation efficiency was reduced keeping distance from the ultrasound probe. This can be explained with the reasons below:

- Multiple scattering of ultrasound waves occurred in far regions from the sound source and it increased with distance. So, a proper standing wave was not established in that region due to formation of cavitations bubble.
- Low acoustic pressure in far area from sound source was the second reason. In that case, energy levels of sound waves were smaller, so the ability
of ultrasound wave to bring oil droplets close together in emulsion decreased.

Although decrease in emulsion distance from ultrasound probe caused light absorbance to diminish (Figure 2B) the effect of ultrasound on emulsion droplets was more in a near zone to the probe. Also cavitations effect decreased there. So a minimum amount of UV absorbance was at a minimum distance (17 cm). In other words, maximum emulsion separation to its two initial phases happened at this distance. Light absorbance reached its highest value at 37 cm distance and 75% sound intensity. Because of that far region, cavitations increased due to high ultrasound intensity as a negative factor for emulsion separation, too the effect of emulsion position in an ultrasound field on intensity as a negative factor for emulsion separation, too the effect of emulsion position in an ultrasound field in different ultrasound intensities and irradiation times were also confirmed above conclusions from emulsion absorbance data.

The evolution of the mean droplet diameter \(d_{32}\) as a function of emulsion position in ultrasound field in different ultrasound intensities and irradiation times were also confirmed above conclusions from emulsion absorbance data. In the ultrasonic emulsion separation process, several changes should be occurred. The first oil droplets must have migrated to high pressure zone in the ultrasonic standing wave field. After oil droplet assembling at this special zone, they came closer and made a flock of oil droplet. If ultrasonic force continued irradiating, coalescence of droplet would happen. In the last stage, oil droplets came up (creaming) and, after the process of oil off, separation was completed. Depending on operation and designed parameters, emulsion separation could be ended in each of the above stages. So, droplet diameter could be applied to quantify the degree of gasoline separation. Droplet diameter showed the efficiency of oil and water separation in emulsion. Emulsion droplet diameter size was increased in most of the experimental states in accordance with initial stable one (1.9 \(\mu m\) for 2% oil in water emulsion), that was shown, emulsions became instable in more states. One clearly point was distinguishable regions in the ultrasound field. The diameter jumped from its initial value about 17.36% in less than 5 minutes in 20% ultrasound intensity or its mean value was multiple after 30 min. The droplet size after the first abrupt decreased for the middle zone (25 cm distance). Then, a second slow decrease took place and the size decreased again for the far region. Whatever the intensity and irradiation time, the emulsion instability behavior passed the same procedure. There was a continuous exchange of matter through the dispersed phase, which increased the average droplets’ diameter while reducing their number. Emulsion droplet diameter value shown that a high level of coalescence led to emulsions separation might occur depending on the emulsion position in acoustic chamber.

The stability of a disperse system could be characterized by the droplet volume fraction distribution.\(^{15-16}\) The size distribution of the droplets largely depended on the rate of their coalescence. In order to get an overall picture of these processes, treated emulsion size distribution was undertaken. The 2% gas oil in water emulsification (part 2.1) leaded to direct emulsion with a typical diameter around 1.9 \(\mu m\) and a narrow size distribution, which can be observed in Figure 4. The graph shown in Figure 4 depicted a fast and steady growth of average droplet sizes (shifting mean value of graph to right) in most cases with ultrasound. Thus it indicated that ultrasonic standing wave field induced rapid o/w emulsion coalescence.

Due to the strong dependence of separation efficiency with emulsions position, differences between distribution shapes were seen in Figure 4. A broader droplet distribution was for all emulsion placed at 17.5 cm distance from sound source (after treating) in all states of ultrasound intensities (Figure 4A–4I). It was the result of oil droplet coalescence and formation of bigger oil flocs. Several picks were seen in the emulsion droplet size distribution for some cases in Figure 4. It could be results of partial oil droplet separation or formation of very big flocs. So it was concluded that emulsion under ultrasound irradiation had larger droplet diameter sizes and droplet size distribution because of oil particle flocculation.

### 4.3. Effects of Ultrasound Intensity

By reviewing the emulsion light absorbance data at different ultrasound intensities, it was concluded that ultrasound intensity had a main effect on absorbance data \((P < 0.05)\). As shown in Figure 2C, increase in ultrasound intensity caused emulsion mean absorbance data to increase, too. In all three intensities, experimental data followed a similar path. It was clear that decrease rate in the absorbance line slope from 75% ultrasound intensity to 45% was larger than from 45% to 20%.

Light absorbance changes with intensity shows that 20% ultrasound intensity had maximum effect on emulsion separation rather than 45% and 75% (Figure 2). Intensity rising caused the formation of cavitations. It also increased bubble activity value. The net result of the above processes was decrease in physical and chemical effect of ultrasound waves. So, positive slope drawn in Figure 2C could be due to intensifying in shear stress that resulted from air bubble decomposition in the growing cavitations field.

Also decrease in emulsion light absorbance in 20% ultrasound intensity certainly was due to mixing and flocculation of oil droplets under properly formed ultrasonic standing wave field. Ultrasound wave interference between the acoustic chamber and ultrasound probe made standing wave with two distinction zones. These areas are called node and anti-node. The difference between density and
the accumulation ability of oil droplets and continues phase (water) under ultrasound force pushed oil droplets to anti-node (an area with high acoustic pressure). In the emigration process, oil droplets gradually came closer and flocculated there. So protective film was ruptured and oil particles were completely amalgamated. The above physical process caused coarser oil droplets, in other words, it decreased emulsion absorbance. Droplet diameter data was measured at different intensities which resulted in the same conclusion. Droplet size value was smaller for 75% ultrasound intensity than 20 and 45% for all corresponding irradiation time and emulsion position. But treated emulsion with 20% intensity made maximum increase in droplet size.

The volume distributions of the dispersed gas oil droplets in the water phase for a given system after 20, 45 and 75% of ultrasound intensity treating are shown in Figure 4. The general trend was the same. Droplet distribution graphs also confirmed the above conclusion but there seemed to be difference in the droplet size distributions in 9 different states. The changes were largest in the finishing time period (30 minutes). A spreader distribution with larger droplet diameters and several peaks were measured for less ultrasound intensity (20%) in Figure 4. The driving forces in the collision frequency were: the creaming of oil droplet and the shear flow. Collision frequency increased the droplet size in the emulsion. So increasing intensity reduced the collision frequency. Since the collision frequency was related to coalescence rate, both flocculation and coalescence were accrued for 20% ultrasound intensity. Also, increase in intensity made larger under-surface area for distribution graph due to slow emulsion separation rate. In the separation of the phases, the process was dominated by the coalescence and the creaming rates of the dispersed phase. The coalescence rate depended on a number of parameters such as droplet size distribution, dispersed phase density and interfacial properties. The creaming rates were determined by the density difference, and the viscosity of the dispersion (computed by Stokes’ law). Other investigations also indicated the same relation between separation efficiency and ultrasound intensity. Effects of ultrasound input power on separation efficiency of grease in water emulsion was studied by Latham J. Stack and better results for lower input power was obtained. Susumu Nii also took the same conclusion for Canola oil in water emulsion.

It must be considered that the correct droplet size distribution was not the number distribution. The big difference between the number distribution and the volume distribution was due to the fact that as the diameter was increased by a factor of 1, the volume was increased by a factor of 3.

Treated emulsion pictures at three different intensities for 30 minutes irradiation time and 17cm distance (Figure 3) implied that the sample irradiated with 20% intensity, completely separated to its initial phase and oiling off occurred (Figure 3D). Creaming rate was improved to 73% for it. But for 45%, partial separation was seen. Numerous oil flocs were formed in continues phase (Figure 3E) and creaming rate reached to 52.1%. Oil droplet was flocculated but the number of oil floc was less in 75% intensity (Figure 3F). Creaming rate was decreased to 36.46%.

### 4.4. Effect of Disperse Phase Concentration

The volume fraction of the disperse phase had a considerable effect on emulsion stability. Increasing oil volume fraction or emulsion average size eased the demulsification processes. As shown in Figure 2D, maximum changes in emulsion average droplet size were for 10% gas oil in water emulsion. A common observation was that smaller droplet size emulsions showed much resistance to separation than coarser on. The above result was confirmed by other studies, too.[18-19] It could be explained in term of collision net rate in high concentrated disperse phase emulsion. Collision frequency (the number of collisions that lead to a successful merging of drops) resulted in drop growth (in the emulsion) and broader distribution.

However, some researcher reported opposite results and implied emulsion separation efficiency descended when oil concentration increased.[12] In another study on the disperse phase concentration effect on Rheological characterization of Mayonnaise emulsion, creaming rate was decreased under hydrodynamic interactions.[20] There might be a relation between droplet size and emulsion disperse phase viscosity. Disperse phase viscosity increase caused droplet movement to the anti-node area to slow down.

### 4.5. Optimum Condition

Ultrasound irradiation time, emulsion position in ultrasound field, ultrasound input intensity and dispersed phase concentration influenced on emulsion instability because their Alpha level for determining statistical significance was below 0.05 (Table 1). Emulsion position in ultrasound field had maximum effects on emulsion absorbance value with comparison amount of $F/P$ value from Table 1. Also, it found that irradiation time then ultrasound input intensity and dispersed phase concentration effected on emulsion absorbance value.

The best state was generated for 10% oil in water emulsion that was treated at 17 cm distance from ultrasound source with 30 minutes treating time and 20% sound intensity. In such case, smaller amount of light absorbance or maximum amount of droplet diameter were read that caused the oil phase to be completely removed from emulsion.
5. CONCLUSION

In conclusion, this study was contributed to improve emulsion separation rate in the high-intensity ultrasonic standing wave field. Study results indicated that ultrasound was an effective treatment to separate oil in o/w emulsions. In spite of cavitations formation at some states, ultrasound standing wave field had enough capability to establish in the acoustic chamber firmly. But the amount of emulsion droplet size and addition light absorbance deduction strongly depended on designing parameter such as emulsion position and processing factor such as irradiation time. Generally outstanding points of the study were as below:

- Using ultrasound technology had an effect on emulsion UV absorbance, droplet diameter and distribution and thus on separation efficiency.
- Emulsion breakage consisted of several processes such as oil droplet emigration, droplet gathering, flocculation, coalescence and oiling of. Depending on the study parameter value, some or all of these stages might occur.
- Emulsion irradiation time increase caused emulsion creaming rate to increase, too.
- Decrease in emulsion distance from ultrasound probe (37–17 cm) caused deduction in emulsion light absorbance, addition in oil droplet diameter and acceleration in o/w separation.
- Ultrasound intensity and shear stress induced by cavitations bubble explosion had an effect on droplet light absorbance. The optimum intensity for oil removal was 20%.
- Increasing oil volume fraction or emulsion average size eased the demulsification processes.
- The optimum experimental states were for 10% oil in water emulsion treating at 17 cm distance from ultrasound source under 30 minutes irradiation time and 20% sound intensity.

REFERENCES