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# Feasibility of low frequency ultrasound for water removal from crude oil emulsions

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ABSTRACT

The feasibility of indirect application of low frequency ultrasound for demulsification of crude oil was investigated without using chemical demulsifiers. Experiments were performed in an ultrasonic bath with frequency of 35 kHz. Synthetic emulsions with water content of 12%, 35% and 50% and median of droplet size distribution (DSD), median $D(0.5)$, of 5, 10 and 25 μm were prepared from crude oil with API density of 19 (heavy crude oil) and submitted to the proposed ultrasound-assisted demulsification procedure. Experimental conditions as temperature, time of exposition to ultrasound and ultrasonic power were evaluated. Separation of water from crude oil emulsion was observed for all emulsions investigated. Demulsification efficiency up to 65% was obtained for emulsion with 50% of water content and DSD of 10 μm. Higher efficiency of demulsification was achieved using US temperature of 45 °C and ultrasound power of 160 W by 15 min. Results obtained in this study showed that ultrasound could be considered a promising technology for industrial crude oil treatment and respective water removal.



## 1. Introduction

The formation of water-in-oil (W/O) emulsions during crude oil production is a problem for crude oil industry. The presence of emulsified water increases oil viscosity which makes difficult its transport through pipelines resulting in the increasing of costs. Furthermore, water usually contains relatively high concentration of dissolved salts, mainly NaCl, leading to corrosion during distillation process and equipment failure [1,2]. Therefore, water and consequently salt must be removed from crude oil after its production.

In order to separate water from crude oil, an initial step is necessary to destabilize the emulsion. It is already known that to make possible the separation of water from crude oil the interfacial film that stabilizes the emulsion must be removed or weakened [3,4]. This step can be performed by means of mechanical, electrical or chemical processes or by the combination of them [5]. Chemical destabilization of W/O emulsion is generally performed using demulsifiers presenting the capability to adsorb onto the water/oil interface and change its properties allowing water drops to aggregate and coalesce. There are several types of demulsifiers and the choice is performed according to emulsion physical and chemical properties. Temperature is a critical parameter that determines demulsifier efficiency because enhancing the temperature will decrease emulsion viscosity and enable easier migration of demulsifier molecules to water/oil interface [6]. Although chemical demulsifiers are widely used in crude oil industry, additional problems are found for removing the demulsifier from oil or aqueous phase and, consequently, contamination of crude oil (and its products) could be observed.

Higher efficiency of demulsification could be achieved by combining demulsifier and physical processes. Among these, the most used for W/O emulsion separation is electrostatic treatment which consists of the application of an external electric field to enhance coalescence of aqueous drops, improving phase separation [7]. However, desalted water (in case of desalting step) as well as demulsifiers must be added to assure suitable demulsification efficiency. Other technologies have been evaluated and advantages in comparison with electrostatic treatment were demonstrated using hydrocyclones [8] and microwave radiation [9–12]. Despite the advantages described in some works about the use of hydrocyclones and microwave radiation for W/O emulsion treatment, these technologies are still not used in industrial crude oil demulsification processes.

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Low frequency ultrasound has been studied as an alternative to overcome drawbacks of the above mentioned technologies for crude oil demulsification [13,14]. Ye et al. [13] evaluated the use of acoustic energy at 10 kHz in an apparatus constructed to generate a standing wave field in combination to chemical demulsifier addition to remove salt and water from crude oil. Schoeppel and Haward [14] also proposed an ultrasonic device at 40 kHz combined to chemical demulsifier for demulsification purposes. One of the main effects attributed to ultrasound is cavitation [15,16] and the resultant shock waves in liquids. Cavitation effects also include heating and intense agitation of liquid medium and can result in the enhancement of heat and mass transference processes [17]. These characteristics have attracted attention for the use of ultrasound mainly in chemical reactions [18–20]. Another effect that can take place under ultrasonic frequencies is the formation of standing waves [21]. There are few works published where the cavitation effect of ultrasound combined with chemical demulsifier was explored [14,22,23] in systems with direct application of ultrasound to emulsion and little is discussed about the mechanisms involved in demulsification process. According to May [22], the separation of water from W/O emulsion (applying frequencies in the range of 200–400 kHz,) was caused by vibration produced by ultrasound when it was directly applied on crude oil emulsions. Additionally, ultrasound was used in some works for particles or emulsions separation using experimental conditions to create standing wave fields [21,24,25].

Based on the above considerations, in the present work, the effect of low frequency ultrasound (35 kHz in an ultrasonic bath) was investigated to crude oil demulsification by indirect application using water as propagation medium and avoiding the use of chemical demulsifiers or desalted water addition. Synthetic emulsions of heavy crude oil (API 19) were used and the operational parameters for ultrasound demulsification procedure as power, temperature and time were studied and all experiments were performed in batch system. W/O emulsions with different water content and drop size distribution (DSD) were evaluated and the demulsification efficiency was measured by the determination of water content remained in emulsion after ultrasonic treatment.

## 2. Materials and methods

### 2.1. Instrumentation

An ultrasonic bath which operates on frequency of 35 kHz (model Elmasonic Xtra-50H) from Elma Ultrasonic (Singen, Germany) equipped with heating system was used. Power of this bath informed by manufacturer is 100 or 160 W for operation modes named as "soft" and "power", respectively. The specific acoustic power entering the system was determined following the calorimetric method proposed by Kimura et al. [26] and discussed by Mason et al. [27]. This method takes into account the volume sonicated and for the system used in the present work the specific acoustic power was $19.2 \pm 2.0\ W\ dm^{-3}$ when equipment power was set on 160 W.

An oven adapted with a mechanical stirrer (model 400-DE, Nova Etica, Brazil) was used for crude oil homogenization with sodium chloride solution during synthetic emulsion production. A Polytron mechanical stirrer (model PT 3100 D, Littau-Lucerna, Switzerland) was also used for the preparation of synthetic emulsions. Droplet size distribution in emulsions was determined by laser diffraction technique using a particle size analyzer Mastersizer 2000 (Malvern Instruments, Malvern, United Kingdom). A transparent mineral oil was used as diluent and 4 – 7 drops of crude oil or W/O emulsion were dispersed in about 40 mL of diluent.

Water content was determined in W/O emulsions and in the demulsified oil by Karl Fisher titration method following ASTM D 4377 method [28]. An automatic titrator (model 836, Metrohm, Herisau, Switzerland) equipped with platinum electrode (model 8.109.1306, Metrohm) was used.

### 2.2. Reagents

Purified water from a Milli-Q® system (Millipore, Billerica, USA) was used to prepare all solutions. Reagent Composite 5 (Riedel-de Häen, Seelze, Germany) was used for Karl Fisher titration. A mixture of toluene (Vetec Química Fina Ltda., Rio de Janeiro, Brazil) and methanol (Carlo Herba Reagents, Milan, Italy) (3:1) was used for sample dissolution for further determination of water content. Sodium chloride solution, used for preparation of synthetic emulsions, was prepared by dissolution of salt (Vetec, Brazil) in water.

### 2.3. Synthesis and characterization of W/O emulsions

Water-in-oil emulsions were prepared by mixing known amounts of a Brazilian heavy crude oil (API 19) and NaCl solution ($100\ g\ L^{-1}$). The characteristics of crude oils investigated are shown in Table 1.

For synthetic emulsions preparation, initially a known amount of NaCl solution was added to crude oil and the mixture was shaken in an oven heated up to 80 °C, adapted with a mechanical stirrer to incorporate the water in the oil phase. Then, the mixture was homogenized by Polytron® stirrer using conditions (frequencies and time) to yield emulsions with monodisperse DSD with median values, $D(0.5)$, close to 10 μm. After preparation, emulsions were characterized by water content and DSD determinations. Operational conditions used in W/O emulsion preparation are shown in Table 2.

Stability of synthetic W/O emulsions was evaluated by successive determination of water content and DSD in intervals of 90 min up to 10 h. Emulsions (W/O) were prepared daily and they could be considered stable since no significant changes in DSD profile, $D(0.5)$ and water content values were observed.

### 2.4. Ultrasound-assisted demulsification experiments

For all the experiments using ultrasonic bath, 20 g of W/O emulsion were transferred to a conic glass vessel, usually employed for BSW (bottom, sediment and water) determination in routine crude oil analysis. A schematic representation of the experimental apparatus using the ultrasonic bath for crude oil demulsification is shown in Fig. 1. More details are available on Fig. S1 (Supplementary material).

The temperature of water in the bath was constantly monitored using a digital thermometer inserted near the conic glass vessel. Since the application of ultrasound increases the water bath temperature, warm water was constantly drained out and water at room temperature was added using pipes to maintain the temperature constant during the experiments. This procedure was especially necessary for experiments carried out at 25 °C while for experiments carried out at 60 °C the heat loss to the

**Table 1**
Characteristics of original crude oil used for preparation of W/O emulsions.

| Parameter | Crude oil |
|---|---|
| Density, API | 19.0 |
| Density, $g\ cm^{-3}$ (45 °C) | 0.9212 |
| Kinematic viscosity, $mm^2\ s^{-1}$ (45 °C) | 133.4 |
| Dynamic viscosity, mPa s (45 °C) | 122.9 |
| Water content, % | 0.025 ± 0.001 |
| Total acid number, mg KOH $g^{-1}$ | 2.06 ± 0.10 |
| NaCl, μg $g^{-1}$ | <10.0 |