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Microwave demulsification of heavy crude oil emulsions: Analysis of acid species recovered in the aqueous phase

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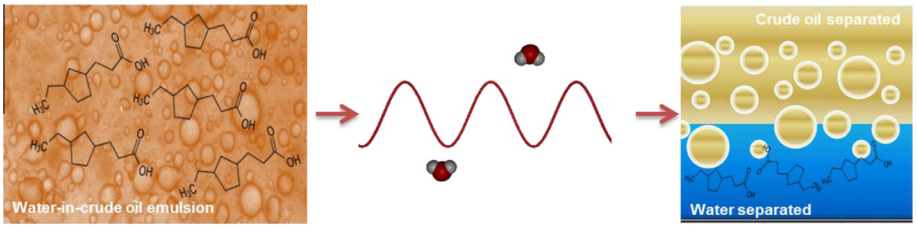
HIGHLIGHTS

- We report the effect of microwaves and conventional heating on the crude oil.
- Microwaves allowed us to remove water and acidic compounds from the oil phase.
- Temperature and pH can be managed to alter the profile of acids recovered.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, the application of microwave technology is investigated for breaking water-in-heavy crude oil emulsions focusing upon the identification of acidic species existing in the aqueous phase recovered by the microwave demulsification process. To accomplish this, a methodology for characterization of acidic species based on GC/qMS (gas chromatography coupled to mass spectrometry quadrupole type) has been developed. An experimental study was conducted to assess the effect of operating conditions, including the heating mode (microwaves/conventional heating), process time (30, 60 min), pH of the aqueous phase (pH = 2, 6, 10) and temperature (90, 120, 150 °C) over the migration of acidic species from the crude oil to the aqueous phase during the demulsification of a heavy crude oil. The most influential variable was the temperature, which favors the partitioning of a larger number of acidic species, including cyclic compounds of low molecular weight that were not extracted at low temperature. The microwave heating allowed a wider distribution profile of monocyclic and bicyclic acids than the conventional heating scheme. Changing the aqueous phase pH from acid to the alkaline range modifies the profile of acidic compounds from predominantly acyclic to monocyclic and bicyclic species.

1. Introduction

The petroleum is a complex mixture composed of hydrocarbons and some heteroatoms such as nitrogen, oxygen and sulfur which contribute to acidity of the crude oil [1]. It has been recognized that crude oils with higher total acid number (TAN) are potentially most toxic and corrosive, which may contribute to generate several complications on production and refinery operations. Among these acidic compounds, much attention has been done to naphthenic acids, which generally are defined by classical formula $C_nH_{2n+z}O_2$ [2–6]. Moreover, the acids behave like natural emulsifiers contributing to stabilize water-in-oil emulsions formed during the oil production [7–9]. Mostly, these compounds are found on the

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immature, biodegraded and heavy oils (viscous and high density) and also on wastewater [10]. Thus, one of the greatest challenges of the oil industry is to develop mechanisms to facilitate the separation of water-in-oil (W/O) emulsions and enhancing the removal of acidic species from the oily matrix. Although there are several methods to extract naphthenic acids, they still have economic and/or operational disadvantages [11].

The problems associated with stabilization of petroleum emulsions are multifaceted and strongly influenced by concentration of the natural emulsifiers and the recovery methods used in the production field [12]. The crude oil production is generally associated with produced water existing in the reservoir. Along the crude oil production, these phases are subjected to agitation and shearing, promoting the dispersion of one phase into another, resulting in highly stable emulsions [13]. Furthermore, the emulsification of water in oil is commonly employed to extract thin solids and salts from the oil in the refinery. The presence of natural emulsifiers in the crude oil, such as asphaltenes, resins, fine solids, naphthenic acids and other polar compounds, favors the formation of these emulsions as they tend to migrate to the water/oil interface to form a hard and viscoelastic film [14–19]. This film may act as a kind of barrier, preventing the droplets coalescence and consequently phase separation [20], making the destabilization of water-in-oil emulsions a very difficult task.

Several emulsion destabilization methods are available in the industry, including chemical treatment, gravity separation, centrifugation, filtration, heating, membrane separation and electrostatic treatment [21]. All of these methods, in combination or separately, are widely used in oil industry especially for processing of water-in-oil emulsions [22]. In order to ensure productivity gains, the improvement of existing techniques and the development of new ones focused on the emulsion processing are of great importance for the oil industry. In this context, microwave irradiation technology has appeared as an alternative process for emulsion separation [23]. Nevertheless, little has been done to evaluate the microwave effects on the partitioning of acidic species existing in the petroleum.

Microwave radiation provides a specific heating mode. The dielectric heating generated by microwaves is associated with the radiation interaction with matter at molecular level. Ionic conduction and dipole rotation provide greater microwave heating efficiency compared to conventional method. This advantage allowed its application in various areas such as organic and inorganic synthesis [24–33], processing of foods and biomass [34–41], processing of effluents, oil characterizations and in a number of other processes of interest for petroleum industry [22,42–49].

The microwave technology is also used to remove acidic components from petroleum. In general these studies evaluate the efficiency of the removal of acidic compounds with the variation in the TAN of specimen between before and after processing by microwave.

Lingzhao et al. [50] developed a study on separation of the naphthenic acids from the diesel fuel by microwave radiation. The authors explain that the microwave radiation causes a decrease in the zeta-potential and electric double layer in the W/O interface, thereby reducing the viscosity of diesel fuel, promoting acceleration of the separation of the naphthenic acids.

Huang et al. [51] conducted a study using microwave for removing naphthenic acids from petroleum distillates, oils and refined oils (lubricants). The optimum conditions for the refining process were as follows: S/O = 0.23:1, pressure of 0.11 MPa, radiation time 5 min (at constant pressure), the radiated power of 375 W and resting time of 25 min. Under these conditions, the acidity was reduced from 0.63 mg KOH/g to 0.0478 mg KOH/g, which was sufficient to meet the standard specifications.

Most recently, Mishra et al. [52] determined the efficiency of a laboratory scale microwave system on naphthenic acids degradation. These acids appear in process water used during petroleum refining and separation from oil sands. They analyzed the effects of TiO_2 catalyst and water source. The microwave radiation favored the catalytic decomposition of naphthenic acids and reduced its toxicity levels considerably.

In a related effort, Freitas et al. [53] described a pioneering method based on GC × GC (comprehensive two-dimensional gas chromatography) for the analysis of organic compounds extracted during microwave demulsification of water-in-crude oil emulsions. In particular, the characterization of polar organic compounds was performed using two analytical techniques: GC/qMS (gas chromatography coupled to mass spectrometry quadrupole type) and GC × GC/TOF-MS (gas chromatography coupled with comprehensive two-dimensional mass spectrometry flying time).These techniques allowed for the identification of a number of natural petroleum compounds that migrate to the water phase during the microwave demulsification process, as a function of temperature and irradiation period.

The objective of this work is to beyond what was done previously and to analyze whether the microwave irradiation process could favor the partitioning of acidic species from the oil phase to the aqueous phase during microwave demulsification runs. An experimental study was conducted to evaluate the effects of microwaves and conventional heating modes, residence time and pH, with the support of chromatographic techniques (GC/qMS).

2. Experimental section

2.1. Crude oil characterization

An experimental study was conducted to assess the demulsification performance of water-in-heavy crude oil emulsions prepared in the laboratory. A Brazilian crude oil was sampled in the petroleum field and used in this study. Table 1 presents its main characteristics and the techniques and standards used for analysis.

2.2. Emulsion synthesis

The emulsions were synthesized with crude oil mentioned in Section 2.1 and distilled water with distinct pH values (2, 6 and 10). Stable emulsions were generated by vigorous mixing of crude oil and water. An amount of water was added stepwise to the petroleum in accordance with previous studies, while the mixture was hand-shaken to completely incorporate water. This mixture was then homogenized using Ultra-Turrax T-25 homogenizer fitted with S25-25G dispersing tool (IKA) with stirring frequency at 6500 and 9000 rpm. The synthesized emulsions had water content between 35–39% and volumetric mean diameter of droplets ranging between 10 μm and 19 μm. This synthesis procedures were based on well-established techniques described previously [46].

Table 1
Main properties of the crude oil employed in this study.

Density (°API)	16.8	ASTM D-5002 [54]
Relative density (20/4 °C)	0. 9506	ASTM D-5002 [54]
Water content (wt.%)	0.1450	ASTM D-1744 [55]
TAN (mgKOH/g crude oil)	3.35	ASTM D-664 [56]
Salinity [NaCl] (wt.%)	0.24	ASTM D-3230 [57]
Hydrocarbons content (wt.%)		
Saturated	44.8	
Aromatic	31.3	
Resins	21.6	
Asphaltenes	2.3	