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Demulsification of heavy crude oil-in-water emulsions: A comparative study between microwave and thermal heating

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HIGHLIGHTS

- A comparative study of demulsification by microwave and oil bath heating.
- Results were confirmed by steady state fluorescence spectrometry.
- The effect of a demulsifier on the oil-in-water (O/W) emulsion stability was studied.
- The effect of salt content on the O/W emulsion stability was evaluated.

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ABSTRACT

Oil-in-water (O/W) emulsions are works in an innovate manner by which otherwise highly viscous heavy and extra-heavy crude oils can be transported from producing sites to transforming sites through pipelines. In spite of the important reduction in viscosity and pressure drops, water must be removed from the crude oil before further process or refining. Hence, the present study discusses the demulsification of an O/W emulsion prepared with Mexican heavy crude oil. A comparative study was carried out between microwave and oil bath heating with regard to water separation time. The effect of a chemical demulsifier and salt content of the O/W emulsion's aqueous phase was also investigated. Microwave dielectric heating of O/W emulsions showed a greater degree of water separation in less time than conventional oil bath heating. Water separation of O/W emulsions increased with microwave power and salt content of the aqueous phase, and in the presence of a chemical demulsifier. Finally, the fluorescence emission spectra of the initial and treated O/W emulsions were in agreement with the water separation results and provide a quick and effective way to study the demulsification processes.

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1. Introduction

Currently, most of the recoverable petroleum in Mexico and in many other countries is heavy crude oil with an API gravity equal to or lower than 20°. The complex composition of these crude oils makes them difficult and expensive to produce and transport through pipelines due to their low mobility and flow near ambient temperature. Also, their high asphaltene and paraffin contents promote pipe clogging, pressure drops, and consequently a lower production rate than lighter crude oils. Various well developed strategies are used to facilitate the transport of heavy crudes, such as dilution with organic solvents, lighter oils, or condensates; heating (and by necessity, thermally isolating) pipelines; and the use of flow improvers and drag reducing additives. Nevertheless,

innovative approaches such as the formation of oil-in-water (O/W) emulsions, known as inverse emulsions within the petroleum community, may contribute as an alternative technology to reduce crude oil's viscosity and increasing flow with only minor operational issues [1].

The formation of O/W emulsions, industrially known as the Orimulsion process [2–4], has proved to be a very reliable method because of its low cost and relative ease in industrial implementation. However, this approach, in which crude oil is transported as drops dispersed in a water continuous phase (20–30% w/w), requires emulsion breakage and water separation before further refining. While there has been fewer studies of O/W emulsions as found in the present article, it is worth mentioning that extensive studies exist on the demulsification of water-in-oil (W/O) emulsions, since emulsion of this type commonly forms during crude oil production and pipelining [5–7].

The presence of emulsions is a common feature in oil processing. Although the formation of emulsions of different types, such

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as W/O, O/W, O/W/O y W/O/W, is possible, the first two are the most common. These are responsible for operational problems such as destabilization and deposition of asphaltenes and paraffin and clogging/blockage and subsequent pressure drops along transport pipes and during drying and desalination processes. In O/W emulsions, water is the continuous phase. This type of emulsion is favored since it effectively carries the otherwise viscous heavy and extra-heavy crude droplets in a far more fluid form through the transport pipes [8–12].

Microwave technology has gained great popularity in recent years owing to its higher efficiency at speeding up most chemical reactions [13]. However, there is still considerable controversy about the action mechanism of microwave dielectric heating with respect to the enhancement of chemical reactions. Some authors attribute such reaction and process acceleration under microwave dielectric heating to the phenomenon known as “specific microwave effect.” This is considered a nonthermal effect of microwaves and generally associated with the selective absorption of energy by polar molecules [14–16]. Another hypothesis states that microwave effect is merely thermal [17,18].

Much attention is focused on the microwave enhancement of chemical reactions and breakage of W/O emulsions because microwave irradiation has demonstrated the ability to accelerate these processes. Although the earlier studies concerning microwave technology for emulsion separation were focused on O/W systems or both O/W and W/O systems [9–12], microwave technology has rarely been considered as a demulsification process of O/W emulsions because this kind of emulsion is an emerging technology for crude oil transportation [19]. Recently, the application of ionic compounds in conjunction with microwave energy was studied in the breaking of W/O emulsions [20,21].

This work discusses the demulsification of an O/W emulsion prepared with a Mexican heavy crude oil and the use of a new ionic glycine-based demulsifier under microwave and oil bath heating. The effects of salt content on the O/W emulsion’s aqueous phase and addition of chemical demulsifier to the water separation fraction were also studied. Finally, fluorescence emission spectra of every initial and treated O/W emulsion were obtained in order to gain further insight about the non-aggregated and aggregated states of the heavy crude oil during the demulsification processes.

2. Experimental section

2.1. Materials and equipment

All reagents were purchased from Aldrich Chemical Co. Microwave experiments were conducted on a CEM Discover Synthesis Unit (Monomode system) operating at 2450 MHz monitored by a PC. The Differential Scanning Calorimetry (DSC) was carried out using a Shimadzu model DSC-60A. Karl Fischer titrator (model Orion AF-8) equipped with a double platinum electrode was employed during the water-content determination tests. Micrographs were taken in a Nikon Eclipse E800 optical microscopy. Particle size determination was performed with a freshly prepared emulsion using a counter and particle size analyzer PPS-Accusizer 780. Zeta potentials of the nanoemulsions were estimated from electrophoretic mobility measurements using phase analysis light scattering (PALS) in the Brookhaven ZetaPALS setup.

2.2. DSC measurements

These assays were carried out under N₂ at a flow rate of 20 mL/min. Every emulsion was precisely weighed (ca. 10 mg) in an aluminum pan which was tightly sealed. The sample’s cooling cycle from 50 to –60 °C was scanned at a rate of –10 °C/min. Emulsion

characterization by DSC was performed twice on the same day that emulsions were prepared.

2.3. Fluorescence spectroscopy

The assays were performed on a RF-5301PC Shimadzu Spectrofluorometer equipped with a 150 W Xe lamp and a cell temperature controller. Emission spectra were recorded between 290 and 410 nm, with an excitation wavelength of $\lambda_{exc} = 280$ nm and a slit width of 3 nm. From each emission spectrum, the slope (m) was determined between 326 and 339 nm. This permits the study of the microenvironment around the fluorophore molecules contained in the heavy crude oil and the effect of demulsifying agents and heating processes [22]. Fixed wavelength data as well as emission spectra were analyzed by means of the panorama software. Appropriate blanks were employed to correct the measurements for any light scattering contribution.

2.4. Crude oil characterization

The sample of heavy crude oil (HCO) utilized in this study was provided by the Mexican Petroleum Company (PEMEX) from a marine well drilled in the south of the Gulf of Mexico. The samples were characterized by the following standard procedures: API gravity (ASTM D-287), Kinematic viscosity (ASTM D-445), salt content (ASTM D-3230), paraffin content (UOP-46), water content (ASTM D-4006), and saturated, aromatics, resins, and asphaltenes (ASTM D-2007) content. Total sulfur was determined in an Antex 9000S, employing the standard procedure ASTM D 5453-05: Standard Test Method for Determination of Total Sulfur in Light Hydrocarbons, Motor Fuels and Oils by Ultraviolet Fluorescence [23]. The cloud points for NPE in salty solutions were determined in accordance with the standard procedure ASTM D 2024-09.

2.5. Preparation of O/W emulsions

Synthetic seawater (total salt content 40,750 ppm, standard method D-1995) was used to prepare O/W emulsions, using commercially available nonylphenol ethoxylate (ethoxyl content 15 mol, NPE) as surfactant. NPE was dissolved in 15 mL of seawater of pH 8 at room temperature to prepare a 1200 ppm solution. This was poured into a jacketed glass reactor with water recirculation at 65 °C. The propeller of the mixer was fixed in order to remain submerged in the aqueous phase. 35 g of HCO was then added to the top of the glass reactor. The reactor and mixer with surfactant seawater solution and HCO were incubated at 25 °C for 10 min. Emulsification proceeded at 8000 rpm for 5 min using an IKA Labortechnik homogenizer. The formation of an O/W emulsion was corroborated by dispersing an emulsion drop in water, DSC analysis, and optical microscopy.

2.6. Emulsion characterization

The initial O/W emulsion was characterized by DSC on the day of preparation. The water content and micrographs were taken before and after each test. The water content reported is the average of three measurements.

2.7. Microwave demulsification tests

The microwave demulsification tests were conducted using sealed-vessels (10 mL) containing 3.0 g of the O/W emulsion. These were separately irradiated from 2 to 60 min at 60 °C without stirring at 60 °C. The reaction temperature was followed by an internal fiber-optic (FO) temperature probe (ruby thermometer) protected by a borosilicate immersion well directly inserted in the reaction

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