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New methodology for heavy oil desalination

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HIGHLIGHTS

- Development of a new methodology to heavy crude oils desalination.
- Monitoring of the desalted crude oil by ionic conductimetry.
- About 99.87% of the salt present in the oil was removed.
- TAN and sulfur content were reduced by around 30% after the desalination process.

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ABSTRACT

The salts present in petroleum interfere in the characterization of its physicochemical properties, and from the measurements of these properties is established the price of crude oil. Therefore the water and salt need to be removed before these analyses. A new desalting apparatus was developed for heavy crude oils desalination by using demulsifier with water. The desalination process is accomplished in several washing steps and the extracted oil salts are monitored by ionic conductivity. Operational conditions were studied before and after the desalting process and the following parameters were evaluated: density, kinematic viscosity, total salinity index, total sulfur, total acid number and ionic conductivity. Using the proposed process it was possible to reduce the chloride content in the crude oil to values lower than 43 mg kg^{-1} of sodium chloride in petroleum with extraction efficiency about 99.87%. After the desalination process it was not observed significant changes in the intrinsic oil properties, and after the fourth wash of the oil there was a reduction of approximately 33% of total sulfur and total acid number content. These results indicate an improvement in oil quality, once the presence of sulfur compounds in the oil is undesirable because it increases the polarity of the oil, thereby increasing the polarity of the emulsions. These compounds are also responsible for the corrosivity of the petroleum products and produce harmful gases during combustion. Variations about 2% in API gravity and 3% in kinematic viscosity were not significant, indicating no change in the physical properties of the oils. The proposed procedure is faster (about 80 min) than the salt extraction method given by ASTM D6470 (about 140 min) for four washing cycles and it was possible to obtain a suitable condition for salt removal from heavy crude oil emulsions without toxic reagents.

1. Introduction

Crude oil is a naturally occurring mixture consisting predominantly of hydrocarbons and organic sulfur derivatives, nitrogen, oxygen and metals, and may usually be accompanied by variable amounts of saline water or produced water, and inorganic gases [1]. The produced water found in the oil must be removed because it usually has a high concentration of salts in its composition and form emulsions with viscosities greater than the dehydrated oil that cause problems such as: changes in the pumping system sizing and transfer, corrosion in the refining towers, fouling in pipelines, higher consumption of chemicals and energy, need of new design of equipment throughout the production process, transportation and refining issues [2,3].

The chemical composition of the salts present in the oils is often found as salts of sodium, calcium and magnesium chloride, in a lower proportion of sulfates. The amount of mineral salts varies according to the geologic formation of the source rock and can be as high as 200,000 mg L^{-1} [4–7]. The processes of water removal

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or dehydration processes also result in removal of salts [7,8]. The water-in-crude oil emulsions for heavy oils (API gravity around 16) are normally more stable than the ones for light oils [3], and separation of liquid phases involves breaking of the emulsion that is a fundamental step for the preparing of oil distillation. Various processes that are used to break the emulsion with removal of water, salts and solids can be mentioned: gravitational separation, electrostatic separation, demulsification, chemical filtration forced by glass wool filter, membrane separation, microwave and ultrasound [5,6,8–11].

In industrial oil processing, the typical water-in-crude oil separation methods are not applied in isolation, they often occur in association with other methods for desalting oil. As an example, we can mention the gravitational separation, which in most cases is used together with the chemical treatment (using demulsifiers) and in some cases heat treatment [4]. The last one includes the application of heat, which has the effect of reducing the kinematic viscosity of the oil and increase the kinetic energy of oil molecules facilitating their separation from water. This facilitates settling and, consequently, salt water separation. Heat also causes changes in the colloidal stability of droplets promoted by emulsifying agents, helping to destabilize the emulsion [4,5]. Another feature is the use of chemical demulsifiers, which adsorb on the water-in-crude oil interface and change its physicochemical properties, promoting coalescence of water droplets. The demulsifiers are nonionic polymeric surfactants which contain a hydrophilic and a lipophilic portion. Hydrophilic are included as parts of ethylene oxides, hydroxyl, carboxyl and amine groups. Among the properties that are sought in demulsifiers it can be mentioned the high speeds of adsorption in oil–water interface, movement of natural emulsifiers that stabilize emulsions and the formation of thin and weak films in the oil–water interface [12,13].

An efficient water-in-crude oil separation method must use heat and some demulsifier to break the emulsion stability. But, it is also necessary to characterize and evaluate the oil through some physicochemical properties such as density (API gravity), kinematic viscosity, total salinity index (TSI), sulfur content, total acid number (TAN) among others. Oil samples with high water content and consequently high amounts of salts render an effective characterization impossible because high concentrations of salts may interfere in the evaluation of physical and chemical properties of the oils [14]. From the measurements of the physicochemical properties is established the price of crude oil, storage and transport conditions.

It is reported that the difficulty of breaking water in oil emulsions of heavy oils is due to the inefficiency of the existing tools for the treatment and monitoring of the salt content in oil. So, it is necessary to make efforts in order to seek how to make the salt extraction process efficient, economic and sustainable [15]. Some laboratory methods are commonly used to extract and quantify salts in oil, as example the method based on titration with silver nitrate by precipitation (Mohr) [14], conductimetry [15] and potentiometric titration [9,16]. These methods are used for the quantification of salt content in oil. However, these methods are not effectively applicable to heavy oils and they are also destructive methods, i.e. using toxic organic or inorganic reagents, generating final product as chemicals waste associated with the oil that is undesirable for the products and the environment [6–9,17]. In this sense, it is necessary to promote the separation of water–oil emulsions and remove the salts present in the heavy crude oils in order to obtain confident results for their physicochemical characterization through the classic methods. Therefore, in this paper we describe a developed apparatus that allows desalting heavy crude oils using washing with deionized water and commercial demulsifiers, under continuous stirring and temperature control. The novelty of this process is the combination of heating control with chemical demulsifiers addition and subsequent removal of water by gravitational separation and simultaneous measurement of the salt content signal by conductimetric technique.

2. Methodology

2.1. Treatment of crude oil samples

In this study, it was used nine heavy crude oils samples from production fields located in the sedimentary basin of the Brazilian coast, identified as "A", "B", "C", "D", "E", "F", "G" , "H" and "I". The oil samples were collected from ducts in 2.0 L flasks and were transported to the laboratory where they were processed within two hour after arrival. The standard method ASTM D5854 [18] was followed for all procedures using one aliquot of the collected crude oils. In the oil characterization process, non-emulsified water in the oil (called free water) is easily separated by applying the gravitational method which requires decanting the oil for one hour. After free water separation, aliquots from oil phase (emulsion) were collected for the characterization procedure before and after desalination process using the developed apparatus shown in Fig. 1. The water content analysis [19] in the oil emulsions was determined. For initial characterization, oils with water content above 1% (v/v) were dehydrated with the addition of 200 μL of a concentrated commercial demulsifier at 60 (±5) °C commonly used in the primary processing of oils and centrifuged at 1600 (±20) rpm for 15 min [5]. These oils were denominated as "dehydrated oils". After removal of water, to verify that the dehydration procedure was effective, the water content in oil emulsion was again determined to verify that the water content was lower than 0.5% (v/v). Then, the physicochemical properties of the dehydrated oils: total salinity index (TSI), API gravity, total acid number (TAN), sulfur content and kinematic viscosity were determined according to the ASTM standard methods.

2.2. Crude oil characterization

2.2.1. Water content

The water content was determined by potentiometric Karl Fischer (KF) titration, in accordance with the ASTM D4377 standard method [19]. The solvent used during the analysis was a

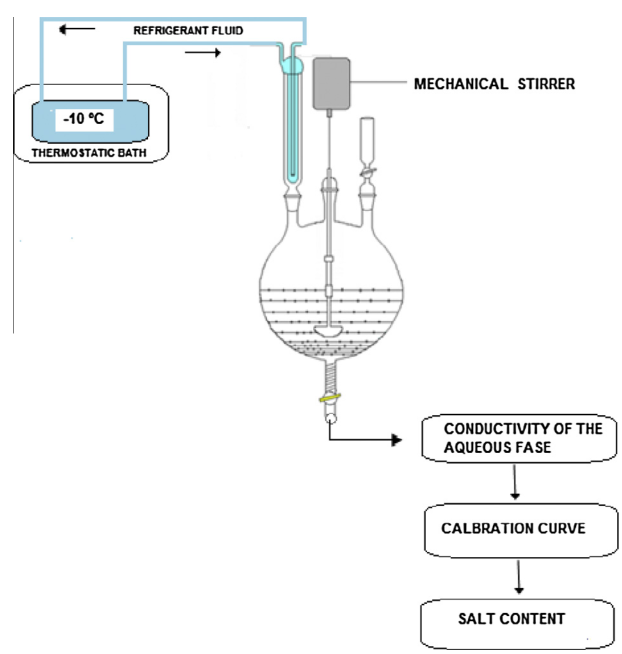

Fig. 1. Desalting apparatus at laboratory.