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Use of near infrared for evaluation of droplet size distribution and water content in water-in-crude oil emulsions in pressurized pipeline

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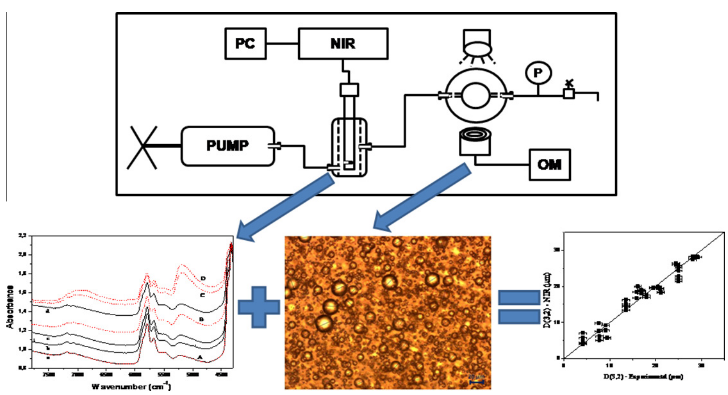
HIGHLIGHTS

- Water/oil emulsions were prepared from Brazilian crude oil.
- DSD was determined by an optical microscope at ambient and pressurized conditions.
- PLS models were built to predict water content and DSD.
- NIR predictions were adequate even in pressurized systems.

GRAPHICAL ABSTRACT



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ABSTRACT

Droplet size distribution (DSD) and water content (WC) are two parameters that affect the type/intensity of treatment of water-in-crude oil (W/O) emulsions in the production fields. Besides, the crude oil viscosity and emulsion stability are strongly dependent of DSD and WC. Several papers have reported different techniques for evaluation of these properties; however, most of them were based on experiments performed at conditions of temperature and mainly pressure far from those found in the production fields. In this work, we demonstrate that optical microscopy and standard PLS models can be combined for calibration of a Near Infrared (NIR) spectrophotometer with regard to DSD of W/O emulsions with different water contents. Additionally, the NIR calibration models were validated considering the prediction of the DSD and WC of a distinct crude oil not used during the calibration step. Then, a new apparatus for online monitoring of W/O emulsions at pressures up to 30 bar is presented. The proposed apparatus employed both techniques (optical microscopy and near infrared spectroscopy) installed in series in the pressurized pipeline. The results indicate that the proposed apparatus is efficient for online monitoring of pressurized emulsions with water contents up to 17 wt% and average diameter (D(4,3)) from 6 to 40 μm.

1. Introduction

Despite the growing concern about environmental problems caused by burning fossil fuels, crude oil is still the most important commodity in the global economy. However, some major oil reser-

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voirs in the world are being depleted, forcing the producers to seek alternatives to increase production capacity, including secondary recovery strategies generally based on the injection of water or gas into the reservoir to maintain or increase the reservoir pressure. Even though water injection schemes are quite successful in enhancing hydrocarbon production, these strategies lead to the generation of large quantities of water-in-oil emulsions [1], which should be separated in the production facilities. Clearly, the efficiency of the separation process is crucial to achieve low levels of water in the treated oil, to ensure the water recovery for reinjection purposes, and to guarantee overall productivity gains.

In order to achieve contaminants specifications in both water and oil phases, a number of separation methods are usually employed, which typically involve settling time, heat, chemicals, electricity or a combination of these methods. Nevertheless, the choice of the proper method and operation conditions of the separation units requires a thorough knowledge of the physical and chemical characteristics of crude oil emulsions and the mechanisms governing the stability of these systems. In addition, separation facilities may be subject to perturbations caused by a number of factors, including water content fluctuations and drifts of temperature and flow rates, among others. For these reasons, it is necessary to include process monitoring instruments in order to provide real-time chemical/physical information, yielding significant improvement of product quality, while minimizing process time.

Real-time monitoring is especially important when pressurized emulsion systems are involved. In this case, sampling procedures should be avoided, because of the difficulty to obtain representative samples and the risk of product characteristics alterations during sampling process [2–4]. Techniques for real-time DSD evaluation based on Focused Beam Reflectance Measurement (FBRM) have been reported in the literature [5–7]. The main advantage related to this tool is the possibility of DSD analyses in opaque systems without the need for sampling or dilution, but only information regarding to physics properties of the sample (as DSD) can be evaluated. Chemical information about the sample under analysis cannot be obtained; besides, all the experiments reported by the abovementioned authors were performed in atmospheric pressure. Thus, the development of a strategy for monitoring petroleum emulsions in pressurized systems remains a gap to be filled.

Near Infrared (NIR) spectroscopy has been successfully used for petroleum products analyses [8–15]. The NIR spectral region comprises the range between 700 nm (14,285 cm^{-1}) and 2500 nm (4000 cm^{-1}) in the spectral region. The increased popularity of the technique is due to its efficiency, simplicity, multiplicity of analysis in a single spectrum and be a non-destructive technique. It should also be considered the rapid development of software for analyzing a large number of variables that assists in the interpretation of spectra and facilitates the use of NIR spectroscopy [16]. Optical fibers can be used to bring the light source to the process stream and bring it back to the detector making it possible to use this equipment for on-line monitoring of processes. It is recognized in the literature that the main advantage of NIR over MIR (mid-infrared) and FIR (far-infrared) is that radiation can be transmitted through optical fiber of silica type, which is relatively inexpensive and available in a variety of types and shapes [17,18].

Besides the molecular absorption, the NIR spectrum depends on several physical parameters. One of the most important is the particle dispersion, because the variation in particle size can cause changes in the amount of radiation scattered by the sample, and this produces an increase in spectra baseline. Due to this fact, the technique can also be applied to determine the physical properties of the sample [16], mainly particle size determinations [18–22]. Recently, NIR spectroscopy was used to predict the average droplet size and water content in water/biodiesel emulsions [23]. The technique showed to be a good alternative to determine the average droplet size and water content in water/biodiesel emulsions with a good potential to application in on-line biodiesel quality control and storage. Araujo et al. (2008) [24] used the Mie theory approach to justify the application of NIR spectroscopy to evaluate the average droplet sizes of W/O emulsions diluted in transparent oil. The authors found experimentally that the increasing of the droplet size yields the NIR spectral signal reduction due to the decrease of the extinction coefficient of the sample, as predicted by the Mie theory for drops between 1 and 100 μm. In the same work the authors presented a measurement setup, including a diluting system equipped with a NIR probe *in-situ*, to predict water content (WC) and volumetric average diameter (D(4,3)) simultaneously. Reliable online predictions of WC and D(4,3) during emulsification runs were provided by the spectrophotometer, even when different crude oils were employed. However, all the experiments were performed at atmospheric pressures.

Despite the flexibility of the NIR technique to analyze both chemical and physical properties, a reliable reference technique is required for each property. The reference techniques are employed in order to obtain NIR calibrations models, generally built by means of multivariate regression techniques. Then, the online implementation of calibration models allows for the in-situ acquisition of process data, consequently allowing for reduction of time delays normally involved with sample preparation.

For DSD analysis of petroleum emulsions, the optical microscopy (OM) is a potential reference technique. The OM technique provides DSD directly from individual droplets measurements, without mathematical data treatment. Another advantage is the ability to examine opaque and concentrated systems without dilution. These characteristics make the OM a standard technique for DSD analysis, and the results provided by others techniques are normally validated with OM data [5,25]. Besides, OM technique can be applied in high-pressure systems if special accessories are employed [22,26]. So, the main objective of this work is to apply optical microscopy technique for calibration of the NIR spectrophotometer with regard to droplet size distribution (DSD) of pressurized water-in-crude oil emulsions with different water content (WC).

2. Experimental section

2.1. Crude oil characterization

The crude oils used in this work were gently provided by Petrobras S.A. and were extracted from two different locations on the Brazilian coast. The main characteristics of these oils are summarized in Table 1.

The crude oil characteristics were determined following the procedures described elsewhere [27]. Briefly, density (°API) data were measured in a digital density meter (Anton Paar, DMA 4500 M). The water content of the crude oil was obtained by the Karl Fischer (KF) reagent method, in accordance with ASTM D-1744 procedures [28]. Asphaltene content was determined

Table 1
Summary of crude oil properties investigated in this work.

Crude oil properties	Oil-O2	Oil-OJ
Density (°API)	19.5	16.8
Water content, wt%	0.21	1.42
Asphaltene content, wt%[a]	2.9	2.3
Viscosity at 25 °C, mPa s	284.0	2070
TAN, mg KOH/g crude oil[b]	1.31	3.35

[a] Defined as the n-heptane-insoluble fraction from the oil.
[b] TAN means total acid number.