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Characterization of polar compounds in a true boiling point distillation system using electrospray ionization FT-ICR mass spectrometry

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HIGHLIGHTS

- We describe the typification of polar compounds of twelve cuts obtained from a true boiling point system.
- We examine changes in the cuts composition by ESI(−) FT-ICR MS analysis.
- A correlation between the composition and TAN, total sulfur and the corrosion process was performed.
- The structures of some naphthenic acids, phenols and pyridines were confirmed using ESI(±)-MS/MS.

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ABSTRACT

In this work, electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI(±)-FT-ICR MS) was applied in the chemical characterization of polar compounds. These compounds were identified as the oxygen-containing compound classes (naphthenic acids, O2 class, and phenols, O1 class), the sulfur-containing compound classes (mainly sulfides, S1 class), and the basic and non-basic nitrogen-containing compound classes (carbazoles and pyridines, N class). For access the sulfur-containing compounds were employed the methylation reactions. As the increasing of distillation cut temperature, the amount of O2 compounds increased (from 9 for cut 2 to 66 for cut 12), and the average molecular weight distribution, M_w, shifted to higher m/z values (M_w = 169 → 321 Da). These results were consistent with the increase of TAN with the boiling point. Plots of the DBE versus the carbon number for the O2 class of heavy distillation cuts (cuts 4–12) suggested a maximum abundance of the carbon numbers located at C_{12}–C_{18} with a constant DBE of 3. For the nitrogen-containing compounds, 100 compounds were detected with m/z ranging from 160 to 414. Similar to O2 class, the amount of nitrogen species increased, and the M_w shifted for high values in function of distillation cut temperature: 6 species and M_w = 206 Da for cut 3; and 64 species and M_w = 340 Da for cut 12. The structures and the connectivity of naphthenic acids, phenols and pyridines were confirmed using ESI(±)-MS/MS. The most abundant sulfur compounds in heavy distillation cuts presented a carbon number of C_{23} (for cut 11) and C_{25} (for cut 12) with constant DBE of 3. Results of ESI(±)-FT-ICR MS contributed to the understanding of the chemical composition of Brazilian crude oil and the establishment of a correlation with the corrosion process.

1. Introduction

The chemical composition of crude oil consists predominantly of hydrocarbon compounds such as naphthenes, paraffins, and aromatic hydrocarbons (~90%). The remainder (~10%) consists of polar compounds containing N, O, and S heteroatoms and metal atoms (only vanadium and nickel exist at concentrations >1 ppm) [1]. Despite the small percentage of polar compounds, approximately 20,000 polar organic compounds with different elemental compositions ($C_cH_hN_nO_oS_s$) have been found in crude oil [2]. These polar compounds sometimes cause problems during the production, refining and storage of petroleum. These problems include corrosion, the formation of emulsions, the poisoning of catalysts,

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coke formation, the development of poisonous and carcinogenic characteristics, and contamination. Oil consumption is continuously growing, which creates the demand to use the limited oil reservoirs and the heavier fractions more efficiently. Therefore, it is extremely important to know the composition of crude oils from different origins to optimize the refining processes.

Among the polar components of petroleum that contain heteroatoms, naphthenic acids and phenols are the two most common oxygen-containing compound classes in crude oil. There are other minor acidic classes, such as aromatic, olefinic, hydroxyl, and dibasic acids [3]. Naphthenic acids are defined as carboxylic acids that include one or more saturated ring structures, with five- and six-membered rings being the most common. In addition to the ring-containing acids, linear carboxylic acids are often included in the naphthenic acid class [4]. Naphthenic acids are known to be a significant source of corrosion in oil-refining equipment [5]. Corrosion is associated with the total acid number (TAN), which is defined as the mass of potassium hydroxide (KOH) in milligrams required to neutralize 1 g of crude oil. However, it has been argued that there is no clear correlation between the TAN and the level of corrosion [6,7].

Recently, there has been growing interest in the chemical characterization of naphthenic acids and sulfur species from crude oils and its distillation cuts because of the problems that these components have caused for the oil refinery business [8]. These compounds induce corrosion in regions of the refineries that operate at temperatures above 100.0 °C. Sulfur compounds are the most notorious and undesirable petroleum contaminants, and a large portion of these compounds can be transferred to diesel oil during refining process. In general, sulfur appears in the form of hydrogen sulfide, organic sulfides and disulfides, benzothiophene, dibenzothiophene, and their alkylated derivatives [9]. Upon diesel combustion, sulfur compounds are converted to sulfur oxides (SOx), which contribute to acid rain and environmental pollution [10]. Although environmental regulation has been applied in many countries to reduce the sulfur levels in diesel and other fuels, sulfur removal still represents a major operational and economic challenge for the petroleum refining industry.

Other well-known polar components in petroleum are the neutral and basic nitrogen species. The non-basic nitrogen compounds usually include pyrrole, indole, carbazole, and their alkylated derivatives, and these compounds correspond to less than 30% of all organic nitrogen compounds [11]. The basic nitrogen compounds include amines, aniline, pyridine, quinoline, benzoquinoline, and their alkylated and hydrogenated derivatives. It is well known that the presence of the nitrogen compounds in liquid hydrocarbon streams, even at very low concentration, strongly deactivates the catalysts that are used in the fuel-refining processes, such as hydrodesulfurization (HDS), hydrodearomatization (HDA), hydrocracking, and reforming [12]. Therefore, the identification and quantification of the various nitrogen compounds and the clarification of their distribution in different liquid hydrocarbon streams are essential to develop either a novel process [13], more efficient catalysts or more efficient adsorbents for the denitrogenation of various liquid hydrocarbon streams and to understand the mechanism in ultradeep HDS, hydrodenitrogenation (HDN), adsorptive denitrogenation (ADN), and extractive denitrogenation (EDN) [14].

Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) offers the highest available mass resolution, mass resolving power, and mass accuracy, which enable the analysis of complex petroleum mixtures on a molecular level [15]. High-resolution MS data have shown that it is possible to discriminate different compounds [16–18] because of the different ionization efficiencies of the crude oil constituents [19]. In this study, one Brazilian offshore acidic crude oil sample (TAN = 3.19 mg KOH g^{-1}) was submitted to primary characterization using a homemade distillation process (where the boiling points changed from 100.4 to 372.9 °C). Twelve cuts and distillation residues were produced and characterized according to the density, TAN, total sulfur and ESI(±)-FT-ICR MS analyzes. The ESI technique is not suitable to detect neutral aromatic compounds such as sulfur compounds. Thus, the methylation reaction was introduced, and the sulfide compounds were converted from the neutral species to methyl sulfonium salts, which can now be easily transferred into the gas phase in the ESI source [20]. Herein, we apply this approach to investigate the sulfur compound species in the heavy-boiling-point cuts and the distillation residue.

2. Experiment

2.1. Reagents

Anhydrous propan-2-ol, toluene, potassium hydroxide (KOH, analytical grades with purity higher than 99.5%), dichloromethane (CH_2Cl_2), and silver nitrate ($AgNO_3$) were used for the TAN measurements and the methylation reactions. These chemicals were supplied by Vetec Química Fina Ltda, Brazil. Ammonium hydroxide (NH_4OH), sodium trifluoroacetate (NaTFA), formic acid (HCOOH), and methyl iodide (CH_3I) were purchased from Sigma–Aldrich Chemicals USA and used for the ESI(±)-FT-ICR MS measurements. All reagents were used as received.

2.2. Petroleum characterization

A sample of offshore oil from Espírito Santo state (ES), Brazil, were collected in 2011 and used in this work. The oil was characterized according to the standards of the American Society for Testing and Materials (ASTM) by Laboratory of Petroleum Characterization of Federal University of Espírito Santo (LabPetro/UFES-Brazil). A primary characterization was conducted to determine the density (ASTM D5002-99) [21], the API degree (ASTM D1298-99) [22], the total acid number (ASTM D664-09) [23], the kinematic viscosity (ASTM D7042-04) [24], and the total sulfur (ASTM D4294) analyses [25]. Because the emulsified water and sediment value was less than 1.0% v/v, it was not necessary to dehydrate the crude oil sample. The data obtained from the characterization of crude oil are as follows: density = 0.9541 g cm^{-3}, API degree = 16.2, TAN = 3.19 mg KOH g^{-1}, viscosity = 150.45 cSt, at 40 °C, and total sulfur = 0.60 wt% (these information are described in more detail in Table 1).

2.3. True boiling point distillation

A homemade distillation process was implemented in accordance with ASTM D 2892 (Standard Test Method for Distillation of Crude Oil) [26] by LabPetro/UFES (Fig. 1). In general, the laboratorial distillation process (homemade) has the basic principle of operation adopted by the Petroleum Refinery Industry. The main differences relate to loading the crude oil (the refinery operates in a continuum mode, whereas the laboratorial process has been conducted in batches). In other words, the furnace is replaced by a glass flask (Fig. 1). In addition, the differences are related to the heating rate (in the laboratorial process, the heating rate is controlled by an electric mantle).

In the homemade distillation system, the process starts by submitting the dehydrate crude oil to a heating rate (from a distillation flask, see to scheme shown in Fig. 1). The light fraction is vaporized and separated by a column fractionation that contains approximately fourteen to eighteen theoretical plates. After liquefying the gases, the cuts of distillation (from gasoline to diesel) and