Study of degradation of acid crude oil by high resolution analytical techniques

Eliane V. Barros[a,b], Heloisa P. Dias[b], Alexandre O. Gomes[c], Rayza R.T. Rodrigues[a], Robson R. Moura[c], Cristina M.S. Sad[d], Jair C.C. Freitas[d,e], Alvaro C. Neto[a], Gloria M.F.V. Aquije[f], Wanderson Romão[a,f,*]

[a] Petroleomic and Forensic Laboratory, Chemistry Department, Federal University of Espírito Santo, 29075-910 Vitória, ES, Brazil
[b] Federal Institute of Education, Science and Technology of Espírito Santo, 29056-255 Vitória, ES, Brazil
[c] CENPES, Petrobras, 21941-598 Rio de Janeiro, RJ, Brazil
[d] Laboratory of Research and Development of Methodologies for Analysis of Oils (LabPetro), Chemistry Department, Federal University of Espírito Santo, 29075-910 Vitória, ES, Brazil
[e] Laboratory of Carbon and Ceramic Materials, Department of Physics, Federal University of Espírito Santo, 29075-910, Vitória, ES, Brazil
[f] Federal Institute of Education, Science and Technology of Espírito Santo, 29106-010 Vila Velha, ES, Brazil

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ABSTRACT

The extraction and refining process of unconventional oils, including heavy and extra heavy oils, has been a challenge to be overcome in the petrochemical industry. These oils typically comprise polar compounds responsible for some undesirable properties, such as naphthenic acids (NAs), which can be associated with the high corrosion rates in refineries. In this context, corrosion caused by NAs is among the most aggressive ones, and it can be accentuated when in presence of other compounds usually found in oil. Herein, a heavy oil sample was subjected to thermal degradation process at 350 °C aiming the understanding of its behavior at the molecular level and to evaluate its physicochemical properties as a function of degradation time. Additionally, the oil was characterized by classic and high resolution analytical techniques. The obtained results showed that the oil exposed to longer degradation times (t≥24 h) presented characteristics of "lighter" oil due to mainly disaggregation of resins and asphaltenes. Total Acid number (TAN) analysis displayed a decrease of 68.3% (from 2.0 to 0.75 mg KOH g^{-1}) of its initial value after 36 h of degradation at 350 °C. Other important changes observed included an increase in API gravity (of two decimal places from 17 to 19), and decreases in the pour point from −12 to −36 °C, in the kinematic viscosity in 86.5% and of total sulfur content in 5.2% (from 0.58 to 0.55 wt%). The HTGC and NMR results showed that the saturated fraction is not affected during the thermal stress process, whereas a subtle increase in the number of aromatic compounds was observed as a function of degradation time. This behavior can be attributed to the disaggregation of resins and asphaltenes as well as to the decarboxylation process. The last process was confirmed by ESI(-)-FT-ICR MS, where a reduction of average mass molar distribution from 466 to 450 Da was observed.

Introduction

The increasing worldwide production of unconventional, heavy and extra heavy oils has been a challenge to be overcome in the petrochemical industry. In general, heavy crude oils have around ~85–90 wt % of hydrocarbons and ~10–15 wt% of polar and moderately polar compounds, which can contain heteroatoms (nitrogen, oxygen and sulfur) and metals (vanadium, iron and nickel) (Mapolelo et al., 2011). Among the polar species present in the crude oil, carboxylic acids (O_2 class) stand out for being associated with the formation of emulsions and naphthenate deposits (Mapolelo et al., 2011) and also are considered the main responsible for the corrosion in oil refineries (Mapolelo et al., 2011; Head et al., 2003; Rowland et al., 2014; Terra et al., 2014).

Corrosion caused by naphthenic acid (NA), or naphthenic corrosion, is among the most aggressive ones and can be enhanced by the presence of other compounds commonly found in oil such as: sulfur compounds, carbon dioxide, chlorides, heavy metals and byproducts of the refining process (Dias et al., 2014).

The amount of NA is usually expressed in terms of the total acid

number (TAN), which is defined as the quantity of potassium hydroxide, in milligrams, needed to neutralize one gram of oil. Refineries are seeking strategies to minimize the effect of the acids, due to fact that oils with TAN > 0.5 mg KOH g^{-1} can cause problems in the refining process, especially in the temperature range at 220–440 °C (Tozzi et al., 2015; Laredo et al., 2004).

Despite the fact that NAs can represent up to 4 wt% of crude oil and are important in the corrosion process in the oil refining, the NA corrosivity of an oil is not always directly related to the its respective TAN value (Headley et al., 2009). The naphthenic corrosion process is complex and can be influenced by the presence of various sulfur species (thiols, mercaptans, *etc.*) and acids with different concentration, molecular structure and molar mass (Laredo et al., 2004; Headley et al., 2009). Studies show that oils of higher thermal evolution degree have better acidity behavior, since mature oils contain less polar compounds (Vaz et al., 2013).

A possible alternative for maturation (or aging) of oil is the process of thermal stress, during which the oil is subjected to sufficiently high temperatures that promote thermochemical reactions (thermal degradation) at a short time with the aim of reducing the concentration of polar compounds (comparing to the naphthenic degradation) and to form light hydrocarbons (Vaz et al., 2013). In addition to the decarboxylation of NA (or elimination of CO_2), this process can cause deamination (loss of nitrogen compounds) and desulfurization (loss of sulfur compounds) (Vaz et al., 2013).

In 2014, Dias et al., (2014) evaluated the thermal degradation *via* the decarboxylation of NA at 350 °C and t=6 h, where a reduction of 80% of TAN value was reached. However, other parameters may provide useful information about the origin and historical evolution of the oil (intrinsic characteristics). Among these parameters, there are: (a) API gravity, which is a hydrometric scale from the American Petroleum Institute (API) used to measure the relative density of oil; (b) the pour point, defined as the lowest temperature at which the oil does not flow under the action of gravity, which can be used to indicate the predominance of oil constituents (Tozzi et al., 2015); (c) kinematic viscosity, which allows predicting conditions related with transfer and processing activities (Tozzi et al., 2015); and (d) sulfur content, which indicates the total amount of sulfur and, depending on the concentration or the type of compounds, might act as agent or inhibitor of corrosion (Yépez, 2005).

The complexity of the composition of the oil and the presence of several polar species limit the chemical information provided commonly by classic physicochemical properties such as API gravity, viscosity, *etc.* Thus, it is important to investigate the use of new analytical techniques to study and characterize these matrices.

Chromatographic methods have been considerably used in the study of these materials. High temperature gas chromatography (HTGC) provides a better resolution than liquid chromatography (LC) for the analysis of saturated compounds; however, it is limited to volatile compounds with boiling point < 330 °C (Rowland et al., 2014; Smith et al., 2007). Nuclear magnetic resonance (NMR) spectroscopy is a powerful analytical tool to determine molecular structure of organic compounds, enabling the identification of different types of carbon and hydrogen atoms present in alkyl groups and in aromatic systems (Gruber et al., 2012; Damasceno et al., 2014; Barbosa et al., 2016). NMR is particularly important to characterize samples of high molecular weight, for instance, asphaltenes, resins, vacuum residues and crude oil (Poveda and Molina, 2012). Besides the NMR technique, Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) enables the characterization of all chemical constituents of oil according to their interactions and reactivity (Marshall and Rodgers, 2004). FT-ICR MS coupled to electrospray ionization (ESI) redefined the analysis of composition of crude oil and its fractions, leading to a new field of study named of petroleomics (Vaz et al., 2013). ESI-FT-ICR MS is able to detect polar species, identifying more than 20,000 distinct compounds ($C_cH_hN_nO_oS_s$), simultaneously, using a minimal

amount of sample and also to characterize the material according to the distribution of class of heteroatoms as well as by aromaticity degree or double bond equivalent (DBE) (Vaz et al., 2013; Marshall and Rodgers, 2004). Particularly, ESI(-) produces negative ions deprotonation ([M-H]$^-$ ion), which is an efficient form to ionize polar species (especially NA) (Rowland et al., 2014; Vaz et al., 2013).

The present study evaluates the naphthenic degradation of an acid heavy oil sample subjected to thermal degradation at 350 °C during different times, using both classical (API degree, viscosity, TAN, total sulfur content, mercaptans, *etc.*) and modern analytical techniques (HTGC NMR and ESI(-)-FT-ICR MS) to understand the behavior of an acid oil in face of a thermal stress process (or maturation).

Materials and methods

Chemicals

All chemicals employed were of analytical grade (purity higher than 99.5%). Toluene, propan-2-ol and potassium hydroxide, Vetec Fine Chemicals Ltda, were used for the TAN analysis. Carbon disulfide (HPLC grade) was used for HTGC analysis, and dichloromethane-d$_2$ (99.5 atom % D, contains 0.03 wt%, TMS), and chromium(III) acetylacetonate for the NMR analysis. Finally, Stearic acid, methanol, ammonium hydroxide (supplied by Sigma–Aldrich Chemicals, USA) were used for FT-ICR MS analysis.

Characterization methods

In this study, one heavy crude oil sample (S$_0$) was selected from a production field located in the sedimentary basin of the Brazilian coast. It was analyzed in the Laboratory of Research and Development of Methodologies for Analysis of Oil (Labpetro) – Department of Chemistry (DQUI) of the Federal University of Espírito Santo (UFES), following the American Society for Testing and Materials (ASTM) standards (Sad et al., 2014):

Water content – The water content was determined by the Karl Fischer (KF) reagent method, in accordance with ASTM D4377 standard procedures (ASTM International, 2006). The solvent used during the analysis was a mixture of dry methanol and chloroform (20% v/v). For standardization of the KF reagent, distilled water was solubilized into the solvents. A Metrohm KF titrator (model 836 Titrant) equipped with a double platinum electrode was employed during the water content analysis. The ASTM D4377 standard covers results in the range of 0.02–2% v/v of water in oil.

API gravity – API gravity of the samples was determined according to ISO 12185-96 standard (International Organization for Standardization ISO, 1996). Density was determined by injecting a sample into the digital automatic densimeter analyzer from Anton Paar model DMA 5000. The measurements were conducted at 40 and 50 °C and then the value at 20 °C was estimated for calculating the API gravity.

Pour point – The maximum pour point was determined according to ASTM D5853 standard (ASTM International, 2011a) in a 531/S PETROTEST semi-automatic pour point tester with five test cameras containing four dependent test cells with an applicability range from 20 to 69 °C. The samples were manually homogenized under stirring for approximately 2 min, and then they were transferred to the test flask at controlled temperature of 5 °C. The test flask containing the sample was left to rest at room temperature for 24 h to achieve equilibrium between the crystallized wax and dissolved wax. After this period, the test flask was heated to 45 °C for 15 min in an oven. To stop the resting period, the sample was slightly stirred with a glass rod, and the walls of the flask were carefully rubbed. The test flask was then inserted in the measurement chamber, and the test started by lowering the temperature. For every temperature decrease of 3 °C, the content of the test flask was poured at an angle of 90° to observe the fluidity of the sample.