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Monitoring the liquid/liquid extraction of naphthenic acids in brazilian crude oil using electrospray ionization FT-ICR mass spectrometry (ESI FT-ICR MS)

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HIGHLIGHTS

- Non-continuum liquid–liquid extraction of naphthenic acids at different pHs from two crude oil samples.
- The residue and the acid fraction were characterized using ESI(−) FT-ICR MS, FTIR and sulfur analysis.
- We observe a decreasing TAN in the original oil with increasing pH (7 → 14), reaching a value of almost zero at pH 14.
- The most abundant naphthenic acids extracted are those with short alkyl chain lengths (<C44) and DBE = 3–4.

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ABSTRACT

Although the term "naphthenic acids" was originally used to describe acids that contain naphthenic rings, today this term is used in a more general sense and refers to all cyclic, acyclic, and aromatic acids in crude oil. In crude oil, naphthenic acids exist as a complex mixture of compounds with broad polydispersity with respect to both molecular weight and structure. Recently, there has been increasing interest in acidic fractions in crude oil because of the corrosion problems that these compounds cause during oil refinery. This corrosion is associated with the total acid number (TAN). However, it has been argued that there is no clear correlation between the TAN and the level of corrosion. Herein, naphthenic acids were extracted from two crude oil samples (TAN = 4.95 and 3.19 mg KOH g^{-1}) using liquid/liquid extraction with alkaline solutions at three different pHs (pH 7, 10 and 14), thus evaluating the efficiency and selectivity among different acidic extraction methods to prevent future corrosion processes in petroleum industry such as regions of the refineries working. The original oil samples and their naphthenic acidic fractions and residues (washed oil from the acidic extraction) were analyzed using negative-ion electrospray ionization (ESI) Fourier transform ion cyclotron mass spectrometry (FT-ICR MS) and Fourier transform infrared spectroscopy (FTIR). The TAN and sulfur content were also determined. We observe a decreasing TAN in the original oil with increasing pH (7 → 14), reaching a value of almost zero at pH 14. Consequently, an intense band at approximately 1700 cm^{-1} was observed for the naphthenic acidic fraction. Fractions produced ESI(−)-FT-ICR MS spectra with average molecular weight distribution, M_w, and m/z values ranging from m/z 200–350 and $M_w = 270$ (for pH 7) to m/z 200–650 and $M_w = 390$ (for pH 14). Therefore, the acidic extraction method at pH 14 was more efficient and the ESI FT-ICR MS analysis reveals that the most abundant naphthenic acids are those with short alkyl chain lengths (<C_{44}) and DBE = 3–4. We associate these compounds as responsible for the TAN observed for the original oil.

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

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

Among the polar components of petroleum containing 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 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].

Crude oil contains both neutral and basic nitrogen compounds. Neutral nitrogen compounds include, for example, carbazoles, indoles, and pyrroles and correspond to less than 30% of all organic nitrogen compounds [7]. Basic nitrogen compounds include, for example, pyridine and quinoline derivatives. Nitrogen compounds are harmful in oil refining because they decrease the efficiency of catalytic processes and increase product instability during storage [8].

Recently, there has been growing interest in the chemical characterization of naphthenic acids and the acidic fractions of crude oils due to the problems that these components cause for the oil refinery business [9]. Naphthenic acids are predominantly found

Table 1
The TAN and sulfur content of the two crude oil samples and their respective residual oils.

Sample	TAN (mg of KOH/g)	Reduction in the TAN (%)	Sulfur (%)
Crude oil I	4.95	0	0.97
Residual oil I – pH 7	3.79	23	0.93
Residual oil I – pH 10	3.08	38	0.93
Residual oil II – pH 14	0.40	92	0.71
Crude oil II	3.19	0	0.59
Residual oil II – pH 7	2.27	29	0.59
Residual oil II – pH 10	2.28	28	0.58
Residual oil II – pH 14	0.46	85	0.51

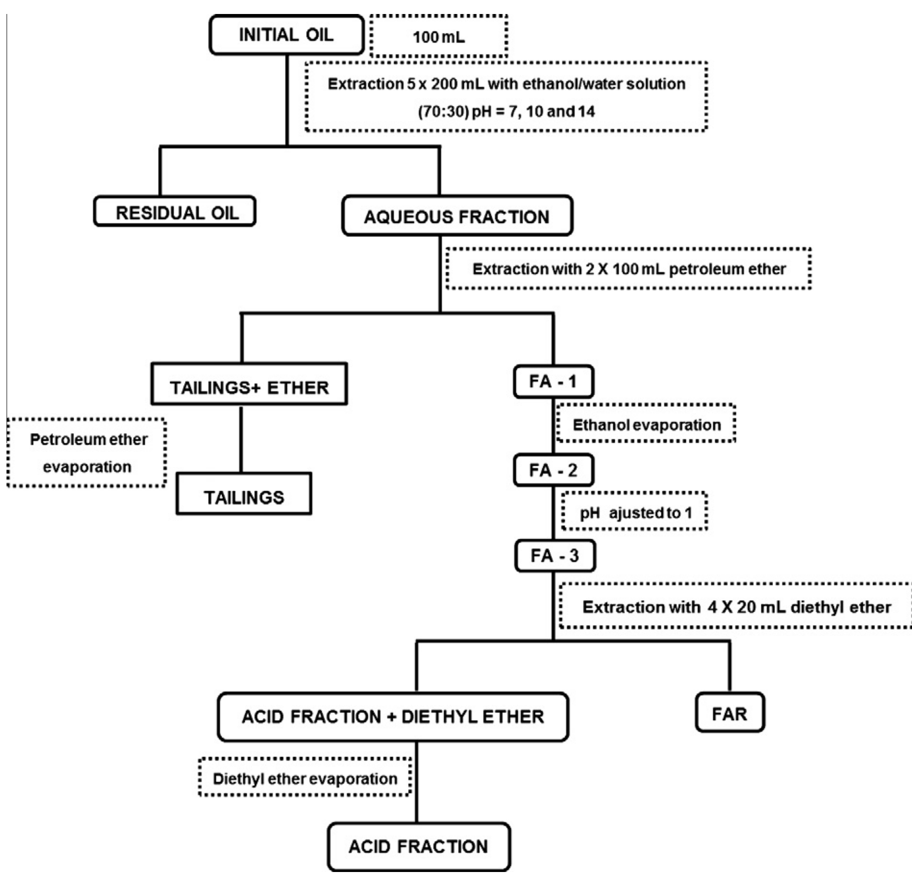

Fig. 1. Scheme of the liquid–liquid extraction of naphthenic acids. (FA – fraction acid, FAR – fraction acid residue).