CHEMICAL ENGINEERING TRANSACTIONS

VOL. 57, 2017

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Sauro Pierucci, Jiří Jaromír Klemeš, Laura Piazza, Serafim Bakalis

ISBN 978-88-95608- 48-8; **ISSN** 2283-9216

Chemical Characterization of Polar Species in Colombian Vacuum Residue and Its Supercritical Fluid Extraction Subfractions Using Electrospray Ionization FT-ICR Mass Spectrometry

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Compositional changes of Colombian vacuum residue and its supercritical fluid extraction fractionation (SFEF) subfractions were analysed by positive- and negative mode electrospray (ESI) coupled with Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR MS). The results showed different distribution of compounds among the SFEF subfractions. The most dominant classes were the nitrogen compounds N_1 and the SFEF end-cut showed to be enriched in multi-heteroatom species. Detailed analysis of double bond equivalent (DBE) distribution revealed that pyridine compounds were more aromatic than pyrrole ones. Planar limit indicated high condensation degree of carboxylic acids species. Therefore, this work evidenced the utility of SFEF fractionation and ESI FT-ICR MS in the detailed characterization of polar compounds in vacuum residua.

1. Introduction

Petroleum has established as the most important and versatile natural resource available for fuel generation and wide variety of products (Hsu et al., 2013). This substance is a complex mixture of thousands of chemically distinct compounds, which define its physicochemical properties (Klein et al., 2006a). Due to global decline of light oil reserves, heavy oil fractions as vacuum residua have become an alternative for refineries obtaining high value-added products. However, their processing presents important difficulties because of their high content of aromatic rings and enrichment in heteroatoms. This problem becomes visible through coke formation and catalyst poisoning (Liu et al., 2013).

Thousands of tons of vacuum residua are generated annually by refineries. These can be better exploited if their composition and chemical behavior is known, allowing to develop appropriated conversion processes (Müller at al., 2005). The conventional characterization of this type of complex samples involves multiple steps of chemical separations, in order to reduce the number of compounds present and thus simplify their identification (Marshall et al., 2004).

Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) has emerged in recent years as the most common technique for analyzing detailed composition of petroleum samples, essentially avoiding long and tedious separation processes. This technique offers high resolving power and mass accuracy, which allows an unambiguously assignment of molecular formula (Pakarinen et al., 2007).

Type of compounds detected in samples by FT-ICR MS depends on the ionization source used. The electrospray (ESI) ionization technique is used for selective ionization of polar molecules present in petroleum (Marshall et al., 2008), very convenient due to the high heteroatom content present in heavy oils.

Fractionating petroleum samples are commonly used, one of them is called supercritical fluid extraction and fractionation (SFEF), which can obtain high yields and allows better characterization of the vacuum residue because it reduces the high complexity of heavy oils (Parra et al., 2010).

This work characterizes a Colombian vacuum residue through its SFEF subfractions, using as the analytical technique of choice FT-ICR MS coupled to ESI source, to explore the different polar chemical species existing in the vacuum residue and note the advantage of fractioning this kind of complex samples.

2. Materials and Methods

2.1 Samples

Vacuum residue (VR) was obtained from Colombian crude oil. Five cuts were derived from VR subjected to SFEF separation. The supercritical solvent was n-hexane and the operating conditions were 265 °C and four different pressures 4.5, 5.5, 6.5 and 7.5 MPa. A subfraction was collected for each programmed pressure and an unextractable end-cut. The SFEF process mentioned in this work has been described elsewhere (Parra et al., 2010). Table 1 summarizes some bulk properties of the VR and its subfractions.

Table 1: Properties of the vacuum residue and its subfractions

	Vacuum residue (VR)	4.5 MPa (S1)	5.5 MPa (S2)	6.5 MPa (S3)	7.5 MPa (S4)	End-cut (S5)
Yield (wt %)		12.57	22.38	23.74	14.49	26.82
Density (g/cm^3)	1.0251	0.9766	0.9838	0.9897	1.0030	1.1296
Sulfur (wt %)	1.85	1.45	1.52	1.64	1.68	2.52
Carbon residue (wt%)	19.50	6.01	8.60	11.77	15.16	55.20
Saturates (wt %)	11.63	35.40	23.01	14.15	8.90	8.75
Aromatics (wt %)	46.34	50.70	59.23	57.70	58.99	24.77
Resins (wt %)	37.12	13.1	17.04	27.91	31.55	17.07
Asphaltenes (wt %)	4.91	0.70	0.73	0.24	0.56	49.41

2.2 ESI FT-ICR MS analysis

Mass spectra were obtained using a Bruker SolariX 15 T FT-ICR mass spectrometer (Bruker Daltonics, Billerica, MA) equipped with a commercially available electrospray source. VR and its subfractions were diluted in 40:60 (v/v) toluene/methanol to yield a 0.05 mg/mL solution (samples S1, S2 and S3), and 0.10 mg/mL (samples S4, S5 and VR). Acetic acid was added (10 µL to each 1 mL of sample solution) to facilitate protonation of basic compounds by positive ion mode, and for negative ion mode, ammonium hydroxide was added (10 µL to each 1 mL of sample solution) to promote deprotonation of acidic compounds. Prepared solutions were directly infused at a flow rate of 300 µL/h. Nitrogen was used as the drying and nebulizing gas. The typical ESI conditions were: a drying gas temperature of 200 °C with a flow rate of 4.0 L/min; a capillary voltage of 3000-4000 V; an ion accumulation time in the collision cell of 0.010 s which was followed by a time-of-flight of 0.1 s to transfer the ions to the ICR cell. Time-domain transient signals were accumulated and averaged (100 scans) to enhanced the signal-to-noise ratio of each spectrum in four mega data size.

FT-ICR mass spectra were initially externally calibrated using a 0.05 mg/mL NaTFA solution, and then externally calibrated using a set of extended homologous alkylated nitrogen compounds abundant in the samples within the mass range of 300-1200 Da. Mass spectra were processed using custom software, PetroOrg (The Florida State University). Molecular formulas were determined on the basis of the m/z values. From the elemental composition ($C_cH_hN_nO_oS_s$) it is possible to obtain the double bond equivalents (DBE) according to Eq(1), where c, h and n are the numbers of carbon, hydrogen, and nitrogen atoms, respectively. DBE is defined as the number rings plus the number of doubles bonds in a chemical structure. The degree of aromaticity of a compound can be related directly to its DBE value.

$$DBE = c - h/2 + n/2 + 1 \tag{1}$$

3. Results

The heteroatom class distribution obtained from positive and negative-mode ESI FT-ICR analyses are shown in Figure 1 and Figure 2, respectively. Only heteroatom classes with considerable relative abundance (≥1%) are presented. Basic polar compounds were detected by positive-ion ESI FT-ICR and high abundance of N_1 class predominates in the distributions of all samples, which can be associated to pyridine-like structures. Pyridine motion would also be present as part of di-heteroatom classes as N_1O_1 and N_1S_1, as well as for triheteroatom class $N_1O_1S_1$. For N_2 class, at least one of the two nitrogen atoms in pyridine form is possible, so also these species could contain two pyridine rings. The SFEF separation allowed detecting new classes such as O_1S_1 and N_2S_1 which were undetectable in the whole vacuum residue.

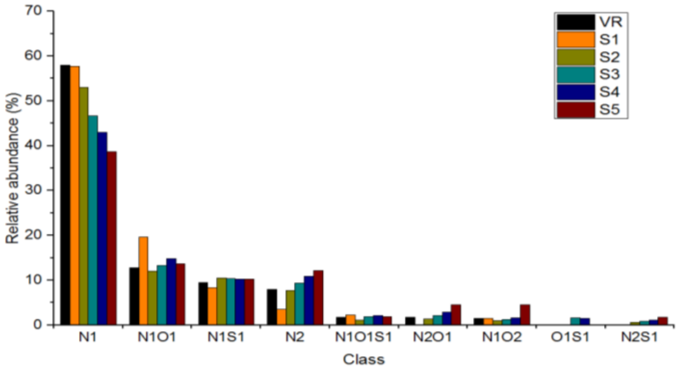

Figure 1: Heteroatom class distribution for vacuum residue and its subfractions from positive-mode ESI FT-ICR MS

Negative-mode ESI FT-ICR offers a selectively ionization of acid compounds and non-basic nitrogen compounds. Although the N_1 class species are the predominant compounds like that observed for positive-mode ESI, in this case, they presumably contain pyrrole-like structures, which would also be present in the other classes with one nitrogen atom. The O_2 class showed a noticeable abundance in all samples, suggesting that the molecular structure of these compounds contain carboxylic acid groups. Oxygen-only compounds are highly predominant in the end-cut (S5), namely, S5 subfraction concentrate most of the carboxylic acid species present in the vacuum residue. Note that O_1 class is detected, corresponding to phenolic analogue species.

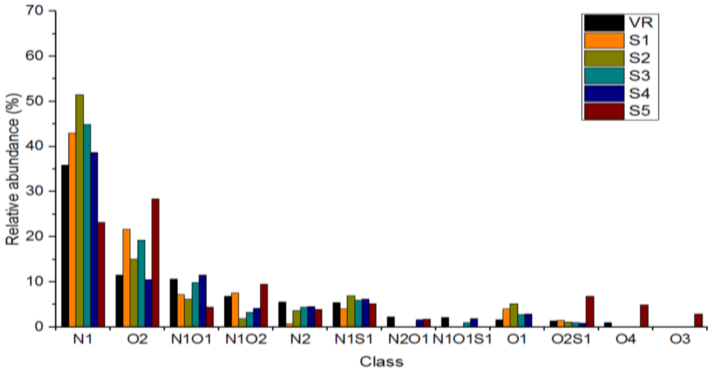

Figure 2: Heteroatom class distribution for vacuum residue and its subfractions from negative-mode ESI FT-ICR MS

Double bond equivalent (DBE) distribution for classes can provide further detailed molecular information, providing evidence about aromatic and/or naphthenic rings attached to alkyl chains. Figure 3 and Figure 4 display the DBE distributions obtained for the VR and its fractions for N_1 class from (+) ESI and (-) ESI respectively. It is possible to note that basic and non-basic nitrogen compounds contain more aromatic cores as the subfraction became heavier. However, pyrrole derivatives (non-basic) distribute a narrower range of DBE values than pyridine structures (basic). The simplest species detected can be tetrahydroquinolines (DBE= 5) for basic compounds and tetrahydrocarbazole (DBE= 7) structure for non-basic compounds.

It is known that the type of nitrogen compounds contained in petroleum samples is important due to the participation of these species in deactivation of catalysts used in hydrotreatment processes (Furimsky et al., 1999). It has been established that the nitrogen removal pathway involves saturation of nitrogen aromatic rings prior to breakdown of carbon-nitrogen bond (Klein et al., 2006b). This could indicate a highly resistance to denitrogenation for the end-cut (S5) due to contain structures with several aromatic rings.

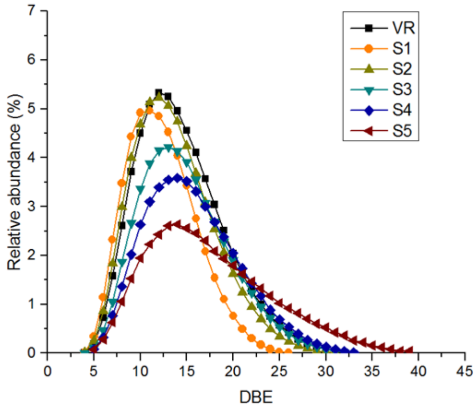

Figure 3: DBE distribution for N_1 class from positive-mode ESI FT ICR MS

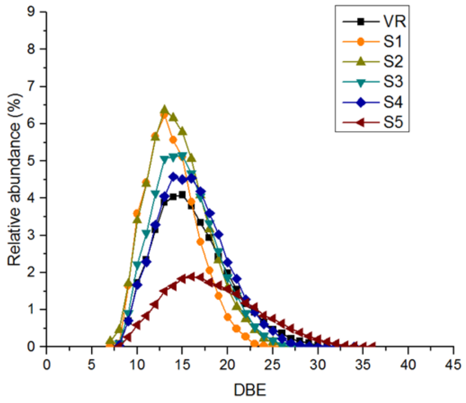

Figure 4: DBE distribution for N_1 class from negative-mode ESI FT-ICR MS

DBE distributions for other classes with nitrogen atoms derived from (+) ESI and (-) ESI, present trends similar to those exhibited by N_1 classes, where pyridine-like compounds are in a wider range of DBE than those obtained for pyrrole species. Table 2 shows the distribution range for N_1O_1, N_1S_1 and N_2 classes for the vacuum residue, taking into account contribution of its subfractions.

Table 2: Range of DBE for some nitrogen-containing classes for the vacuum residue.

	(+) ESI	(-) ESI
N_1O_1	4 - 38	8 - 30
N_1S_1	6 - 38	9 - 33
N_2	8 - 40	10 - 32

Among the compounds of interest in characterization of vacuum residua are carboxylic acids, which are related to corrosion in refining units, increasing costs to process acid petroleum (Barrow et al., 2004). These oxygen compounds can be selectively ionized by negative-mode ESI, being grouped into O_2 class. In the vacuum residue the O_2 and N_1O_2 classes were detected with considerable abundance. The DBE distribution obtained for these classes is shown in Figure 5 and Figure 6.

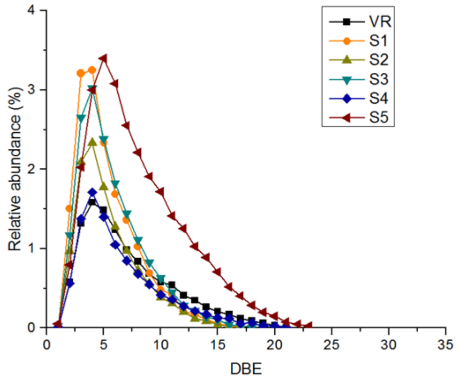

Figure 5: DBE distribution for O_2 class from negative-mode ESI FT ICR MS

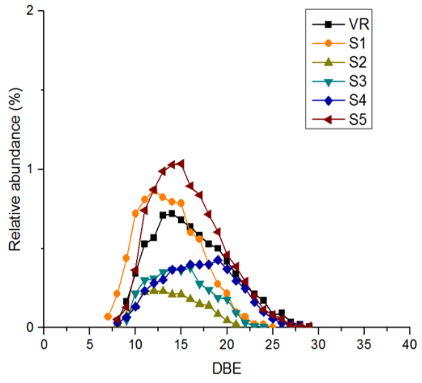

Figure 6: DBE distribution for N_1O_2 class from negative-mode ESI FT-ICR MS

If the class O_2 is associated with carboxylic acids, the compounds detected at DBE less than 4 would correspond exclusively to naphthenic acids derived from cyclohexanoic and cyclopentanoic acids. From DBE 4 to 24 it is possible contain aromatic carboxylic acids, involving complex structures with several aromatic rings. For the case of N_1O_2 class, although there is absence of compounds constituted only by cycloaliphatic acids, these species within the range of DBE 7 – 29 can be associated to naphthenic-aromatic acids. Note that in this case, the nitrogen can exist either as pyridine or pyrrole form, for example, DBE 7 may be associated to an indole carboxylic acid.

It is common to related O_2 class with carboxylic acids, but the presence of compounds that contain hydroxyl groups (R-OH) which can be found as phenols or saturated alcohols is also feasible (Wang et al., 2013). This fact makes possible that diols such as naphthalenediol derivatives (DBE= 7) can be present in the vacuum residue.

Data obtained by FT-ICR may be related with structural information of components in crude oils. The planar limit is a recent concept proposed to understand the molecular structure of petroleum compounds. The planar limit has been defined as the imaginary line generated by connecting the highest DBE values for a given carbon number in a plot of DBE versus carbon number obtained from FT-ICR data (Figure 7), where the corresponding slope is related to the condensation degree of species (Purcell et al., 2010). It has been reported how this slope varies from a saturated to an asphaltenes fraction of a crude oil, found slope values of ≈ 0.3 and ≈ 0.9, respectively. The slopes calculated for the most abundant classes detected in the vacuum residue and its fractions are shown in Table 3.

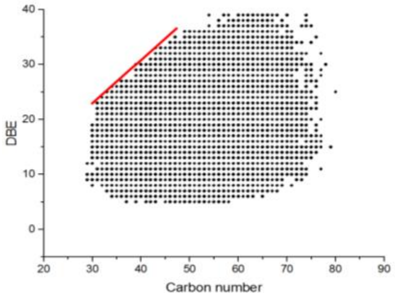

Figure 7: Planar limit (red line) on a plot of DBE versus carbon number for N_1 class from positive-mode FT-ICR MS

Table 3: Slopes of planar limit of N_1 and O_2 classes.

	VR	S1	S2	S3	S4	S5
N_1 (+) ESI	0.54	0.45	0.53	0.55	0.60	0.68
N_1 (-) ESI	0.65	0.50	0.51	0.53	0.66	0.67
O_2 (-) ESI	0.69	0.45	0.57	0.66	0.73	0.74

The slope results indicate the presence of more condensed structures as the subfraction become heavier. Therefore, each subfraction contains compounds with different condensation degree. The condensation degree increases as S1 < S2 < S3 < S4 < S5. These results are in agreement with the highest potential of coke formation for S5 sample, which is consistent with the carbon residue percent (%CCR) obtained (Table 1). Comparing between classes, carboxylic acid structures exhibit high condensed compounds compared to pyridine- and pyrrole-like species.

4. Conclusions

Positive- and negative- mode electrospray FT-ICR MS allowed selective ionization of polar compounds of Colombian vacuum residue and its SFEF subfractions. It was possible to identify chemical compositional differences between the subfractions, being likely even the detection of compounds not found in the unfractionated vacuum residue. The nitrogen-containing compounds were the most predominant in the vacuum residue. Among these nitrogen classes, the N_1 class species were the most abundant. Pyridine-like structures exhibited wider range in aromatic ring content than pyrrole compounds. Moreover, acid species with two oxygen atoms were identified likely derivatives of carboxylic acids and phenols. The end-cut showed to be enriched in multi-heteroatom compounds attributed to the concentration of asphaltenes in this subfraction, also, this subfraction content the most condensed aromatic compounds derived from the vacuum residue.

SFEF fractionation combined with FT-ICR MS provide a potential tool for the understanding of the molecular composition of the vacuum residue. Although the results obtained in this work are characteristic of a vacuum residue available only in a specific region of the world, these findings can be compared with the characterization of other vacuum residua in order to determine compositional differences or similarities that explain their particular properties.

Acknowledgments

The development of this work was supported by the Research Agreement No 5211770 Universidad Industrial de Santander – ICP (ECOPETROL S.A.) and COLCIENCIAS under the project No. FP44842-039-2015. Juan Arenas-Diaz and Diana Palacio thank to COLCIENCIAS for the Graduate Fellowships.

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