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SEPARATION AND CHARACTERIZATION OF ASPHALTENIC SUBFRACTIONS

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The structure of the various asphaltenic subfractions found in crude oil was evaluated. For this purpose, C5 asphaltenes were extracted from an asphaltic residue using n-pentane as the flocculant solvent. The different subfractions were isolated from the C5 asphaltenes by the difference in solubility in different solvents. These were characterized by infrared spectroscopy, nuclear magnetic resonance, X-ray fluorescence, elementary analysis and mass spectrometry. The results confirmed that the subfractions extracted with higher alkanes had greater aromaticity and molar mass. However, small solubility variations between the subfractions were attributed mainly to the variation in the concentrations of cyclical hydrocarbon compounds and metals.

Keywords: crude oil; asphaltenes; characterization.

INTRODUCTION

Petroleum is a highly complex mixture of organic components, ranging from small molecules in a gaseous state to larger liquid molecules. The separation of these compounds at refineries is generally performed according to the boiling point ranges, thus producing commercial products. The chemical composition of a crude oil is classified according to its SARA content (saturates, aromatics, resins and asphaltenes). Generally, waxes make up around 14%. In turn, branched and cyclical (naphthenic) compounds account for 16 and 30%, respectively, while aromatics make up around 30% and asphaltenes-resins 10%.[1]

The asphaltenes are present in the heaviest fraction of crude oil and represent one of the main sources of problems for the petroleum industry, among them precipitation during production and transport, poisoning during refining, besides the stabilization of water-in-oil emulsions. The asphaltene fractions are the most polar in the crude oil and appear as dark solids that do not melt and decompose at 300 to 400 °C. They increase the crude oil's viscosity and density, hindering its transport and are also responsible for its color (brown to black). During oil refining in a fractionation column, the asphaltenic fraction is not distilled, remaining solidified along with the resins. This distillation residue is called asphaltic residue.[2-5]

Asphaltenes can be separated from resins by the addition of a non-polar solvent (paraffinic) such as n-pentane or n-heptane, forming precipitates that dissolve in aromatic compounds such as toluene.[6] The asphaltenes isolated are named C5I and C7I when using n-pentane and n-heptane as flocculant, respectively. A higher yield is obtained when using n-pentane and this fraction constitutes molecules with a broader distribution of molar masses and polarities. In fact, asphaltenes C5I contains all molecules of asphaltenes C7I.[4,6,7]

The profile of the asphaltenes separated during refining depends on the type of crude oil, its origin and the type and quantity of flocculating agent added during the process, in the last case expressed as the flocculant/oil ratio.[8,9]

The structure of asphaltenes is formed by aromatic polycondensate nuclei linked to the cyclical and aliphatic chains, containing heteroatoms such as oxygen, nitrogen and sulfur along with metals including iron, vanadium and nickel. Their exact structure is unknown due to the variety and complexity of their chemical structure. They are a highly heterogeneous polydispersed mixture in relation to molecule size and composition. Various structural models have been proposed and the macromolecular model of asphaltene fractions remains the focus of intense study. Currently, the main models suggested are the archipelago and continental models.[10-14]

The deposition of asphaltenes is associated with the flocculation of particles, which starts due to variations in the composition of the crude oil and temperature, pressure and flow regime.[15-17] The flocculation can be promoted by the addition of apolar solvents to the oil (such as n-pentane and n-heptane). When a large quantity of aromatic solvent is present, molecular aggregates can be formed in the dispersed medium.[18-20]

The objective of this work was to describe the extraction and characterization of the asphaltene fractions and subfractions starting from an asphaltic residue. For this purpose, first the flocculant solvent n-pentane was used to obtain the C5 fraction. After this extraction, different subfractions were isolated by the difference in solubility in various solvents. The flocculants for the subfractions obtained were n-hexane, n-heptane, n-octane, n-nonane and n-decane. These fractions and subfractions were characterized by Fourier transform infrared spectroscopy (FTIR) for comparative analysis of the chemical structures, by X-ray fluorescence to determine the levels of inorganic elements, by nuclear magnetic resonance spectrometry (NMR) of hydrogen to ascertain the ratio between aromatic and aliphatic carbons, by elementary analysis to determine the concentrations of carbon, hydrogen and nitrogen (CHN), and finally by matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF/MS) to determine the average molar masses.

EXPERIMENTAL

Materials

The asphaltic residue (ASPR) was supplied by the Petrobras Research Center – CENPES (Rio de Janeiro, Brazil). The solvents n-pentane, n-hexane, n-heptane, n-octane, n-nonane, n-decane and

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toluene were obtained from Vetec Química Fina (Rio de Janeiro, Brazil), all P.A. grade, except for the toluene, which was distilled and dried in alumina. HPLC-grade toluene was supplied by Tedia Brasil (Rio de Janeiro, Brazil).

The Da ProteoMass calibration standards – MALDI-MS peptides and proteins, with molar mass ranging from 185.2 to 5,730.6 – were supplied by Sigma-Aldrich (São Paulo, Brazil).

METHODS

The asphaltic residue and n-pentane (proportion of 15 g:1 L) were placed under stirring for 24 h. The insoluble fraction was placed in a Soxhlet extractor with n-pentane (proportion of 1 g:45 mL). This extraction step continued until the paraffinic solvent appeared clear in the extractor. The solvent in the extractor was then replaced with dry toluene (proportion of 1 g of precipitate:35 mL of solvent) and the extraction process was repeated until this new solvent appeared clear. The dissolved asphaltenes were recovered after evaporation of the toluene in a rotary evaporator. All the material soluble in n-pentane was placed in the evaporator to recover the C5 resins.

The asphaltenes and resins obtained in the rotary evaporator were dried for 3 days in a chapel to evaporate the residual solvent. The fractions obtained were placed in dark sealed flasks to prevent oxidation by the action of light.

Successive extractions were performed from the C5 asphaltenes to obtain different subfractions, separated by the difference in solubility in various solvents (n-hexane, n-heptane, n-octane, n-nonane and n-decane).

The C5-C6 subfraction corresponds to that extracted by solubilization in n-hexane, starting from the C5 asphaltenes. The remaining precipitate (asphaltenes C6) was then subjected to another extraction, this time with n-heptane, to obtain the C6-C7 subfraction dissolved in n-heptane. The other subfractions (C7-C8, C8-C9, C9-C10 and C10) were obtained following the same procedure, as shown in Figure 1. All the dissolved subfractions were dried for around 3 days and weighed to calculate the yield.

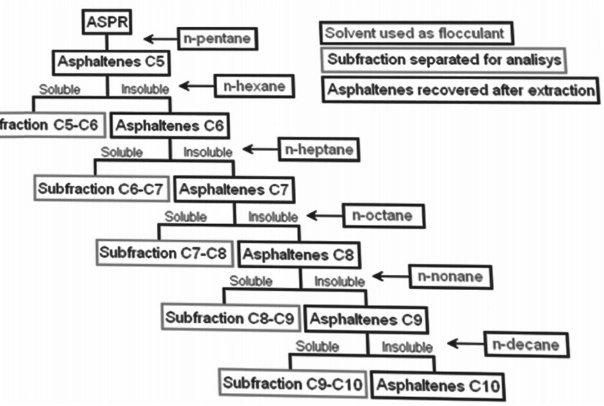

Figure 1. *Scheme of extraction of asphaltenes subfractions*

The Fourier transform infrared absorption spectroscopy was carried out on a Varian 3100 Excalibur Series FTIR spectroscope by casting film on a KBr cell. The spectra were scanned from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}, at room temperature.

The X-ray fluorescence analyses were performed in an EDX-720 X-ray fluorescence spectrometer, on Mayla film, at room temperature and under vacuum, with reading from sodium to uranium.

The quantitative hydrogen nuclear magnetic resonance analyses were performed on a Varian Mercury 300 spectrometer at a frequency of 300,067 MHz. A sample concentration of 0.1% wt/v was used in a 5-mm test tube. The data were treated with the Mestrenova® Software.

The elementary analysis was carried out using a Perkin-Elmer 2400 CHN analyzer.

The mean molar mass values were obtained by matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF/MS), using a Shimadzu Axima Confidence model with an N$_2$ (50 Hz) laser, in the range 1-80 kDa in reflectron mode. Asphaltene solutions at 0.05% wt/v in HPLC-grade toluene were used, prepared 24 h in advance. The device was calibrated with a ProteoMass kit (185.2 to 5,730.6 Da).

RESULTS AND DISCUSSION

The fractioning employed in this work is depicted in Figure 2, based on the classical representation of asphaltene fractions in function of their molar mass and polarity.[4]Each subfraction separated has a specific polarity corresponding to the solvent utilized to dissolve it (shown in Figure 1).

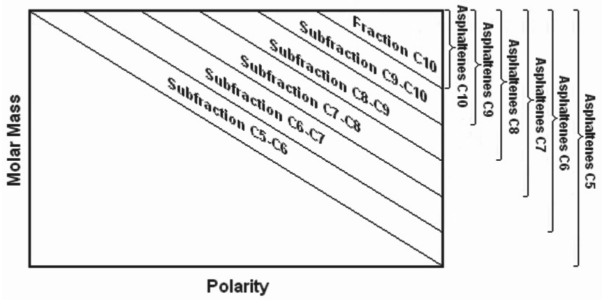

Figure 2. *Asphaltenes subfractions obtained by C5 asphaltenes*

The yields of the extraction process are given in Table 1. A significant loss of material (18%) occurred during the separation of the C5 resins and C5 asphaltenes from the ASPR: 62% of the material was recovered as C5 resins and 20% as C5 asphaltenes. On the other hand, the separation of the subfractions from the C5 asphaltenes caused losses of under 1%. Among the subfractions separated, C5-C6 had the highest yield. The other subfractions (C6-C7, C7-C8, C8-C9 and C9-C10) had yields of around 1% in relation to the ASPR or 5% in relation to the C5 asphaltene fractions.

Table 1. Yield of the asphaltenes fractions and subfractions

RASF (100%)						
Resins C5 (62%)	Asphaltenes C5 (20%)					
	C5-C6 (3.48%)	C6-C7 (1.01%)	C7-C8 (0.72%)	C8-C9 (1.15%)	C9-C10 (0.27%)	C10 (13.02%)

In the infrared absorption spectra of the ASPR, the C5 resins and C5 asphaltenes showed essentially the same peaks (Table 2), which were in agreement with those reported in the literature.[21,22]The differences observed were in the relative intensities.

A comparison between the spectra of the ASPR and C5 asphaltenes showed more accentuated peaks in the bands corresponding to the assignments B and G for the C5 asphaltenes. Besides this, the relative intensities of the B and A peaks (B/A) were higher for the C5 asphaltene spectrum than for the ASPR spectrum. This indicates a greater quantity of aromatic groups (bands B and G) in relation to the aliphatic groups (band A), evidencing, as expected, that the C5 asphaltene sample is more polar than the ASPR sample. The B/A ratios were approximately 1/11, 1/8 and 1/5 in the ASPR, C5 resins and C5 asphaltenes, respectively. The ASPR contains all the molecules

Table 2. Groups and assignments of FTIR spectra

Peak	Wave number (cm-1)	Group	Assignment
A	2923 and 2853	CH2 and CH3	CH_2 and CH_3 stretching vibration
B	1605	C=C and C=O	Aromatic nucleus vibrations
C	1457	CH_3	CH_3 symmetrical stretching vibration
D	1376	CH_3	CH_3 asymmetrical stretching vibration
E	1032	Sulfoxide (C2S=O)	---
F	870 and 800	C-H	Out-of-plane vibration of ring C-H
G	750	---	Vibration of four hydrogen adjacent to the aromatic ring

Table 3. Metals in the composition of ASPR, resins C5 and asphaltenes fractions and subfraction

Elements	ASPR (%)	Res C5 (%)	Asp C5 (%)	C5-C6 (%)	C6-C7 (%)	C7-C8 (%)	C8-C9 (%)	C9-C10 (%)	Asp C10 (%)
Ca	0.000	3.992	0.768	1.258	1.470	1.282	0.922	2.613	0.000
Cu	0.356	0.120	0.284	0.270	0.000	0.000	0.000	0.000	0.000
Fe	0.813	0.332	0.735	0.644	0.864	0.909	0.526	2.428	1.193
Ni	1.178	0.185	1.607	0.000	0.000	0.000	0.000	0.000	2.772
P	0.000	0.000	3.331	3.714	3.463	3.499	3.646	0.118	3.533
S	88.841	95.332	85.941	84.880	85.626	86.238	86.192	84.117	83.187
Si	7.290	0.000	4.326	7.334	5.084	5.272	5.247	7.809	5.971
V	1.522	0.039	2.733	1.901	2.882	2.802	2.635	2.915	3.345

present in the C5 asphaltenes fraction, but after separation by solubility difference, the more polar compounds become more concentrated in the C5 asphaltenes fraction while the less polar ones become more concentrated in the remaining fraction (C5 resins fraction).

As expected, the asphaltene subfractions showed the same peaks. The same behavior discussed above was also seen when comparing the spectra of the C5-C6 subfractions (less polar) and C10 asphaltenes (more polar). Nevertheless, no significant correlation was found between the other subfractions regarding variation in intensities of B and G bands. In other words, the subfractions presented polarity differences based on the extraction method, but these variations were not perceptible in the molecular structure using the FTIR technique.

The X-ray fluorescence results of the samples of ASPR, resins and asphaltenes are shown in Table 3 and are expressed in terms of percentage related to the total amount of the detectable elements. Significantly higher amounts of sulfur were detected in all samples compared with the amounts of calcium, copper, iron, nickel, phosphorous, silicon and vanadium. This sulfur in crude oil can impair the refining process, besides causing corrosion, deactivation of catalysts and pollution. The presence of metals in the samples might have contributed to the higher polarity of resins and asphaltene fractions compared to other crude oil fractions.

In the case of the analyses with the ASPR sample, some of the elements (Ca and P) present in the asphaltenes were not observed. This behavior may have been due to the fact the ASPR sample contains a high number of components, since it is a residue of distillation, making it harder to detect elements with lower concentrations.The X-ray fluorescence analysis was useful to identify metals in resins and asphaltene fractions but the results were not sufficiently conclusive to explain the polarity differences between the asphaltene subfractions.

The hydrogen nuclear magnetic resonance (H^{1}NMR) spectra of the asphaltene subfractions showed peaks related to aromatic and aliphatic hydrogen atoms, as expected.[23] The relative percentage results of these aromatic (Haro) and aliphatic (Hali) hydrogens are shown in Table 4, which corroborate, in part, those obtained by FTIR. A significant difference between the C5-C6 subfraction and C10 fraction is evident, with Haro/Hali percentage ratios of 0.17 and 0.28, respectively, indicating higher aromaticity of the C10 fraction. The C5-C6 subfraction, which had the highest yield among the subfractions extracted, also had the greatest difference in Haro/Hali ratio. Among the intermediate subfractions, no significant variation was found in the results of the Haro/Hali ratios, which were between 0.21 and 0.23, without any pattern. These subfractions certainly exhibit polarity differences, but these differences must be attributed to other factors (suggested below), or the differences between Haro and Hali are so small that it is not possible to detect them using the resonance technique.

Table 4. Percentage of aromatic and aliphatic hydrogen

	H aromatic (%)	H aliphatic (%)	Haro/Hali ratio
Subfraction C5-C6	14.0	86.0	0.17
Subfraction C6-C7	17.5	82.5	0.21
Subfraction C7-C8	18.5	81.5	0.23
Subfraction C8-C9	18.3	81.7	0.22
Subfraction C9-C10	18.6	81.4	0.23
Asphaltenes C10	22.0	78.0	0.28

The levels of carbon, nitrogen and hydrogen were determined by elementary analysis. The percentages of C, H and N, as well as the H/C and N/C ratios, are given in Table 5.

A comparison of the results obtained for the C5-C6 and C8-C9 subfractions and the C10 fraction shows that the carbon and hydrogen content tend to diminish as polarity increases, while the nitrogen content tends to increase along with the concentrations of the unquantifiable components. This group, which cannot be quantified by this technique, can include the elements iron, nickel, vanadium and mainly sulfur, detected in higher quantity by X-ray fluorescence for the C10 fraction, and possibly oxygen. These elements might be responsible for the increased polarity, in detriment to the influence of

Table 5. Content of carbon, hydrogen and nitrogen in asphaltenes samples

Samples	Elements (%)					
	C	H	N	Total	H/C	N/C
Asphaltenes C5	86.72	8.35	1.76	96.83	0.096	0.020
Subfraction C5-C6	86.40	10.53	1.55	98.48	0.122	0.018
Subfraction C8-C9	86.35	8.96	1.60	96.91	0.104	0.019
Asphaltenes C10	81.16	7.93	1.69	91.05	0.098	0.021

the aromatic compounds only. In addition, the H/C ratio also varies among the subfractions. Since no significant aromaticity differences were detected among the subfractions on the FTIR and NMR analyses, the differences in the H/C ratios could be due to the higher levels of cyclical compounds in the more polar subfractions.

One characteristic of a molecule that contributes to its solubility is molar mass. Molecules with the same structure become less soluble as the molar mass increases. The classic diagram of separation of asphaltenic fractions predicts higher molar mass for more insoluble fractions. Comparing the C5 and C10 fractions, the results obtained by MALDI-TOF/MS (Figure 3) confirm that the C10 fraction contains a concentration of molecules with higher average molar mass (434 Da) than does the C5 fraction (369 Da). However, upon comparing the subfractions with each other, only the C5-C6 subfraction (327 Da), which had the highest extraction yield, showed a difference in average molar mass in relation to the other subfractions. This means that the differences in polarity of the majority of the subfractions separated in this work do not stem from differences in average molar mass.

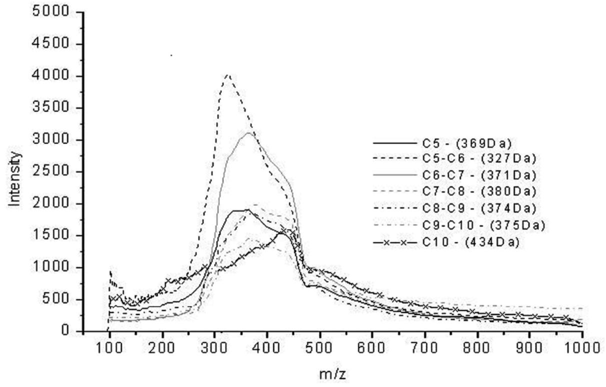

Figure 3. MALDI-TOF/MS spectra of asphaltenes subfractions and respective average molar masses

CONCLUSIONS

The method of separating asphaltenes used in this work permitted obtention of fractions containing molecules exclusive to each of the subfractions, which differed in solubility.

The variation in aromaticity was detected by FTIR and NMR analyses when comparing C5 and C10 asphaltenes samples. Besides the aromaticity, the presence of elements such as nitrogen, sulfur, phosphorous, silicon, nickel, iron and vanadium (observed by X-ray fluorescence) might also contribute to the increase in polarity of these fractions.

The elementary analysis showed that the samples separated are mainly composed of carbon, and there are small differences in terms of H/C ratio between the various subfractions, i.e., the more polar fractions have a lower H/C ratio. Since this difference does not stem from significant differences in aromaticity, it can be attributed to the variation in the cyclical compounds content.

The increase in molar mass of the fractions extracted with larger n-alkanes was also confirmed. However, different molar masses were not observed among those subfractions presenting low yield.

Thus, small variations in solubility can be attributed only to the variation in levels of cyclical hydrocarbon compounds and metals.

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