

## Properties of heptol sub-fractions extracted from Brazilian asphaltenes

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Asphaltene continue attracting much attention and controversy in spite of the considerable advances in their description and characterization that have appeared in the recent literature [1]. Their tendency to flocculate and precipitate during both oil production and refining is a strong incentive for the development of more efficient processes that can be applied to heavy petroleum fractions. A better knowledge of the chemical structure of this class of substances and their properties under certain conditions may hold the key to understanding their behavior in different stages of petroleum processing.

In the present work, a combination of characterization techniques was applied to different asphaltene fractions in order to get new insights into the way they aggregate. Asphaltene fractions were obtained by precipitation of samples A and B, obtained from vacuum residues, and of sample C, from pipeline deposits, using mixtures of heptane and toluene (referred to as Heptol) in different concentrations as a precipitation solvent. Our recent work [2], evidences important differences among asphaltene sub-fractions and reveals that aromatic species with higher content of ring fusion aromatic carbons, can concentrate in specific sub-fractions. It is noteworthy that they are not always in the least soluble fraction, nor in the one with the highest average molecular weight. The results of sub-fractionation indicated that the yield of asphaltene decreased as the proportion of toluene in Heptol increases, for both vacuum residues. This behavior agrees with solubility principles, but the solubility limit depends on the asphaltene type. Asphaltene C reveal a completely different solubility behavior. The solubility of asphaltene C doesn't seem to be affected by increasing the amount of toluene in the precipitant mixture up to values in which A and B are practically completely soluble (Table 1). In terms of techniques, there is no significant variation in elemental composition of sub-fractions, as indicated by C, H, N and S analysis for A and B asphaltene, however, C asphaltene show different values for this analysis. Hydrogen NMR (<sup>1</sup>H NMR) (Table 2), nevertheless, reveals that the relative proportions of aromatic to aliphatic hydrogens may be used as an indicator for some of these variations. The behaviour of the two vacuum residues is similar, except for small differences for the aromatic carbon in vacuum residue B [2]. For all C asphaltene sub-fractions larger differences are observed, showing a higher proportion of aromatic hydrogens in comparison to A

and B asphaltene for all the sub-fractions. Carbon-13 NMR (<sup>13</sup>C NMR) indicates that these changes may be traced to the fusion of aromatic ring systems. The results also show that a specific sub-fraction (A-10%) had a higher proportion of aromatic carbons, and is important to point out than this sub-fraction is the same that showed highest percentage of ring junction aromatic carbons calculated by NMR in a previous work [2]. This result helps to validate the importance of sub-fractionating of this specific vacuum residue, once it was found that aromatic species are concentrated in the less soluble asphaltene sub-fraction. And, could serve as an indication that this sub-fraction could have fundamental importance for the association of these complex molecules [2].

**Table 1.** Solubility behavior (weight %)

% Toluene	%Asphaltene A	% Asphaltene B	% Asphaltene C
0	11.3	8.3	48.6
10	7.1	4.6	47.5
20	3.3	1.1	47.9

**Table 2.** <sup>1</sup>H NMR Integrated Area

Molecular parameter	Chemical Shift (ppm)	Integrated area (%)		
		A - 0%	A - 10%	A - 20%
H Saturated, Hsat	4 - 0	90.4	86.9	92.6
H Aromatic, Har	9 - 6	9.6	13.1	7.4
		B - 0%	B - 10%	B - 20%
H Saturated, Hsat	4 - 0	89.4	89.1	91.5
H Aromatic, Har	9 - 6	10.6	10.9	8.5
		C - 0%	C - 10%	C - 20%
H Saturated, Hsat	4 - 0	86.8	81.3	79.9
H Aromatic, Har	9 - 6	13.2	18.7	20.1

Some structural observations could be made from the measured values of aromatic hydrogen (Har). The A-10% and all the C asphaltene sub-fractions reveal high values for Har. This strongly suggests extensive aromatic ring fusion and explains the tendency of the C asphaltene sub-fractions to deposit in pipelines and also consistent with the suggestion that the A-10% sub-fraction can be responsible for the association of asphaltene in vacuum residue A [2]. The results show that <sup>1</sup>H NMR can be used to make a preliminary evaluation of the behaviour of asphaltene, from the oil reservoir to the production lines and storage tanks.

### References

- [1] Wiehe, L.A., Process Chemistry of Petroleum Macromolecules (2008), CRS Press, Boca Raton, 2.
- [2] Navarro, L, Seidl, P; Tasic, L; Leal, K.; Menezes, S. (2008) Prepr. Pap. - Am. Chem. Soc., Div. Fuel Chem. 53 (1).