

Selective extraction of asphaltenes from Brazilian heavy oils by solvent blends

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Supplies of conventional petroleum have been steadily dwindling, increasing the demand for heavier crudes and processes that are able to recover lighter fractions from residues. [1] Particularly in Brazil, where most of the fields under exploration yield crude oils of under 20 API, refining operations require considerable investments in additional units and the development of more efficient chemical processes for the conversion of highly aromatic and naphthenic constituents into smaller paraffinic molecules that can be separated into fuels, lubricants or petrochemical raw materials.

Even in low concentrations, asphaltenes (the main constituents of heavier fractions), tend to aggregate and precipitate and may pose serious problems for upstream operations. They may also form coke when heated and concentrate heteroatoms, such as nitrogen, that may deactivate catalysts used in conversion processes. On the other hand, as they are rather large and contain aromatic, naphthenic and paraffinic groups, solvents of these types or their mixtures should be to afford a certain degree of selectivity to their fractionation. [2]

In order to verify this possibility, asphaltenes were extracted from a vacuum residues (VR) obtained from two off-shore fields, A and B, that are geographically close in space. Combinations of pairs of naphthenic and paraffinic reagent grade solvents were tested as selective precipitation agents under carefully controlled conditions for VR A. [3] As it was found to be completely soluble in both naphthenic solvents, one of them, N1, was selected for tests in combinations with the two paraffinic solvents, P1 and P2. Constituents of “asphaltenes” that were precipitated for each combination of solvents were monitored by hydrogen NMR.

Table 1. Percentage of Extraction vs Type of Extractant

Samples	Blends	$\delta/\text{MPa}^{1/2,*}$	Fraction (%)	
			Insoluble	Soluble
VRA	N1/P1	16,8/14,5	11.72	88.28
	N1/P2	16,8/15,3	3.8	96.2
VRB	N1/P1	16,8/14,5	3.4	96.6
	N1/P2	16,8/15,3	1.96	98.04

* δ = Solubility parameter determined by: $\delta_{blend} = \delta_A \phi_A + \delta_B \phi_B$

(ϕ = volume fraction of solvent).

From Table 1 it is clear that P1 is a better solvent for VRA and VRB than P2. However both solvents extract a larger amount of asphaltenes from A than from B.

Table 2. ¹H NMR Analyses of asphaltenes with different solvent blends

Types of Hydrogen	Percentage* (%) VR A		Percentage* (%) VR B	
	N1/P1	N1/P2	N1/P1	N1/P2
Aromatic	8.8	14.3	7.5	11.6
H α	10.2	5.2	20.0	1.8
H β	63.5	68.5	53.9	73.6
H γ	17.6	12.0	18.5	13.0
Total Saturated	91.2	85.7	92.5	88.4

*Percentage of peak area.

From Table 2 it appears that blends N1/P1 and N1/P2 may extract asphaltene constituents selectively. For VR B, P1 extracted asphaltenes with a larger proportion of H α than for VR A.

The different types of carbons and hydrogens are represented in Figure 1.

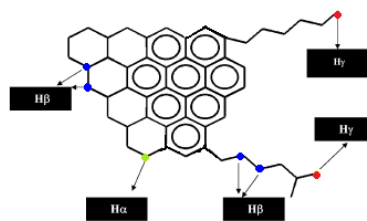


Fig.1. Types of carbons and hydrogens [4]

References

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