

Characterization of Pendant Groups in Asphaltenes by Cracking under Hydrogenation Conditions

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Quantitative evidence of bridged-structures in asphaltenes has been previously reported¹, along with the identification of different homologous series of compounds, including saturated, aromatic, and naphthenoaromatic structures^{1,2}. The petroleum asphaltenes, defined by solubility as the *n*-heptane or *n*-pentane insoluble, but toluene soluble fraction of oil, are complex structures that self-associate even in the presence of strong solvents, and cause problems during oil production and processing. The study of the asphaltenes structures can provide a better understanding of their behaviour, but is hampered by their complexity. In this study, we crack the asphaltenes and quantitatively recover the distillates, which constitute the analyzable fraction. Asphaltenes were cracked under hydrogenation conditions that favoured the yield of products in the distillate range, ensuring minimal change in the molecular structures during the reaction.

Asphaltenes from different geological origins were obtained by precipitation in *n*-heptane, using a ratio of 40:1 solvent to vacuum residue. The asphaltenes were cracked in 15 mL stainless steel batch microreactors, in a hydrogen atmosphere with tetralin solvent as a hydrogen-donor solvent, and with catalyst with mild hydrogenation activity, prepared by wet impregnation of iron sulphate on sub-bituminous coal. Gases, coke and liquids were quantitatively recovered, giving mass balances above 97%, as shown in Figure 1. Gases were analyzed by GC-TCD. SimDis analysis of the raw asphaltenes and liquid products, after tetralin removal, provided an estimate of the conversion of the vacuum residue fraction.

Reaction conditions of 450°C, residence time of 3 hours, H₂ pressure of 4.1 MPa at ambient temperature, tetralin to asphaltenes ratio of 2.5/1, and 2 wt% of catalyst, led to yields of coke below 10% and distillates above 50%, for all the samples evaluated. Analyses of the distillates (< 538 °C fraction) by gas chromatography–field ionization–time-of-flight high-resolution mass spectrometry (GC-FI-TOF HR-MS), illustrated in Figure 2, showed similar distributions of pendant groups for the asphaltenes from the different origins. Overall yields, shown in Figure 3, suggest that large aromatic clusters, approximated by coke yield plus the unconverted vacuum residue fraction, would account for 35 wt% (Gudao) up to 45 wt% (Safaniya) in *n*-C₇ asphaltenes.

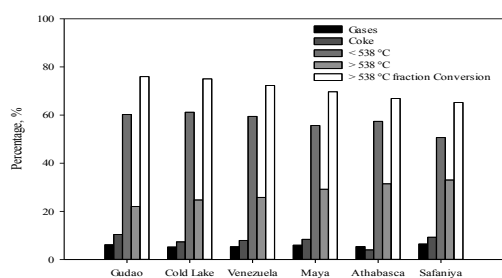


Figure 1. Yields of products (ash-free basis) from the cracking of *n*-C₇ asphaltenes under hydrogenation conditions.

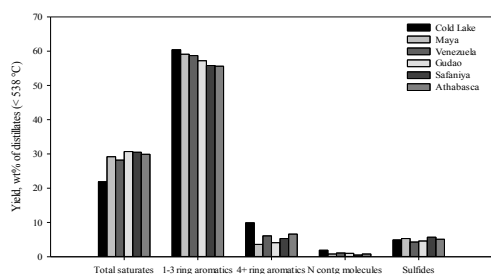


Figure 2. Distribution of saturate, aromatic, nitrogen containing and sulfide structures in *n*-C₇ asphaltenes, obtained by GC-FI-TOF HRMS analysis of the distillable fraction of the cracked products.

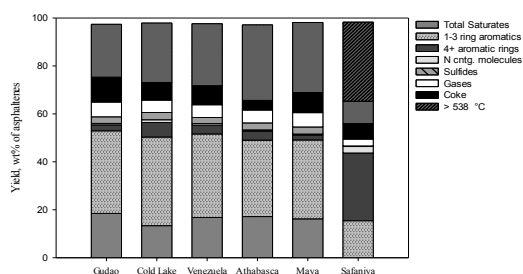


Figure 3. Overall yields from the cracking of asphaltenes.