Cluster Analysis of Asphalt Constituents Determined by NMR

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Abstract: *The quality of asphalts is related to the constituents of crude oils processed in a refinery ^{1}H and ^{13}C NMR were used to analyze variation in constituents of five asphalts produced in Brazilian refineries and their fractionation products (asphaltenes, maltenes, resins and aromatics) extracted by IP-143 method and separated by liquid chromatography, We assesed the extent to which NMR can be an appropriate technique to be used for this investigation. Cluster analysis of NMR chemical shift regions revealed considerable differences in the chemical constitution of the asphalts. The asphaltene fraction reflected the highest similarity between the constituents of two different asphalts.*

The quality of asphalts depends on their crude oil sources, as crude oils have different chemical compositions. The relationship between composition and performance properties have long been recognized, and several studies clearly demonstrate the importance of asphalt chemical composition on pavement durability.[1]

Asphalt is a complex mixture of organic molecules that vary widely in composition. Although they are composed predominantly of carbon and hydrogen, most of its molecules contain one or more heteroatoms (nitrogen, oxygen and sulfur) as well as trace amounts of metals, mainly vanadium and nickel. Molecular type and structure information are necessary for a fundamental understanding of how composition affects physical properties and chemical reactivity. Thus, we have used the IP 143 method to separate asphaltene and maltene (heptane soluble) fractions of different asphalt samples.[2] The maltene fraction was further separated into its respective saturated, aromatic, and resin (polar) components by preparative liquid chromatography.[3,4] The fraction´s constituents were analysed by ^{1}H and ^{13}C NMR spectroscopy, elemental analysis, and cryoscopic molecular weight determination. Cluster analysis of NMR data for five asphalts of different origins reveals the degree of correlation between the constituents of the separated fractions.

NMR experiments were run on a Varian INOVA-300 Spectrometer. Hydrogen spectra were run at 300 MHz on 5% (weight/volume) samples dissolved in a 1:1 mixture of deuterochloroform and tetrachloroethylene at ambient temperature, using 4.9μs (45°) pulses and 128 transients. ^{13}C spectra were run at 75.4 MHz on a solution of about 100 mg of

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sample dissolved in 1ml of a solution of 0.05M of chromium acetilacetonate in deuterochloroform as a relaxation reagent and tetramethylsilane as an internal reference. The acquisition used 90º pulses, 10s intervals between pulses, 5000 transients and the decoupler in the gated mode to avoid NOE.

All samples were submitted to statistical analysis. MINITAB release 13 software was used to generate the respective clusters for integrated areas of asphalts, asphaltenes, maltenes, resins, and aromatics. The parameters employed for each fraction are displayed for the asphaltene fraction in Table 1. Cluster analysis is a valuable tool for the identification of similarities in a large volume of data. Statistical treatment allows the aggregation of similar results and the quantification of their respective degrees of similarity. Treatment of each asphalt and its fractions reveals the similarities among them as well as those of their respective fractions. Similarities are given as percentages.

Table 1. NMR Parameters for the Asphaltene Fraction

Molecular parameters of asphaltenes	**A**	**B**	**C**	**D**	**E**
% aromatic C	46,2	57,3	51,3	52,1	50,4
% aliphatic C	53,8	42,7	48,8	47,9	50,4
% arom. alkyl or heteroatom C	17,3	12,6	14,6	15,2	13,7
% arom C - H	14,6	28,0	24,7	24,1	24,2
% arom. ring junction C	14,3	16,8	11,9	12,8	11,7
Fa (aromaticity factor)	0,5	0,6	0,5	0,5	0,5
% aromatic H	15,3	7,3	4,7	14	5,0
% alfa H	22,6	20,4	19,0	21,2	19,2
% beta H	47,1	53,7	58,4	48,6	58,5
% gama H	15,0	18,6	18,0	16,2	17,6
% saturated H	84,7	92,7	95,3	86,0	95,0

The largest similarity (79%) among asphalts is found between samples A and D and, when B and E are included in the same cluster, this value is reduced to 60%. With regard to the constituents of different fractions, the resin fraction of the maltenes reveals the highest correlation among all constituents.This value (47%) is, nevertheless, rather low, indicating that the constituents are quite different. The highest correlation between inidividual constituents was found for the asphaltene fraction, in which samples C and E reveal a correlation of 92% (this value falls to below 50% if the remaining samples are included). These results indicate that there is a considerable variation in the chemical composition of asphalts produced in different Brazilian refineries, but analysis of asphalts

without fractionation would not reveal this fact. The similarities of the constituents of each fraction may be conveniently identified by cluster analysis of carbon 13 and hydrogen chemical shift regions.

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