Article

Structural Characterization of Unfractionated Asphalts by 1H NMR and 13C NMR

FERNEY BETANCOURT CARDOZO, Eliseo Avella-Moreno, and Carlos Alexander Trujillo

Just Accepted

Structural Characterization of Unfractionated Asphalts by ^{1}H NMR and ^{13}C NMR

Ferney Betancourt Cardozo, [†] Eliseo Avella Moreno,[*,‡] *and Carlos Alexander Trujillo*[‡]

†Department of Civil and Agricultural Engineering, ‡Department of Chemistry, Universidad Nacional de Colombia, Avenue 30th 45-03, Building 451, postal code 111321, Bogotá, Colombia.

ABSTRACT. An improved methodology for the structural characterization of heavy fractions of petroleum by hydrogen-1 and carbon-13 nuclear magnetic resonance was applied to three fresh and unfractionated asphalts in solution. The results were compared with those generated by other two known characterization methods applied to the same NMR spectra. The comparison revealed inconsistencies in the traditional methods for the structural characterization of this type of materials. The improved methodology can be applied to unfractionated samples, and it provides a more detailed structural characterization of the asphalts than previously obtained. The new method provides a better correlation between physicochemical properties and the chemical structure of the complex mixtures of hydrocarbons.

1. INTRODUCTION

Asphalt is a general term used to denominate complex mixtures of organic compounds, predominantly hydrocarbons. It has several applications, but its primary use is as cementitious

material for road construction. Asphalt is a non-renewable resource that is not easily replaceable

in most of its uses. The study of the asphalt includes its physical and chemical characterization,

and it frequently pursues finding materials with better performance in the construction of roads.

Researchers try to associate physical and chemical properties found in the laboratory with the

performance of the material under traffic.

The characterization of asphalts should provide information on chemical, structural and

physical properties of the material as a whole regardless of the complexity of the mixture. The

ideal situation is to analyze the unfractionated material because the sum of the properties of the

parts does not necessarily match the properties of the original sample. Nevertheless,

characterization of such complex mixtures is not an easy task. To simplify the problem, the

traditional characterization of the asphalts is done dividing the sample in particular fractions, and

the ensemble of its characteristics is interpreted as if they were of the whole sample. Typically,

asphalts are separated into fractions, according to the solubility in diverse organic solvents or

chromatographic systems. Commonly the constituents of the asphalt are separated by solvent

extraction and chromatography in four broad groups: saturated fraction, aromatics, resins and

asphaltenes (i.e. SARA fractionation).[1,2] The results of the analysis of the SARA fractions and

individual indexes inferred from its physical and mechanical properties are commonly used as

indicators of asphalt quality.

Nuclear Magnetic Resonance (NMR) has been used as an analytical tool to characterize the

composition of fractions asphalt in an attempt to correlate its structure with the performance and

service life of these materials in roadworks. NMR has gained acceptance by its ability to provide

information about the structure and composition of the samples, and the non-destructive

character of the analysis.[3-9] Traditionally, asphalt fractions are analyzed by NMR in similar ways

as petroleum, coal or its derivatives.[4,7,9,10-26] A comprehensive search of the literature showed the absence of publications about the characterization of unfractionated asphalts by NMR spectroscopy.

Ramsey et al.[12] published the first structural characterization of asphalts by hydrogen-1 nuclear magnetic resonance (^{1}H NMR). After them, Hasan et al.[16] published a more structured analytical approach to characterize a petroleum vacuum distillation residue (bp > 454 °C); later, this methodology was slightly modified by Siddiqui and Ali[4]. Since then other authors have used ^{1}H NMR spectrum, sometimes carbon-13 nuclear magnetic resonance (^{13}C NMR) spectrum, and elemental analysis for the structural characterization of asphalts fractions or similar materials to define indexes that intend to correlate with the properties and future behaviors of asphalts in roadworks.[4,7,9,20-23,27-44]

Avella and Fierro[25] applied a distinct approach to characterize the structural composition based on the elemental analysis, ^{1}H NMR, and ^{13}C NMR spectra of some heavy fractions of petroleum. They proposed a methodology useful to characterize oil, coal or its fractions. In their analysis, they found inaccuracies in previous publications (1972-2006) on the limits of the integration intervals and the assignments of the signals of the NMR spectra.[45] Their proposal includes integrating a higher number of intervals (with statistically optimized limits) and adjusting the allocations taking into account the partial overlapping of some signals in the same integration interval of the NMR spectrum. They suggested a way of data processing and spectra interpretation to benefit from the advances of NMR, in hardware and software, since Hasan et al.[16] or Siddiqui and Ali[4] did their researches. Avella-Fierro's proposal achieved a more detailed structural characterization which allowed calculating the same known indexes from the NMR spectra of heavy fractions of petroleum.[25,45]

This article reports the application of the procedure proposed by Avella and Fierro[25] for the structural characterization by NMR of three fresh asphalts (unfractionated). This new methodology is compared with those proposed by Hasan et al.[16] and Siddiqui and Ali[4]. A new way to use NMR spectra to gain more detailed information about the structural composition of the asphalt is proposed. It is hoped this research helps to develop more accurate correlations between structural properties and the future performance of asphalts in roadworks.

2. MATERIALS

2.1. Samples and Reagents. Three unfractionated fresh commercial asphalts named P1, P2 and P3, produced in Colombia by the Empresa Colombiana de Petróleos (ECOPETROL) at its industrial complex in Barrancabermeja were used. Samples were collected in the feeding ducts of three plants that produce asphaltic mixtures in Bogotá.

Chromarod SIII (Iatron Laboratories), n-hexane, toluene, chloroform, di-chloromethane, methanol, hexamethyldisiloxane (HMDS), tetramethylsilane (TMS), chromium(III) acetylacetonate [$Cr(acac)_3$] and deuterated chloroform ($CDCl_3$ -d); ACS reagents for analysis, were acquired from Sigma Aldrich and used without further treatment.

2.2. Instruments and Methods. The following properties of the samples were determined: penetration (ASTM D5[46]), ductility (ASTM D113[47]), softening point (ASTM D36[48]), specific gravity (ASTM D3289[49]), and viscosity (ASTM D4402[50]).

Elemental analysis (C, H, N, and S) was performed by dynamic combustion (Dumas' modified method) at 900-1000 °C. Oxygen was determined by pyrolysis in a Thermo Scientific Flash-

Energy & Fuels

2000 Series. CO_2, H_2O, N_2, SO_2, and CO, the reaction products, were separated and analyzed by gas chromatography with thermal conductivity detector.[51]

The SARA fractionation (ASTM D4124[2]) was carried out in an IATROSCAN-TLC/FID provided with an MK6 analyzer using Chromarod SIII as the stationary phase and a flame ionization detector. Hexane, toluene, toluene/chloroform, and dichloromethane/methanol, in this order, were used as eluents. The quantification of the fractions was performed measuring the area of each signal in the chromatogram.

NMR spectra were acquired on a Brucker Avance 400 spectrometer, provided with a broadband observe (BBO) probe, using the conventional sequence (delay time, d_1; flip angle, θ, 30°x, and acquisition delay, AQ) for ^{1}H NMR, inverse gated decoupling sequence for ^{13}C NMR spectra of samples in standard 5 mm NMR tubes (Norell). Other specifications are consigned in Table 1.

Each free induction decay (FID) was processed using MestReC 4.9.8.0[52] by Fourier transform, baseline correction by Bernstein polynomials, and manual adjusting of the signals phase, following previously published indications to obtain the NMR spectrum.[25,45] The assignment and the integration of the NMR spectra signals to quantify the nuclei were performed separately on the same spectrum according to the indications of (1) Hasan et al.[16], (2) Siddiqui and Ali[4], and (3) Avella and Fierro[25], and Avella[45], respectively. Data processing from the FID was repeated at least six times in ^{1}H NMR spectra, or ten or more times in ^{13}C NMR spectra, until obtaining a coefficient of variation lower than 5% in the average-total integral.[53] Those signals that Hasan et al.[16] or Siddiqui and Ali[4] allocate at only one distinct chemical shift (δ) were integrated at the interval $\delta \pm 0.1$ ppm.

3.   RESULTS AND DISCUSSION

3.1.   Preliminary Characterization. The viscosity, the penetration (80/100), the softening

point, and the colloidal instability index (Table 2) indicate that P1 and P2 have a softer

consistency than P3. The three asphalts show high thermal susceptibility, according to the

criteria of Pfeiffer and Van Doormal[54,55], being P3 the most sensitive (penetration index, -1.4).

This result agrees well with the common origin, the similar elemental composition, and other

properties certified by ECOPETROL.

The SARA fractionation data (Table 2) suggest that their higher content of resins and their

smaller fraction of aromatics justify the softer consistency of P1 and P2 compared to P3.

However, the lower proportion of resins and the highest thermal susceptibility of P3 is not

coherent with the criterion that associates higher thermal susceptibilities with higher contents of

resins (EN 12591:2009)[55]. It is important to realize that the SARA analysis[1,2] provides general

information about the composition depending on the solubility, the adsorption, and the partition

coefficient of the compounds in each solvent, all of them affected by mutual interactions

between the sample components. Therefore, the SARA fractionation has limitations to provide

an accurate description of the particular structural and chemical composition of the sample. Data

from Table 2 are important to predict some physical behavior of the asphalts, but they are not

enough to distinguish between P1, P2, and P3, by their structural and chemical characteristics.

3.2.   Structural Characterization of Asphalts by NMR. Hasan et al.[16] and Siddiqui and Ali[4]

resorted to fractionate the asphalt before acquiring the NMR spectra. They obtained NMR

spectra using samples in concentrated solutions (up to 50% w/v) with 0.50-0.75% of iron(III)

acetylacetonate [Fe(acac)$_3$] as relaxation agent in ^{13}C NMR. They processed the FID, assigned

and integrated the signals into intervals or discrete values of δ (six or seven for ^{1}H NMR, and three to five for ^{13}C NMR spectra). Their structural characterization of the samples depends on 14 defined fragments and 9 indexes calculated from the integral of the signals in the spectra and the average C/H ratio determined by elemental analysis.

In this work the asphalt was not fractionated, the spectra were taken on more diluted solutions (^{1}H NMR: 3-4% of sample in $CDCl_3$ 99.8%-d with TMS, 0.03-0.05% v/v, and HMDS, 0.05-0.10 M; ^{13}C NMR: 20-25% of sample in $CDCl_3$ 90%-d with TMS, 0.2-0.4% v/v, and $Cr(acac)_3$, 0.05 M). The signals were processed according to the following criteria (1) integration intervals (33 for ^{1}H NMR, and 43 for ^{13}C NMR) chosen within limits defined by statistical treatment of previously published data (Tables A1 and A2, Supporting Information), (2) subtraction of the integral of those signals that do not belong to the sample, and (3) definition of a factor f to convert reciprocally integrals between ^{1}H NMR, and ^{13}C NMR spectra, and to get coherent quantification of the nuclei in one same sample.

The structural characterization of the sample is done considering a greater number of structural fragments (37 in ^{1}H NMR, and 39 in ^{13}C NMR) and using more equations to distribute such fragments into three general assignment categories (Tables 3 and 4). The equations used allow finding the integral for each particular allocation in a way that the adverse effects on the quantification that are caused by the overlapping of the signals in the sample spectrum are diminished.[25,45]

The percentage distribution of hydrogen, H_i, or carbon, C_i, into the different structural fragments of P1, P2 and P3 (Tables 3 and 4) were calculated from the integral of each corresponding allocation, I_{H_i}, or I_{C_i}, in the NMR spectra, and related to the average of the total

integral, I_{Htotal} or I_{Ctotal}, in the spectrum of the sample (Tables A1-A3, Supporting Information) according to equations 1 and 2.

$$H_i(\%) = 100\frac{I_{H_i}}{I_{Htotal}} \qquad (1)$$

$$C_i(\%) = 100\frac{I_{C_i}}{I_{Ctotal}} \qquad (2)$$

Where, $I_{Htotal} = \frac{\sum_{i=1}^{i\geq6}\sum_{j=1}^{m}(I_{H_{ij}})}{i\geq6}$, and $I_{Ctotal} = \frac{\sum_{i=1}^{i\geq10}\sum_{j=1}^{m}(I_{C_{ij}})}{i\geq10}$ for all number, i, of replications of

the measure, and, j intervals of δ integrated in the respective spectrum.

The elemental composition (Table 2) and the ^{1}H NMR spectra (Table 3) show very similar quantities of hydrogen in the different structural fragments (aliphatic, aromatic, olefinic, or phenolic) of P1, P2 and P3. Although these data do not allow discriminating clearly between the three asphalts, they evidence a predominance of alkyl substituents with a length of four or more carbon atoms in their average structure. Most of the hydrogen in its aliphatic fraction belongs to CH_n moieties located at three or more bonds from the aromatic fragment. In total, more hydrogen was found bonded to carbons in positions β, γ, δ, or farther (H_β, H_γ, H_δ, ...) than bonded to carbons in position α to aromatic fragments, H_α. Hydrogen in methyl groups represent a little more than 45% of all H_α; this is 27% of the total hydrogen of the sample, and it is almost 26% of the sum $H_\beta + H_\gamma + H_\delta$ or farther to an aromatic ring.

^{13}C NMR spectra (Table 4), viscosity, penetration, and the softening point (Table 2) confirm some degree of similitude between P1 and P2, and show differences between them regarding P3. Table 4 data show that the content of carbon bonded to hydrogen present as methyl, methylene, or methine in the structure of P1, P2 or P3 is quite similar. The quaternary carbon content in alkyl or aryl fragments is practically equal in the structure of P1 or P2. P3 has the lowest content of quaternary carbon in its aliphatic fragments and the highest content of quaternary carbon in

polycondensed aromatic fragments (most of these are catacondensed carbons bonded to a heteroatom or an alkyl group distinct to methyl). The calculated molar ratio of aliphatic carbon to aromatic carbon in the structure of these asphalts is 2.51 (P1), 2.59 (P2) or 2.22 (P3).

Both CH in chain branching points as CH or CH_2 in naphthenic fragments are scarce in the aliphatic fragments, and there is a predominance of quaternary carbons in the aromatic portions of the structure (94.5% in P1, 94.2% in P2, and 94.8% in P3). Most of their sp^2 carbons are on the peripheral of polycondensed aromatic fragments and approximately 25% of these acts as bridgehead (25.5% in P1, 28.0% in P2 and 25.6% in P3).

3.2.1.   A Comparison of the Methods for the Structural Characterization of Asphalts by NMR. The procedures originally proposed by Hasan et al.[16] and by Siddiqui and Ali[4] to characterize asphalts have been used practically unmodified since their original publications, despite advances in NMR as analytical technique and the improvements in the technologies and methods to characterize such materials.[15,21,40,56-63] In this work, both NMR spectra of the same sample (P1, P2 or P3), were processed from its FID, according to indications of Avella and Fierro[25,45] and the other two methods. Results were compared correspondently (Tables 5 and 6).

The two traditional methods gave very similar results to each other, but different to those obtained from the approach proposed by Avella and Fierro[25,45] (Tables 5 and 6). In general, the three methods showed that the structures (average) of P1, P2 or P3 have a similar content of total hydrogen, but the structure of P3 has more carbon in alkyl than in aryl fragments. The new approach of analysis, unlike the other two, evidences the predominance of alkyl branches with a length of three or more carbons, and establishes $H_\gamma > H_\beta > H_\alpha$; $C_\beta > C_\alpha > C_\gamma$, with a minor

participation of $H_{\alpha\text{-alk}}$, H_β or H_n (Table 5). It also shows a scarce presence of C_n, $C_{ar\text{-H}}$, $C_{ar\text{-b}}$ or $C_{ar\text{-J}}$, and a higher content of C_β, $C_{Me\text{-b}}$ and $C_{ar\text{-alk}}$ (Table 6).

The methods proposed by Hasan et al.[16] and Siddiqui and Ali[4] for the characterization of asphalt by NMR differ only in the allocation of some signals and within the limits of certain integration intervals (0.0-4.0 ppm in ^{1}H NMR spectrum; 137-160 ppm, and 29.7 ppm in ^{13}C NMR spectrum). The approach proposed by Avella and Fierro[25] takes into consideration aspects such as the sample preparation, the acquisition, the processing and the unified assignment of the signals in the spectra.

The traditional procedures prescribe the acquisition of ^{1}H NMR and ^{13}C NMR spectra using solutions with 50% or more of the sample, although, in NMR, ^{1}H is 62.5 times more sensitive than [13]C.[64,65] Such so higher concentration of sample could lead to a suspension instead of a solution, something that could induce adverse effects on the quantification due to the loss of spectral resolution in ^{1}H NMR. Those methodologies also resorted to acquire ^{13}C NMR spectra adding $Fe(acac)_3$ as paramagnetic relaxation agent. However, it was found that the quality of ^{13}C NMR spectra of heavy fractions of petroleum is notably altered due to $Fe(acac)_3$, because it hinders or prevents the shimming in the preparation stage for the acquisition of the spectra.[45] According to the literature (Table 7),[4,28,58,60,61,66-84] it is not customary the use of $Fe(acac)_3$ for the structural characterization by NMR of coal, petroleum or their derivatives.[45] Paramagnetic relaxation agents are added to the solutions to decrease the time constant for longitudinal relaxation, T_1, and consequently the experimental time for NMR spectra acquisition[85], however, there is no consensus about the nature or the concentration of the relaxation agent (Table 7). Avella and Fierro[25] recommended the use of diluted solutions (item 3.2), acquiring NMR spectra by similar acquisition sequences as utilized by Hasan et al.[16], or by Siddiqui and Ali[4] and the

quantification of the nuclei by the integration of its signals in the spectrum. This new approach indeed provides more details about the structure of the sample.

Hasan et al.[16] and Siddiqui and Ali[4] characterize the structure of the asphalts with NMR spectra acquired by sequences with long recycle delay, d_1; up to 25 s for ^1H or 15 s for ^{13}C, or too short d_1 (sometimes, zero) which compile a relatively small number of data in the time domain for ^1H NMR and ^{13}C NMR, and a high number of scans for ^{13}C (Table 1). Acquiring such ^{13}C NMR spectra could require from 12.5 h up to 139.0 h; this is a considerable time; enough to affect in some extension the quantification of the nuclei by the distortion of the signal shape due to the drift of the magnetic field. The use of d_1 equal to zero affects or hinders the re-equilibrium of the longitudinal magnetization between consecutive scans, so it also deteriorates the measure.

Avella and Fierro recommend using shorter d_1 (1 s for ^1H and 5 s for ^{13}C), to compile 65 536 data points and to register a different number of scans for the NMR spectra acquisition (16 to 64 for ^1H NMR, and 1024 to 4096 for ^{13}C NMR; Table 1).[25] In this way, they obtained NMR spectra that fit to quantify the nuclei, and acquired ^{13}C NMR spectra in three hours or fewer.[45]

The approach proposed by Avella and Fierro[25] gives specific details about the spectra processing such as the baseline adjustment, the phase correction of the signals and calibration for the quantification of the nuclei.[45] It also prescribes using integration intervals with statistically unified δ limits; sets criteria to replicate the processing of the FID a given number of times in order to get reproducibility; discounts the integral of all signals extraneous to the sample; evenly distributes the integral between the different overlapped signals into one same interval; converts reciprocally the integral from one to another spectrum (^1H NMR - ^{13}C NMR) and applies a larger

number of equations (Tables A1-A3 in the Supporting Information) to get a more detailed

structural characterization of the sample.[25,26,45] Their results also allow calculating the indexes

used by Hasan[16], Ali and Siddiqui[4], and some other authors for the structural characterization of

coal, petroleum, or its fractions.[14,86]

According to the traditional methods, the structural fragments ($H_{\alpha\text{-alk}}$, $C_{\text{ar-H}}$, $C_{\text{ar-Me}}$) and the

indexes (Table 6) are calculated using the average atomic C/H ratio determined by the elemental

analysis of the sample regardless if the fragment is aliphatic or aromatic. This ratio is indeed

different for an alkyl or an aryl fragment {alkyl [C/H $\geq n_C/(2n_C+1)$], aryl [C/H $\geq n_C/(n_C-1)$]; n_C is

number of carbons}. The new approach does not recommend using the average C/H ratio

indiscriminately, instead it proposes a factor f calculated from a ratio (f^*) between the integral of

signals corresponding to one millimol of carbon in one millilitre of the solution used to acquire

the ^{13}C NMR spectrum (I_C), and the integral of the respective signals corresponding to one

millimol of hydrogen atoms in one millilitre of the solution used to acquire the ^{1}H NMR

spectrum of the same sample (I_H), as indicated by equations 3-5.

$$f^* = \frac{I_C}{I_H} = 12 \frac{m_H(\%H)(V_C)(I_{C\text{total}})}{m_C(\%C)(V_H)(I_{H\text{total}})} \qquad (3)$$

Where f^* depends on (1) the sample masses, m_H or m_C, (2) the dissolution volumes, V_H or V_C,

used to acquire the NMR spectra, (3) the hydrogen, *%H*, or carbon, *%C*, percentages determined

by elemental analysis of the sample, and (4) the total integral measured in the ^{1}H NMR spectrum

($I_{H\text{total}}$), or in the ^{13}C NMR spectrum ($I_{C\text{total}}$), respectively.

Factor f^* converts corresponding integrals of the signals, from the ^{1}H NMR spectrum to the

^{13}C NMR spectrum, or vice-versa, taking into account the number of hydrogen atoms, n_H,

directly bonded to the carbon in each particular group (CH_3, CH_2 or CH) to normalize and to keep the proportionality of the data (eq 4).

$$I_{H_i} = \frac{n_H I_{C_i}}{f^*} \quad \text{or} \quad I_{C_i} = \frac{f^* I_{H_i}}{n_H} \qquad (4)$$

The factor f (eq 5) is a system of homogeneous fractions, useful to simplify the use of f^* into the raised equations to determine the integral of the signals in the NMR spectrum which are attributed to any of such groups in one given structural fragment (Tables A1-A3, Supporting Information).

$$f = \frac{f^*}{6} = \frac{2I_{H_{CH_3}}}{6} + \frac{3I_{H_{CH_2}}}{6} + \frac{6I_{H_{CH}}}{6} \qquad (5)$$

Where, $I_{H_{CH_3}}$, $I_{H_{CH_2}}$, $I_{H_{CH}}$, are the integrals of the signals of methyl, methylene or methine groups in the ^1H NMR spectrum of the sample, respectively.

In this way, the new approach makes possible to calculate the integral corresponding to all the carbon bonded to hydrogen from the integral of the signals of the respective groups in the ^1H NMR spectrum. Therefore, it allows deducting the integral corresponding to quaternary carbons in the structure simply by subtracting the calculated integral of the protonated carbons from the total integral of the signals in the ^{13}C NMR spectrum of the same sample, when it is acquired by a sequence similar to that used by traditional approaches. This is an advantage of the new method in comparison with the traditional schemes for characterization of this type of materials because these do not determine the participation of the quaternary carbons in the structure of the sample or do it but with a higher uncertainty.

Data in Table 8 show the comparison of the results obtained from the three approaches for the structural characterization of P1, P2 and P3. Notable differences appear whether the average C/H ratio or the factor f is used, with integrals of identically processed spectra of the same sample.

From the footnotes in Table 5 it is possible to infer that Hasan et al.[16], and Siddiqui and Ali[4] characterized asphalts structures by calculating $H_{\alpha\text{-alk}}$ only as function of methylene groups in position alpha to aromatic rings. They calculated $H_{\alpha\text{-alk}} = 2(C/H)C_{ar\text{-alk}}$. It is something that indeed affects the determination of $H_{\alpha\text{-Me}} = H_\alpha - H_{\alpha\text{-alk}}$ in the asphalt structure.

The different participation of C_α and C_γ in the structures of P1, P2 or P3 when it is calculated by one of these three approaches (Table 6) depends on the criteria applied to allocate the signals in the NMR spectrum. Hasan et al.[16] and Siddiqui and Ali[4], following indications of Grandt and Paul,[87] and Lindeman and Adams,[88] attributed wrongly the signals appearing at 14.1 ppm to C_α, and those at 32.2 ppm to C_γ. Probably, they dismissed the electronic effects and the anisotropy that operate on the carbons of the alkyl substituents due to the proximity to aromatic rings. In the spectra of benzenes mono-substituted by normal alkyl chains of 6 up to 18 carbons length, the signals of C_α commonly appear near to 36 ppm or slightly downfield (if these are part of a branched fragment) and the signals of C_γ appear around 29 ppm; not at 14.1 ppm, nor at 32.2 ppm. At 14.1 ppm usually appear signals of CH_3 in γ, δ or farther to aromatic fragments.[89]

The three approaches determine different contents of C_n, $C_{Me\text{-b}}$ and C_β in the structures of P1, P2 or P3 (Table 6). These results depend on the limits of the interval integrated (29-30 or 29.7 ± 0.1 and 19.7 ± 0.1 or 18-28 ppm) and the calculation used in each case (factor f, or integration in 22.9 ± 0.1 ppm). It should consider that other signals different to those assigned to C_n also can

contribute to the integral between 29 and 30 ppm. The Avella and Fierro's approach allows appreciating that C_n is only 0.44% or 0.40% of total carbon of P1, P2 or P3 (see CH_2 γ, δ or more to aromatic and to CH_3, Table 4).[25]

3.2.2. Other indexes for structural characterization of asphalts. Average empirical formula: average empirical formulas of P1, P2 or P3 from the elemental analysis (Table 2) and the NMR spectra (Tables 3 and 4) were calculated as appears consigned in Table 9. It is notable an average mass of the empirical formula around 2000 atomic mass units.

   Most probable average length of alkyl substituents determined by the new method: data in Table 10 show the most probable participation of the normal long chains (eight or more carbons, LC, %), the participation of normal short chains (seven or less carbons, SC, %) and the average length (as number of carbons) of the short chains (ALSC) as function of an assumed average length of the long chains (ALLC) in the structures of P1, P2 and P3, just as it was determined by NMR data (Table 6). Chains until 40 carbons were taken into account. These participations were deducted from the ratio C_n/$CH_{3-\gamma}$ (Table 9) assuming that there is (n_C - 8) internal methylenes in the longer chains ($n_C > 8$) and at least one, in an eight carbon chain. The participation of LC (%) was compared with the participation of SC (%) which were determined using the *f* factor (Tables 3 and 4; footnotes in Table 8) by mean of the ratio CH_3/CH_2 in γ, δ or farther to aromatic in the structure. The most probable average length of the normal alkyl substituents in the structures of P1, P2 and P3 (10 carbons) is similar to the minimal chain length calculated from ^{13}C NMR (Avella and Fierro[25]; Table 6). The integral's value between 29 and 30 ppm (CH_2 −γ or δ or more to aromatic and to CH_3) in ^{13}C NMR (Table 4) admits only two or up to three internal methylenes in the normal alkyl substituents. The ratio C_n/$CH_{3-\gamma}$ (Table 9) is approximately 3 and ALSC tends to 9.6 or 9.8 carbons if the assumed ALLC increases.

Naphthenic hydrogen and carbon contents: the percentage of hydrogen and carbon of naphthenic fragments in the structures of P1, P2 or P3 is the value obtained with higher uncertainty, however it is the unique index known and it is currently used for the characterization of asphalts. In accordance with the new approach, the structure of P1, P2 or P3 has shortages of alicyclic or olefinic fragments. This was inferred from (1) the smaller hydrogen deficiency index (HDI, Table 9) in its aliphatic fraction, (2) the smaller content of shorter alkyl substituents, (3) the minor percentage of hydrogen (Tables 3 and 5) or carbon (Tables 4 and 6) in naphthenic fragments, (4) the predominance of methyl and methylene (CH_3 is more than 25% of all C_α), and (5) the presence of just a few methines in alpha to polycondensed aromatic fragments (large HDI).

Content of aromatic quaternary carbon: any of these approaches for the characterization of asphalts by NMR concludes that quaternary carbon is the most abundant type of carbon in the aromatic fraction of the structure of P1, P2 or P3 (Tables 4 and 8). The new approach allows inferring that, on average, in the aromatic fraction of its structures there are two, or up to three, external quaternary carbons (substituted and catacondensed) for each internal quaternary carbon (pericondensed) and that at most one of them serves as bridgehead. In effect, it is calculated that 83.0% of the average structures of P1, and 85.1% of those of P2 or P3 have a bridgehead aromatic carbon and that there are two catacondensed aromatic quaternary carbons for each pericondensed aromatic carbon existing in the 57.0% of the average structures of P1, in 81.0% of P2 and in 53.0% of P3.

4.   CONCLUSIONS

The method proposed recently by Avella and Fierro[25,45] is appropriate to characterize unfractionated asphalts and affords more information about its composition and structure from ^{1}H NMR and ^{13}C NMR spectra. The new methodology showed greater potential for the structural characterization of three fresh and unfractionated asphalts in comparison with methodologies previously used only on fractions of asphalts (Hasan et al.[16]; Siddiqui and Ali[4]). Their procedure (1) optimizes the acquisition of the spectra, (2) unifies the limits of integration intervals using the statistics, (3) recommends a specific way to process the FID, (4) integrates a larger number of intervals in the spectrum, (5) discounts the integral corresponding to signals that do not belong to the sample, (6) raises and uses a larger set of equations taking into account the overlapped signals and the intersection of allocations, (7) incorporates a useful factor to convert the integrals between NMR spectra (^{1}H NMR or ^{13}C NMR) of the same sample, (8) allows to indirectly determine the quaternary carbons content, and (9) discriminates those bonded to an heteroatom, among other favorable aspects observed.

The new method enabled determining content of different types of carbons in the aliphatic and aromatic fractions, as well as the distinct distribution of several kinds of quaternary carbons in the structures of the asphalts P1, P2, and P3. This is something that the NMR can establish with more certainty than conventional physicochemical analysis, and that the new method achieves better than the traditional ones. This way, it were found structural characteristics of these asphalts such as (1) a predominance of quaternary sp^3 carbon, (2) a large content of catacondensed aromatic quaternary carbons attached to alkyl groups, and (3) an abundance of CH$_n$ (protonated groups) at γ, δ or farther from any aromatic ring, into aliphatic chains of ten carbons (its average length more likely). The procedure proposed by Avella and Fierro[25,45] allows to calculate the same indices used by diverse authors in other approaches for the structural

characterization of oil, coal, its fractions or similar materials. It also permits to determine in the

asphalt (1) an average empirical formula, (2) an approximate molecular mass, and (3) an average

degree of unsaturation or polycondensation.

By comparing results between the three approaches for the structural characterization of this

type of materials, the work published here detected some inconsistencies in the traditional

approaches, such as (1) misallocation of some signals, (2) integration of signals at a single

discrete δ, (3) distinct allocation of signals appearing into one same δ interval, (4) the use of a

same average C/H ratio to indistinctly calculate structural indices of aliphatic, or aromatic

fragments, and (5) a lack of information about the specific way to acquire and process the NMR

spectra of such samples, and to apply these structural characterizations of the asphalts fractions

on unfractionated asphalts.

Table 1. Sample Preparation and Some Parameters Used to Acquire NMR Spectra of Asphalts or

Similar Petroleum Fractions.

experimental condition	Hasan et al.[16]	Siddiqui and Ali[4]	Avella and Fierro[25]
^{1}H NMR spectra acquisition			
samples preparation			
sample	petroleum residue[a]	asphalt[b]	asphalt
initial state	oil fraction	fractionated	unfractionated
asphalt	0.7 mL	1.0 g	0.028 g
solvent	2.0 mL[c] + TMS[d]	2.0 mL	0.7 mL[e]
HMDS			0.05%
acquisition parameters			
spectrometer	Varian XL-200 PFT	Varian XL-200 (PFT)	Brucker Avance 400
operation frequency	200.0 MHz	200.0 MHz	400.13 MHz
NMR tubes	5 mm	5 mm	5 mm
recycle delay, d_1	25 s	0 s	1 s
number of scans	10	64	64
time domain data points	15 680	15 680	65 536
flip angle	45°	45°	90°

spectral window wide	14 ppm (2800 Hz)	14 ppm (2800 Hz)	14 ppm (5602 Hz)
window center			6 ppm (2401 Hz)
^{13}C NMR spectra acquisition			
samples preparation			
sample	petroleum residue[a]	asphalt[b]	asphalt
initial state	oil fraction	fractionated	unfractionated
sample size	0.7 mL	1.0 g	0.140 g
solvent	2.0 mL[c] + TMS[d]	2.0 mL	0.7 mL[f]
relaxation agent	Fe(acac)$_3$, 15 mg	Fe(acac)$_3$, 10 mg	Cr(acac)$_3$, 0.05 M
acquisition parameters			
operation frequency	50.3 MHz	50.3 MHz	100.6 MHz
sequence	gated decoupling	gated decoupling	igd[g]
NMR tubes	10 mm	10 mm	5 mm
recycle delay, d$_1$	15.0 s	0.0 s	5.0 s
number of scans (transients)	20 000	16 000	2048
time domain data points	24 000	24 000	32 768
flip angle	45º	45º	90º
spectral window wide	198.8 ppm (10 000 Hz)	198.8 ppm (10 000 Hz)	240 ppm (24 144 Hz)
window center			110 ppm (11 066 Hz)

[a]Vacuum distillation residue, bp > 454 ºC. [b]Generic fractions obtained by ASTM D4124[2] (Corbett). [c]CDCl$_3$-d.
[d]Tetramethylsilane (TMS, scale reference). [e]CDCl$_3$ 99.8%-d, 0.03% v/v TMS. [f]CDCl$_3$ 90.0%-d, 0.30% v/v TMS. [g]igd, inverse gated decoupling.

Table 2. Physical-Chemical Properties of Fresh and

Unfractionated Asphalts.

assay	units	samples		
		P1	P2	P3
conventional assays				
viscosity at 60 °C	Poises	1403	1263	2193
viscosity at 135 °C	Poises	3.10	2.89	4.23
viscosity at 150 °C	Poises	1.27	1.17	1.46
ductility at 25 °C	cm	> 150	> 150	> 150
penetration at 25 °C	0.1 mm	84	93	64
specific gravity		1.004	1.006	1.008
softening point	°C	45.8	44.4	47.0
colloidal instability index		0.36	0.36	0.38
SARA separation				
saturates[a]	%	14.18	13.86	13.54
aromatics[b]	%	39.59	39.59	43.43
resins[c]	%	33.69	33.06	29.03
asphaltenes[d]	%	12.53	13.48	13.99
elemental analysis				

carbon	%	85.69	85.73	85.84
hydrogen	%	10.50	10.45	10.42
nitrogen	%	0.94	0.99	1.02
sulfur	%	1.64	1.65	1.65
oxygen[e]	%	1.24	1.19	1.07

Uncertainty of [a]± 0.50, [b]± 0.83, [c]± 0.54, [d]± 0.67. [e]Measured values, not deducted as the difference from 100%.

Table 3. Hydrogen Percentage determined by ^{1}H NMR, According to Avella and Fierro[25], in Structural Fragments of Fresh and Unfractionated Asphalts.

type (assignments)	interval (ppm)	samples		
		P1	P2	P3
general				
aliphatic or saturates[a]	0.5-4.5	94.48	94.33	94.35
olefinic	4.6-6.2	0.26	0.21	0.21
aromatic	6.3-9.3	5.23	5.44	5.43
phenolic OH	5.0-9.0	0.02	0.02	0.02
particular undefined				
CH_n γ, δ or more to aromatic	0.5-2.0	46.04	46.08	45.92
CH_n β, γ, δ or more to aromatic	0.5-2.0	81.37	81.26	80.95
CH_n β to aromatic	0.5-2.0	35.32	35.19	35.04
CH_n α to aromatic	2.0-4.5	13.10	13.05	13.38
CH_n α to C=C (it is CH_n-C=C)	1.9-2.1	0.01	0.01	0.01
CH_n in a C sp^3 joined to oxygen[b]	3.1-3.3	0.01	0.01	0.01
CH_3, CH_2 or CH γ, δ or more[c]	0.5-1.0	16.08	16.34	16.32
$CH_{3-β}$, $CH_{2-β\ or\ γ}$, $CH_{-β\ or\ γ}$ [d]	1.0-2.0	59.93	59.48	59.19
CH in monocyclic aromatic[e]	6.3-7.3	1.85	2.07	1.94
CH in polycyclic aromatic	7.2-9.3	3.38	3.37	3.49
particular defined				
CH_3 γ, δ or more to aromatic	0.5-1.0	12.13	12.35	12.34
CH_2 γ, δ or more to aromatic	0.5-4.5	1.06	1.05	1.03
CH γ, δ or more to aromatic	0.5-4.5	0.18	0.17	0.17
CH_3 β to aromatic	1.0-1.4	9.35	9.11	9.05
CH_3 β to aromatic or internal CH_2[f]	1.0-1.4	14.02	13.67	13.58
H in naphthenic fragment	1.4-2.0	3.66	3.77	3.76
CH_2 or CH β to aromatic	1.4-2.0	25.97	26.08	25.99
CH_2 β to aromatic	1.4-2.0	20.70	20.74	20.66
CH β to aromatic	1.4-2.0	5.28	5.34	5.32
CH_3 α to monocyclic aromatic	2.0-2.4	1.29	1.38	1.32
CH_3 α to aromatic	2.0-2.8	5.69	5.69	5.80
CH_3 α to polycyclic aromatic	2.3-2.8	4.40	4.31	4.48
CH_2 or CH α to aromatic	2.4-4.0	7.40	7.36	7.57
CH_2 α to aromatic	2.4-4.0	5.92	5.88	6.06
CH α to aromatic	2.4-4.0	1.48	1.47	1.51
CH_2 α to two aromatic rings	3.5-4.5	0.63	0.64	0.64

type (assignments)	interval (ppm)			
CH$_2$= in *gem*-disubstituted olefins[g]	4.6-4.8	0.07	0.05	0.06
CH$_2$= in monosubstituted olefins[g]	4.8-5.0	0.05	0.03	0.04
internal CH= in branched olefins	5.1-5.3	0.02	0.01	0.01
CH= in normal (straight chain)[h]	5.3-5.6	0.03	0.04	0.03
CH= in monosubstituted olefins[g]	5.6-6.0	0.00	0.03	0.01
monocyclic aromatic CH	6.5-7.3	1.74	1.96	1.83
dicyclic aromatic CH	7.2-8.2	1.04	1.06	1.09
tricyclic aromatic CH	7.4-8.5	0.85	0.88	0.89
tetracyclic aromatic CH	7.2-9.3	1.60	1.54	1.62

[a]Paraffins and naphthenes. [b]CH$_n$-C-O. [c] to aromatic. [d]To aromatic and CH$_2$ or CH. [e]Estimated by excess (6.3-7.3). [f]In aliphatic fragments. [g]Vinyl. [h]Olefins

Table 4. Carbon Percentage determined by NMR, According to

Avella and Fierro[25], in Structural Fragments of Fresh and

Unfractionated Asphalts.

type (assignments)	interval (ppm)	samples		
		P1	P2	P3
general				
aliphatic or saturates[a]	10-60	70.50	71.35	68.11
olefinic	105-153	1.38	1.05	1.14
aromatic	102-165	28.12	27.60	30.74
particular undefined				
total CH$_3$	10-23 U			
	24-28	2.69	2.66	2.66
total CH$_2$	23-60	8.27	8.17	8.13
total aliphatic CH$_n$ (C sp^3)	25-60	3.45	3.42	3.41
quaternary sp^3	10-60	56.09	57.10	53.91
total aromatic CH	102-131	1.55	1.60	1.59
quaternary sp^2	123-165	26.57	26.00	29.15
particular defined				
CH$_3$-γ or more to aromatic	10-15	1.20	1.21	1.21
CH$_3$-β to aromatic, in ethyl group	15-18	0.46	0.42	0.45
CH$_3$-α to aromatic	18-22	0.56	0.56	0.57
CH$_3$ attached to CH in alkyl[b]	18-28	2.16	2.16	2.13
CH$_3$-α to protected aromatic ring	18-21	0.26	0.24	0.25
CH$_3$-β to aromatic, in isopropyl group	24-28	0.11	0.10	0.10
naphthenic CH$_2$ α to aromatic[c]	23-24	0.00	0.00	0.00
CH$_2$-α to CH$_3$ in alkyl[b] of ≥4 C	23-24	0.11	0.11	0.12
CH$_2$-β to aromatic in *n*-propyl group[d]	24-28	0.36	0.34	0.35
CH$_2$-α to aromatic	23-43	0.88	0.87	0.89
CH$_2$ α to aromatic in 1,2-diarylethanes[e]	28-37	0.40	0.39	0.40
CH$_2$ α to aromatic in diarylmethanes[f]	33-43	0.02	0.02	0.02
CH$_2$ not linked to CH in alkyl[b]	28-37	3.62	3.52	3.55
CH$_2$-γ,-δ or more to aromatic and to CH$_3$	29-30	0.44	0.40	0.40
CH$_2$-β to aromatic and ≥10 bonds from CH$_3$	30-31	0.03	0.03	0.03
CH$_2$-β to CH$_3$ and ≥10 bonds of aromatic[g]	32-33	0.06	0.06	0.06
CH$_2$ attached to alkyl CH	37-60	4.33	4.32	4.25
naphthenic CH	25-58	0.32	0.33	0.33
alkyl or naphthenic CH, not isopropyl	37-60	0.15	0.21	0.21
naphthenic CH or CH$_2$	25-60	0.70	0.72	0.71
aromatic CH ortho to OH or OR	102-116	0.01	0.00	0.01
C$_{ar-q}$[h] pericondensed (internal)	123-129	6.24	6.43	6.74

C_{ar-q}^h not attached to heteroatom	127-148	14.88	14.69	15.74
C_{ar-q}^h catacondensed (external)	128-165	20.33	19.57	22.41
C_{ar-q}^h bridgehead	129-135	5.18	5.47	5.74
C_{ar-q}^h attached to nitrogen	130-149	1.50	1.62	1.65
C_{ar-q}^h bonded to alkyl, other than CH_3	133-151	9.13	8.66	9.44
C_{ar-q}^h attached to naphthenic fragment	135-141	0.02	0.02	0.02
C_{ar-q}^h attached to heteroatom (N, S, O)	147-165	6.51	5.85	7.67
C_{ar-q}^h attached to oxygen	149-164	0.13	0.07	0.10

[a]Paraffins and naphthenes. [b]Substituent. [c]In tetralines. [d]Naphthenic or in indane. [e]Ar-CH₂CH₂-Ar. [f]Ar-CH₂-Ar. [g]And alkyl or napthenic. [h]C_{ar-q}, aromatic quaternary carbon.

Table 5. Hydrogen Percentages in Comparable Structural Fragments of Fresh and

Unfractionated Asphalts Determined From a Same Spectrum of the Sample by ¹H NMR

According to Different Characterization Approaches.

	Hasan et al.[16]				Siddiqui and Ali[4]				Avella and Fierro[25]			
type	interval ppm	samples			interval (ppm)	samples			interval ppm	samples		
		P1[a]	P2[a]	P3[b]		P1[a]	P2[a]	P3[b]		P1[a]	P2[a]	P3[b]
H_{sat}^c	0.0-4.0	95.18	94.55	94.84	0.5-4.0	95.14	94.49	94.78	0.5-4.5	94.48	94.33	94.35
H_γ^d	0.5-1.0	21.58	21.66	21.73	0.5-1.0	21.76	21.89	22.01	0.5-2.0	46.04	46.08	45.92
H_β^d	1.0-2.0	60.31	59.18	59.07	1.0-1.6	52.00	50.70	50.77	0.5-2.0	35.32	35.19	35.04
H_n^e	1.6-1.9	7.40	7.69	7.60	1.6-1.9	7.46	7.77	7.69	1.4-2.0	3.66	3.77	3.76
Total H_β					1.0-1.9	59.45	58.46	58.46				
H_α^d	2.0-4.0	12.50	12.67	12.79	1.9-4.0	13.93	14.15	14.31	2.0-4.5	13.10	13.05	13.38
H_{ar}^f	6.0-9.0	4.82	5.45	5.16	6.0-9.0	4.86	5.51	5.22	6.3-9.3	5.23	5.44	5.43
$H_{\alpha-alk}$		11.39[g]	9.84[g]	11.37[g]		11.95[g]	10.43[g]	12.03[g]	2.0-4.5[h]	7.40	7.36	7.57
$H_{\alpha-Me}$		1.11[i]	2.83[i]	1.42[i]		1.98[i]	3.72[i]	2.28[i]	2.0-2.8[h]	5.69	5.69	5.80

[a]Asphalt penetration, 80-100. [b]Asphalt penetration, 60-70. [c]H_{sat}, Aliphatic protons. [d]H_α, H_β and H_γ, protons attached to saturated carbon in α, β, γ or further removed to aromatic, respectively. [e]H_n, cycloalkyl protons (naphthenic hydrogen). [f]H_{ar}, aromatic hydrogen. [g]$H_{\alpha-alk}$, aliphatic protons on carbon in α-position respect to aromatic, calculated based on $H_{\alpha-alk} = 2(C/H)C_{ar-alk}$, where C_{ar-alk} is aromatic carbons attached to alkyl (except methyl) in the ¹³C NMR spectrum. [h] $H_{\alpha-alk}$ (methylene or methyl protons on carbon in α-position to aromatic) or $H_{\alpha-Me}$ (methyl protons on carbon in α-position respect to aromatic) both calculated as $H_{\alpha-alk} = I_{A13*}^H = I_{A003*}^H - I_{A34*}^H$ or $H_{\alpha-Me} = I_{A34*}^H$, on base of the integral in the respective interval of the ¹H NMR spectrum (the original[25] corrected and unified nomenclature, Supporting Information, Table A1 eqs 23 and 25, was preserved). [i]$H_{\alpha-Me} = H_\alpha - H_{\alpha-alk}$.

Table 6. Carbon Percentage in Comparable Structural Fragments of Fresh and Unfractionated Asphalts Determined From a Same Spectrum of the Sample by NMR According to Different Characterization Approaches.

type	Hasan et al.[16] interval (ppm)	samples $P1^a$	$P2^a$	$P3^b$	Siddiqui and Ali[4,23] interval (ppm)	samples $P1^a$	$P2^a$	$P3^b$	Avella and Fierro[25] interval (ppm)	samples $P1^a$	$P2^a$	$P3^b$
percentage distribution determined by integration of the signals in the δ range												
$C_{sat}{}^c$	0.0-70.0	71.61	72.38	69.67	0.0-70.0	71.61	72.38	69.67	10-60	70.50	71.35	68.11
$C_\alpha{}^d$	14.1^e	1.41	1.35	1.33	14.1^e	1.41	1.35	1.33	f	1.88	1.86	1.90
$C_{Me-b}{}^g$	19.7^e	1.14	1.10	1.08	19.7^e	1.14	1.10	1.08	18-28	2.16	2.16	2.13
$C_\beta{}^d$	22.9^e	0.30	0.34	0.28	22.9^e	0.30	0.34	0.28	f	5.57	5.51	5.47
$C_n{}^h$	29.7^e	6.97	6.75	6.65					$29\text{-}30^{i,j}$	0.44-11.74	0.40-11.04	0.40-10.60
$C_n{}^k$					29.7^e	6.97	6.75	6.65	f,i	0.54-1.09	0.55-1.11	0.55-1.10
$C_\gamma{}^d$	32.2^e	0.46	0.50	0.43	32.2^e	0.46	0.50	0.43	10-15	1.64	1.62	1.61
$C_{ar}{}^l$	110-160	28.39	27.62	30.33	110-160	28.39	27.62	30.33	102-165	28.12	27.60	30.74
$C_{ar-alk}{}^m$	137.5-160	8.31	7.15	8.23	137-160	8.73	7.57	8.70	133-151	9.13	8.66	9.44
percentage distribution determined as structural indexes calculated from the integrals												
C_α/C_γ		3.07	2.70	3.08		3.07	2.70	3.08		1.15	1.15	1.18
$C_{alk}{}^n = C_\alpha + C_\beta + C_\gamma + C_n$		9.14	8.94	8.69		9.14	8.94	8.69		9.53-20.83	9.38-20.02	9.38-19.58
$n^o = 2(C_\alpha + C_\beta + C_\gamma + C_n)/C_\alpha$		12.97	13.28	13.07		12.97	13.28	13.07		10.12-22.13	10.11-21.58	9.88-20.63
$C_{ar-H}{}^p = H_{ar}/(C/H)$		7.04	7.91	7.46		7.04	7.91	7.46	$102\text{-}131^j$	1.55	1.60	1.59
$C_{ar-Me}{}^q = H_{\alpha-Me}/[3(C/H)]$		0.54	1.37	0.68					$18\text{-}22^j$	0.56	0.56	0.57
$C_{ar-J}{}^r = C_{ar-H} + C_{ar-Me} + C_{ar-alk}$		15.89	16.43	16.38		16.30	16.86	16.84	$128\text{-}165^j$	11.25	10.82	11.59
$C_{ar-b}{}^s = C_{ar} - C_{ar-J}$		12.50	11.19	13.95		12.09	10.76	13.49	$129\text{-}135^j$	5.18	5.47	5.74
$f_a{}^t = C_{ar}/(C_{sat} + C_{ar})$		0.28	0.28	0.30		0.28	0.28	0.30		0.29	0.28	0.31
$f_{ar-H}{}^u = C_{ar-H}/C_{ar}$		0.25	0.29	0.25		0.25	0.29	0.25		0.06	0.06	0.05
$f_{ar-alk}{}^v = C_{ar-alk}/C_{ar}$		0.29	0.26	0.27		0.31	0.27	0.29		0.32	0.31	0.31
$f_{ar-Me}{}^w = C_{ar-Me}/C_{ar}$		0.02	0.05	0.02		0.02	0.05	0.02		0.02	0.02	0.02
$f_c{}^x = C_{ar-b}/C_{ar}$		0.44	0.41	0.46		0.43	0.39	0.44		0.18	0.20	0.19
$f_p{}^y = C_{ar-J}/C_{ar}$		0.56	0.59	0.54		0.57	0.61	0.56		0.40	0.39	0.38

[a]Asphalt penetration, 80-100. [b]Asphalt penetration, 60-70. [c]C_{sat}, aliphatic carbons. [d]$C_{\alpha, -\beta, -\gamma}$, aliphatic carbon α, β, γ or further removed to aromatic (Ar-C_α-C_β-C_γ...). [e]Integrating the cited discrete value ± 0.1 ppm. [f]Data obtained according to Supporting Information (SI),Table A3[25]. [g]C_{Me-b}, branched methyl. [h]C_n, δ or further removed carbons in a paraffinic straight chain. [i]Minimum or maximum values assuming that all the naphthenic hydrogen is only methylene or methine, respectively (SI, Table A3). [j]Data obtained according to SI, Table A3[25]. [k]C_n, carbons in cycloalkyl groups. [l]C_{ar}, aromatic carbons. [m]C_{ar-alk}, aromatic carbons attached to alkyl (except methyl). [n]C_{alk}, carbon into aliphatic fragments. [o]n, average chain length. [p]C_{ar-H}, aromatic carbons attached to hydrogen. [q]C_{ar-Me}, aromatic carbons attached to methyl group. [r]C_{ar-J}, peripheral aromatic carbons (non-bridgehead). [s]C_{ar-b}, aromatic carbons in bridgehead. [t]f_a, aromaticity factor. [u]f_{ar-H}, fraction of aromatic carbons attached to hydrogen. [v]f_{ar-alk}, fraction of aromatic carbons attached to alkyl (except methyl). [w]f_{ar-Me}, fraction of aromatic carbons attached to methyl group. [x]f_c, fraction of aromatic carbons in bridgehead. [y]f_p, fraction of peripheral aromatic carbons (non-bridgehead).

Table 7. Samples Composition Used to Acquire ^{13}C NMR Spectra of Crude Oil, Coal or its

Fractions that Appears Published Since 1972 to 2006. [45]

relaxation agent[a]	sample dissolved in CDCl$_3$, TMS
Cr, 0.1 M	synthetic blends, mineral base oil and a blend of mineral base oil, 30-40%.[66]
Cr, 0.08-0.15 M	petroleum fractions, boiling point below 200 °C.[67]
Cr, 0.2 M	asphaltenes obtained from bitumen processed at three Indian refineries.[68]
Fe or Cr, 0-0.1 M	asphaltenes, vacuum residue and distillate of light Arabian petroleum.[69]
Cr, 0.01 M	Bitumens, 20%.[58]
Cr, 0.15 M	base oils, 40-50%.[70]
Cr, 0.6%	petroleum fractions, fuels, middle fractions and synthetic blends, 20-30%.[28]
Cr, 1.0%	intermediate boiling fractions (175.5-254.5 °C) of an Alwyn crude oil.[71]
Fe, 1.0%[b]	anthracene oil and East Texas lignite extract.[72]
Cr, 0.2 M	vacuum gas oil.[73]
Cr, 0.1 M	straight run and fluid catalytic cracked gasolines and coker kerosine, 30-40%.[74]
⋯	synthetic blends and aromatic fraction of diesel, 50%.[75]
Fe, 5.0%	fractions of Kuwait petroleum (37-200 °C), 2/1 v/v.[76]
⋯	petroleum waxes insolubles in acetone-petroleum ether mixtures, 40-80%.[77]
Fe, 0.5%	asphalt fractions (asphaltenes, resins, naphthenes and saturates), 50%.[4]
Cr, 0.1 M	vacuum residua and vacuum gas oils from RFCC[c] feed samples, 30%.[78]
Cr, ⋯ %	several fractions of oils and synthetic blends.[61]
Cr, 0.3 M	narrow-cuts from petroleum residua, 10%.[79]
⋯	shale oils by pyrolisis and hydropyrolisis, 13/7 v/v.[80]
Cr, 3.0%	coal tar pitches, 20%.[60]
Cr, %	oil shale-derived asphaltenes and pre-asphaltenes, 50%.[81]
Cr, %	asphaltenes isolated from crude oil, vacuum or atmospheric residua.[82]
Cr, 0.01 M	asphaltenes of light, medium and heavy oils.[83]
Fe, 0.05 M	petroleum asphalts, 10%.[84]

[a]Iron(III) or chromium(III) acetylacetonate. [b]Iron(III) trifluoroacetylacetonate. [c]RFCC, residue fluid catalytic cracking.

Table 8. Distinct Values of Some Same Indexes (%) Calculated According to Different

Approaches for the Structural Characterization by NMR of Asphalts.

carbon type	Hasan et al.[16]			Siddiqui and Ali[4]			Avella and Fierro[25]		
	samples								
	P1	P2	P3	P1	P2	P3	P1	P2	P3
C$_{ar-H}$[a]	1.43	1.60	1.51	1.44	1.62	1.53	1.55	1.60	1.59

$C_{ar\text{-}H}$[b]	7.04	7.91	7.46	7.04	7.91	7.46			
$C_{ar\text{-}alk}$[a]	1.69	1.45	1.67	1.78	1.53	1.76	9.13	8.66	9.44
$C_{ar\text{-}alk}$[b]	8.31	7.15	8.23	8.73	7.57	8.7			
$C_{ar\text{-}Me}$[a]	0.11	0.28	0.14	0.20	0.36	0.22	0.56	0.56	0.57
$C_{ar\text{-}Me}$[b]	0.54	1.37	0.68	0.54	1.37	0.68			
$C_{ar\text{-}q}$[a]	26.96	26.02	28.82	26.95	26.00	28.80	26.57[c]	26.00[c]	29.15[c]
$C_{ar\text{-}q}$[b]	21.35	19.71	22.87	21.35	19.71	22.87			

[a]$\%C_i = 6f(\%H_i)(I_{Htotal})/(n_H I_{Ctotal})$; f is the factor calculated according to Avella and Fierro[25] from the NMR spectra. [b]Calculated by the average C/H ratio as Hasan et al.[16], and Siddiqui and Ali[4] from ^{1}H NMR. [c]$C_{ar\text{-}q}$, only sp^2 quaternary carbons. Where:

	P1	P2	P3			P1	P2	P3
I_{Htotal}	3.66	3.62	3.57		C/H	0.68	0.69	0.69
I_{Ctotal}	31.73	32.01	32.22		Factor f	0.43	0.43	0.44

Table 9. Some Other Structural Indexes of the Asphalts Obtained by NMR According to Avella and Fierro.[25]

index	samples		
	P1	P2	P3
calculated average empirical formula			
unfractioned sample	$C_{139.5}H_{203.6}N_{1.3}O_{1.5}S$	$C_{138.7}H_{201.4}N_{1.4}O_{1.4}S$	$C_{138.9}H_{200.9}N_{1.4}O_{1.3}S$
aliphatic fraction	$C_{98.3}H_{192.4}$	$C_{98.9}H_{190.0}$	$C_{94.6}H_{189.5}$
olefinic fraction	$C_{1.9}H_{0.5}$	$C_{1.5}H_{0.4}$	$C_{1.6}H_{0.4}$
aromatic fraction	$C_{39.2}H_{10.7}$	$C_{38.3}H_{11.0}$	$C_{42.7}H_{10.9}$
structural index			
average mass (g/empirical formula)	1955.1	1943.2	1943.0
HDI[a] of the empirical formula	38.8	39.2	39.6
HDI[a] of the aliphatic fraction	2.6	4.4	0.4
HDI[a] of the olefinic fraction	2.2	1.8	1.9
HDI[a] of the aromatic fraction	34.4	33.3	37.7
C_n[b]$/CH_3\text{-}\gamma$[c]	2.72	2.99	2.99
$CH_3\text{-}\alpha/C_\alpha$ (%)[d]	29.8	30.1	30.0
$CH_2\text{-}\alpha/C_\alpha$ (%)[d]	46.8	46.8	46.8
$CH\text{-}\alpha/C_\alpha$ (%)[d]	23.4	23.1	23.2

[a]HDI, hydrogen deficiency index (number of unsaturations and/or cycles). [b]C_n, δ or further removed carbons in a paraffinic straight chain. [c]$CH_3\text{-}\gamma$, methyl in γ, δ or more to aromatic. [d]$CH_3\text{-}\alpha$, $CH_2\text{-}\alpha$ and $CH\text{-}\alpha$, methyl, methylene or methyne in an aromatic fragment, respectively, and C_α is total carbon in α to aromatic fragment.

Table 10. Average Length and Percentage of Short Chains in the Structure of Three Asphalts

Calculated from the Assumed or Estimated Long Chain Length by NMR (According to Avella

and Fierro[25]).

If ALLC is	then P1			then P2			then P3		
	LC (%)[a]	ALSC[b]	SC (%)[c]	LC (%)[a]	ALSC[b]	SC (%)[c]	LC (%)[a]	ALSC[b]	SC (%)[c]
8	36.8	11.4	63.2	33.4	11.2	66.6	33.5	10.8	66.5
10	18.4	10.1	81.6	16.7	10.1	83.3	16.7	9.9	83.3
12	9.2	9.9	90.8	8.4	9.9	91.6	8.4	9.7	91.6
14	6.1	9.9	93.9	5.6	9.9	94.4	5.6	9.6	94.4
16	4.6	9.8	95.4	4.2	9.9	95.8	4.2	9.6	95.8
18	3.7	9.8	96.3	3.3	9.8	96.7	3.3	9.6	96.7
20	3.1	9.8	96.9	2.8	9.8	97.2	2.8	9.6	97.2
30	1.7	9.8	98.3	1.5	9.8	98.5	1.5	9.6	98.5
40	1.2	9.8	98.8	1.0	9.8	99.0	1.0	9.6	99.0

ALLC, assumed average length (as number of carbons) of normal long chain. [a]LC(%), percentage of normal long chain [LC(%) = $100(CH_{3-\gamma}$ in long chain)/(% Total $CH_{3-\gamma}$ in the sample]. [b]ALSC, average length of the normal short chain {ALSC = 100[Minimum average length of chain (Table 6)]/[LC(%)(ALLC)]}. [c]SC (%), percentage of normal short chain [SC(%) = $100(CH_{3-\gamma}$ in short chain)/(% Total $CH_{3-\gamma}$ in the sample)].

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information**

Equations to determine the integral of the signals in the NMR spectra of the sample (Tables A1

and A2) and some additional information to calculate percentage of certain carbon types

included into Table 6 (Table A3) for the structural characterization of petroleum, coal or their

derived fractions, such as it was proposed by Avella and Fierro,[25,45] can be found in this section.

The material is available free of charge on the ACS Publications website at DOI: …

AUTHOR INFORMATION

Corresponding Author

* E-mail: eavellamo@unal.edu.co.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The Authors declare no competing financial interest.

ACKNOWLEDGMENT

ABBREVIATIONS

The required abbreviations were defined in the main document and in the associated content at its first mention into the text.

REFERENCES

(1) Corbett, L. W. Composition of asphalt based on generic fractionation. Using solvent deasphaltening, elution-adsorption chromatography and densimetric characterization. *Anal. Chem.* **1969**, *41*, 576-579.

(2) ASTM D4124. Standard Test Method for Separation of Asphalt into Four Fractions. *American Society for Testing and Materials (ASTM)*, West Conshohocken, PA, 2009.

(3) Siddiqui, M. N.; Ali, M. F. Studies on the aging behavior of the Arabian asphalts. *Fuel* **1999,** *78*, 1005-1015.

(4) Siddiqui, M. N.; Ali, M. F. Investigation of chemical transformations by NMR and GPC during the laboratory aging of arabian asphalt. *Fuel* **1999,** *78*(12), 1407-1416.

(5) Lamontagne, J.; Dumas, P.; Mouillet, V.; Kister, J. Comparison by Fourier transform infrared (FTIR) spectroscopy of different ageing techniques: Application to road bitumens. *Fuel* **2001,** *80*(4), 483-488.

(6) Siddiqui, M. N.; Ali, M. F.; Shirokoff, J. Use of X-ray diffraction in assessing the aging pattern of asphalt fractions. *Fuel* **2002,** *81*(1), 51-58.

(7) Siddiqui, M. N. Alkylation and oxidation reactions of Arabian asphaltenes. *Fuel* **2003,** *82*(11), 1323-1329.

(8) Ouyang, C.; Wang, S.; Zhang, Y.; Zhang, Y. Improving the aging resistance of asphalt by addition of Zinc dialkyldithiophosphate. *Fuel* **2006,** *85*(7-8), 1060-1066.

(9) Siddiqui, M. N. Effect of oxidation on the chemistry of asphalt and its fractions. *Arab. J. Sci. Eng. Sect. A Sci. (Special Issue)* **2009,** *21*, 25-31.

(10) Williams, R. B. Characterization of Hydrocarbons in petroleum by nuclear magnetic resonance spectrometry. In: Symposium on composition of petroleum oils, determination and evaluation. *ASTM Spec. Technol. Publ.* **1958,** *24*(STP224), 168-194.

(11) Brown, J. K.; Ladner, W. R.; Sheppard, N. A Study of the Hydrogen Distribution in Coal-like Materials by High-Resolution Nuclear Magnetic Resonance Spectroscopy. I. The Measurement and Interpretation of the Spectra. II. A Comparison with infra-red measurement and the conversion to carbon structur. *Fuel* **1960,** *39*, 79-96.

(12) Ramsey, J. W.; McDonald, F. R.; Petersen, J. C. Structural study of asphalts by nuclear magnetic resonance. *Industrial and engineering chemistry product research and development* **1967,** *6*(4), 231-236.

(13) Knight, S. A. Analysis of aromatic petroleum fractions by means of absorption mode carbon-H NMR spectroscopy. *Chemistry and Industry* **1967,** *11*, 1920-1923.

(14) Clutter, D. R.; Petrakis, L.; Stenger, R. L.; Jensen, R. K. Nuclear magnetic resonance spectrometry of petroleum fractions. Carbon-13 and proton nuclear magnetic resonance characterizations in terms of average molecular parameters. *Anal. Chem.* **1972,** *44*, 1395-1405.

(15) Rongbao, L.; Zengmin, S.; Bailing, L. Structural analysis of polycyclic aromatic hydrocarbons derived from petroleum and coal by ^{13}C and ^{1}H NMR Spectroscopy. *Fuel* **1988,** *67*, 565-569.

(16) Hasan, M. U.; Ali, M. F.; Bukhari, F. Structural characterization of Saudi Arabian heavy crude oil by n.m.r. spectroscopy. *Fuel* **1983,** *62*, 518-523.

(17) Hasan, M. U.; Ali, M. F.; Bukhari, F. Structural characterization of Saudi Arabian medium crude oil by n.m.r. spectroscopy. *Fuel* **1985,** *64*, 839-841.

(18) Hasan, M. U.; Ali, M. F.; Arab, M. Structural characterization of Saudi Arabian extra light and light crudes oil by ^{1}H and [13]C n.m.r. spectroscopy. *Fuel* **1989,** *68*, 801-803.

(19) Romero, C. M.; Gómez, A. Propiedades físicas y químicas de asfaltos colombianos tipo Barrancabermeja y de sus respectivas fracciones de asfaltenos [Physical and chemical properties of Colombian Barrancabermeja type asphalts and their respective fractions of asphaltenes]. *Acad. Colomb. Cienc.* **2002,** *26*(98), 127-132.

(20) Siddiqui, M. N. NMR Finger printing of chemical changes in asphalt fractions on oxidation. *Petroleum Science and Technology* **2009,** *27*, 2003-2045.

(21) Huang, J. Characterization of asphalt fractions by NMR Spectroscopy. *Petroleum Science and Technology* **2010,** *28*, 618-624.

(22) Ma, L. X.; Wu, S. P.; Huang, J. F. Investigation of chemical properties by NMR during the laboratory aging of asphalt. Wuhan Ligong Daxue Xuebao. *Journal of Wuhan University of Technology* **2010,** *32*(17), 43-46.

(23) Siddiqui, M. N. NMR fingerprinting of chemical changes in asphalt fractions on oxidation. *Petroleum Science and Technology* **2010,** *28*(4), 401-411.

(24) Siddiqui, M. N. Catalytic pyrolysis of Arab Heavy residue and effects on the chemistry of asphaltene. *J. Anal. Appl. Pyrolysis* **2010,** *89*(2), 278-285.

(25) Avella, E.; Fierro, R. Intervalos de integración unificados para la caracterización estructural de petróleos, carbones o sus fracciones por RMN ^{1}H y RMN [13]C [Unified integration intervals for the structural characterization of oil, coal, or fractions thereof by ^{1}H NMR and ^{13}C NMR]. *Revista Colombiana de Química* **2010,** *39*(1), 87-109.

(26) Avella, E.; Gómez, S.; Fierro, R. Determinación rápida y precisa del contenido de hidrógeno en mezclas de hidrocarburos por RMN [1]H [Fast and precise determination of the hydrogen content in hydrocarbons mixtures by ^{1}H NMR]. *Revista Colombiana de Química* **2012,** *41*(1), 7-30.

(27) Shirokoff, J. W.; Siddiqui, M. N.; Ali, M. F. Characterization of the structure of Saudi crude asphaltenes by X-ray diffraction. *Energy Fuels* **1997,** *11*(3), 561-564.

(28) Lee, S. W.; Glavincevski, B. NMR method for determination of aromatics in middle distillate oils. *Fuel Process. Technol.* **1999,** *60*(1), 81-86.

(29) Srivastava, M.; Singh, I. D.; Singh, H. Structural characterization of petroleum based feedstocks for carbon black production. *Petroleum Science and Technology* **1999,** *17*(1-2), 67-80.

(30) Bhandari, D. S.; Bathia, B. M.; Madhwal, D. C.; Rawat, M. S.; Nagpal, J. M.; Aloopwan, M. K. Physico-chemical and compositional studies on vaccum gas oils from North Gujarat crudes. *Indian Journal of Chemical Technology* **2000,** *7*(3), 116-120.

(31) Kohli, R.; Bhatia, B. M.; Madhwal, D. C. Compositional studies on hydrocarbon type fraction from deasphalted oils and asphalts by NMR spectrometry. *Petroleum Science and Technology* **2001,** *19*(7-8), 885-898.

(32) Duquesne, S.; Bras, M. L.; Bourbigot, S.; Delobel, R.; Camino, G.; Eling, B.; Lindsay, C.; Roels, T.; Vezin, H. Mechanism of fire retardancy of polyurethanes using ammonium polyphosphate. *J. Appl. Polym. Sci.* **2001***, 82*(13), 3262-3274.

(33) Bathia, B. M.; Goyal, B. S.; Aswal, D. S.; Aloopwan, M. K.; Kothari, G. C. Structural characterization of VGOs from western region crudes by NMR spectrometry. *Petroleum Science and Technology* **2003,** *21*(1-2), 125-132.

(34) Ali, F.; Khan, Z. H.; Ghaloum, N. Structural studies of vacuum gas oil distillate fractions of Kuwaiti crude oil by nuclear magnetic resonance. *Energy Fuels* **2004,** *18*(6), 1798-1805.

(35) Brebeanu, G. The influence of the hydrocracking process parameters on the oils characteristics. *Revista de Chimie* **2004,** *55*(8), 648-651.

(36) Sutcu, H.; Toroglu, I.; Piskin, S. Structural characterization of oil component of high temperature pyrolysis tars. *Energy Sources* **2005,** *27*(6), 521-534.

(37) De Peinder, P.; Visser, T.; Petrauskas, D. D.; Salvatori, F.; Soulimani, F.; Weckhuysen, B. M. Prediction of long-residue properties of potential blends from mathematically mixed infrared spetra of pure crude oils by partial least-squares regression models. *Energy Fuels* **2009,** *23*(4), 2164-2168.

(38) Elbaz, A. M.; Gani, A.; Hourani, N.; Emwas, A-H.; Sarathy, S. M.; Roberts, W. L. TG/DTG, FT-ICR Mass Spectrometry, and NMR Spectroscopy Study of Heavy Fuel Oil. *Energy Fuels* **2015**, 29(12), 7825-7835.

(39) Min, K. E.; Jeong, H. M. Structures and properties of semi-blown petroleum asphalt. *Journal of the Korean Industrial and Engineering Chemistry* **2011,** *22*(6), 664-671.

(40) Xiao, Y.; Feng, R.; Cao, S.; Liu, X.; Gao, T.; Pan, Z. Characterization of coal tar pitch and paving pitch by UV, EA and NMR. *Chemical Industry and Engineering* **2011,** *28*, 11-17.

(41) Honse, S. O.; Ferreira, S. R.; Mansur, C. R.; Lucas, E. F.; González, G. Separation and characterization of asphaltenic subfractions. *Quim. Nova* **2012,** *35*(10), 1991-1994.

(42) Masili, A.; Puligheddu, S.; Sassu, L.; Scano, P.; Lai, A. Prediction of physical-chemical properties of crude oils by ^{1}H NMR analysis of neat samples and chemometrics. *Magn. Reson. Chem.* **2012,** *50*(11), 729-738.

(43) Pourabdollah, K.; Mokhtari, B. Application of 1H NMR in the flow surveillance of oil wells. *Magn. Reson. Chem.* **2012,** *50*(3), 208-215.

(44) Hauser, A.; Alhumaidan, F.; Al-Rabiah, H. NMR investigations on products from thermal decomposition of Kuwaiti vacuum residues. *Fuel* **2013,** *113*, 506-515.

(45) Avella, E. Aplicación de resonancia magnética nuclear para la caracterización de fracciones pesadas del petróleo en el proceso de desasfaltado por extracción (DEMEX). [Application of NMR to characterize heavy oil fractions in the deasphalting process by extraction (DEMEX)], Doctoral dissertation available at http://www.bdigital.unal.edu.co/3977/, Tesis, Universidad Nacional de Colombia, Bogotá, Colombia, 2011.

(46) ASTM D5. Standard Test Method for Penetration of Bituminous Materials. *American Society for Testing and Materials (ASTM)*, West Conshohocken, PA, 2013.

(47) ASTM D113. Standard Test Method for Ductility of Bituminous Materials. *American Society for Testing and Materials (ASTM)*, West Conshohocken, PA, 2007.

(48) ASTM D36. Standard Test Method for Softening Point of Bitumen (Ring-and-Ball Apparatus). *American Society for Testing and Materials (ASTM)*, West Conshohocken, PA, 2014.

(49) ASTM D3289. Standard Test Method for Density of Semi-Solid and Solid Bituminous Materials (Nickel Crucible Method). *American Society for Testing and Materials (ASTM)*, West Conshohocken, PA, 2008.

(50) ASTM D4402. Standard Test Method for Viscosity Determination of Asphalt at Elevated Temperatures Using a Rotational Viscometer. *American Society for Testing and Materials (ASTM)*, West Conshohocken, PA, 2015.

(51) Thermo Scientific. *Thermo scientific Flash 2000 series, organic elemental analyzers.* https://www.thermoscientific.com/content/dam/tfs/ATG/CMD/CMD%20Documents/BR-11007-FLASH-2000-Series-Organic-Elemental-Analyzers.pdf (accesed Jan 20, 2015).

(52) Compostela, Universidad Santiago de. *Mestrelab Research S.L. Software licenciado MestRe-C 4.8.6.0*. http://mestrelab.com/?s=mestrec+4.8.6.0 (accesed Jun 1, 2014).

(53) Martínez, C. *Estadística y muestreo*; Ecoe Ediciones: Bogotá, 2003; pp 86-95, 149, 156, Tabla II.

(54) Pfeiffer, J. P.; Van Doormal, P. M. The reological properties of asphaltic bitumens. *Journal of Institute of petroleum technologists* **1936,** *22*, 414-440.

(55) EN 12591, Appendix A. Bitumen and Bituminous Binders - Specifications for Paving Grade Bitumens. *European Standard*, Avenue Barnix 17, B-1000 Brussels, 2009.

(56) Bouquet, M.; Bailleul, A. Routine method for quantitative ^{13}C NMR spectra editing and providing structural patterns. Application to every kind of petroleum fractions including residues and asphaltenes. *Fuel* **1986,** *65*, 1240-1246.

(57) Bestougeff, M. A.; Byramjee, R. J. Chemical constitution of asphaltenes (Chapter 3). In: Yen, T. F. and Chilingarian, G. V. Asphaltenes and asphalts, I. *Developments in Petroleum Science* **1994,** *40*, 67-94.

(58) Michon, L.; Martin, D.; Planche, J.-P.; Hanquet, B. Estimation of average structural parameters of bitumens by 13C nuclear magnetic resonance spectroscopy. *Fuel* **1997,** *76*, 9-15.

(59) Kazhaev, R. S.; Kemalov, A. F.; Diyarov, A. N.; Fakhrutdinov, R. Z. Relation between parameters and service characteristics of asphalts: The role of structural ordering. *Chemistry and Technology of Fuels and Oils* **1999,** *35*, 98-103.

(60) Díaz, C.; Blanco, C. G. NMR: A powerful tool in the characterization of coal tar pitch. *Energy Fuels* **2003,** *17*, 907-913.

(61) Khadim, M. A.; Wolny, R. A.; Al-Dhuwaihi, A. S.; Al-Hajri, E. A.; Ghamdi, M. A. Determination of hydrogen and carbon contents in crude oil and petroleum fractions by NMR Spectrosocpy. *The Arabian Journal for Science and Engineering* **2003,** *28*, 147-162.

(62) Nielsen, K. E.; Dittmer, J.; Anders Malmendal, J. A.; Nielsen, N. C. Quantitative analysis of constituents in heavy fuel oil by ^{1}H nuclear magnetic resonance (NMR) spectroscopy and multivariate data analysis. *Energy Fuels* **2008,** *22*(6), 4070–4076.

(63) Ahmad, I.; Shakirullah, M.; Rehman, H.; Ishaq, M.; Khan, M. A.; Shah, A. A. NMR analysis of cracking products of asphalt and assessment of catalyst performance. *Energy* **2009,** *34*, 127-133.

(64) Jacobsen, N. E. *NMR spectroscopy explained: Simplified Theory, Applications and Examples for Organic Chesmistry and Structural Biology*; John Wiley: New Jersey, 2007; pp 3, 75.

(65) Richards, S. A.; Hollerton, J. C. *Essential practical NMR for organic chemistry*; Jhon Wiley: Singapore, 2011; pp 12-13.

(66) Sastry, M. I.; Mukherjee, S.; Kapur, G. S.; Sarpal, A. S.; Jain, S. K.; Srivastava, S. P. Modified method for hydrocarbon type analysis of blended base stocks by infrared spectroscopy. *Fuel* **1995,** *74*, 1343-1346.

(67) Ozubko, R. S.; Clugstone, D. M.; Furimsky, E. Comparison of mass spectrometry and nuclear magnetic resonance spectrometry for determination of hydrocarbon type. *Anal. Chem.* **1981,** *53*, 183-187.

(68) Christopher, J.; Sarpal, A. S.; Kapur, G. S.; Krishna, A.; Tyagi, B. R.; Jain, M. C.; Jain S. K.; Bhatnagar, A. K. Chemical structure of bitumen-derived asphaltenes by nuclear magnetic resonance spectroscopy and X-raydifractometry. *Fuel* **1996,** *75*, 999-1008.

(69) Gillet, S.; Delpuech, J.-J.; Valentin, P.; Escallier, J.-C. Optimum conditions for crude oil and petroleum product analysis by carbon-13 nuclear magnetic resonance spectrometry. *Anal. Chem.* **1980,** *52*, 813-817.

(70) Sarpal, A. S.; Kapur, G. S.; Mukherjee, S.; Jain, S. K. Characterization by ^{13}C NMR spectroscopy of base oils produced by different processes. *Fuel* **1997,** *76*, 931-937.

(71) Dosseh, G.; Rousseau, B.; Fuchs, A. H. Identification of aromaticmolecules in intermediate boiling crude oil fractions by 2D NMR spectroscopy. *Fuel* **1991,** *70*, 641-646.

(72) Cantor, D. M. Nuclear Magnetic Resonance spectrometric determination of average molecular structure parameters for coal-derived liquids. *Anal. Chem.* **1978,** *50*, 1185-1187.

(73) Kapur, G. S.; Chopra, A.; Sarpal, A. S. Estimation of total aromatic content of vacuum gas oil (VGO) fractions (370-560 ºC) by ^{1}H NMR spectroscopy. *Energy Fuels* **2005,** *19*, 1065-1071.

(74) Bansal, V.; Sarpal, A. S.; Kapur, G. S.; Sharma, V. K. Estimation of bromine number of petroleum distillates by NMR spectroscopy. *Energy Fuels* **2000,** *14*, 1028-1031.

(75) Kapur, G. S.; Findeisen, M.; Berger, S. Analysis of hydrocarbon mixtures by diffusion-ordered NMR spectroscopy. *Fuel* **2000,** *79*, 1347-1351.

(76) Abu-Dagga, F.; Rüegger, H. Evaluation of low boiling crude oil fractions by NMR spectroscopy. Average structural parameters and identification of aromatic components by 2D NMR spectroscopy. *Fuel* **1988,** *67*, 1255-1262.

(77) Musser, B. J.; Kilpatrick, P. K. Molecular Characterization of Wax Isolated from a Variety of Crude Oils. *Energy Fuels* **1998,** *12*, 715-725.

(78) Bansal, V.; Krishna, G. J.; Chopra, A.; Sarpal, A. S. Detailed Hydrocarbon Characterization of RFCC Feed Stocks by NMR SpectroscopicTechniques. *Energy Fuels* **2007,** *21*, 1024-1029.

(79) Zhao, S.; Xu, Z.; Xu, C.; Chung, K. H.; Wang, R. Systematic characterization of petroleum residua based on SFEF. *Fuel* **2005,** *84*, 635-645.

(80) Netzel, D. A.; Miknis, F. P. NMR study of US eastern and western shale oils produced by pyrolysis and hydropyrolysis. *Fuel* **1982,** *61*, 1101-1109.

(81) Canel, M; Canel, E.; Borrego, A. G.; Blanco, C. G.; Guillén, M. D. Characterization of the Göynük oil shale-derived asphaltenes and preasphaltenes by ^{1}H and ^{13}C nuclear magnetic resonance and by gas chromatography. *Fuel Process. Technol.* **1995,** *43*, 111-122.

(82) Calemma, V.; Rausa, R.; D'Antona, P.; Montanari, L. Characterization of Asphaltenes Molecular Structure. *Energy Fuels* **1998,** *12*, 422-428.

(83) Ibrahim, H. H.; Idem, R. O. Correlations of Characteristics of Saskatchewan Crude Oils/Asphaltenes with Their Asphaltenes Precipitation Behavior and Inhibition Mechanisms: Differences between CO_2- and n-Heptane-Induced Asphaltene Precipitation. *Energy Fuels* **2004,** *18*, 1354-1369.

(84) Delpuech, J.-J.; Nicole, D.; Daubenfeld, J.-M.; Boubel, J.-C. Method to evaluate benzonaphthenic carbons and donatable hydrogens in fossil fuels. *Fuel* **1985,** *64*, 325-334.

(85) Claridge, T. D. *High-Resolution NMR Techniques in Organic Chemistry;* Elsevier: Amsterdam, 2005; pp 27-33, 38, 112-114, 279-282, 368-371.

(86) Michael, G.; Al-Siri, M.; Khan, Z. H.; Ali, F. A. Differences in average chemical structures of asphaltene fractions separated from feed and product oils of a mild thermal processing reaction. *Energy Fuels* **2005,** *19*, 1598-1605.

(87) Grant, D. M.; Paul, E. G. Carbon-13 Magnetic Resonance. II. Chemical Shift Data for the Alkanes. *J. Am. Chem. Soc.* **1964,** *86*(15), 2984-2990.
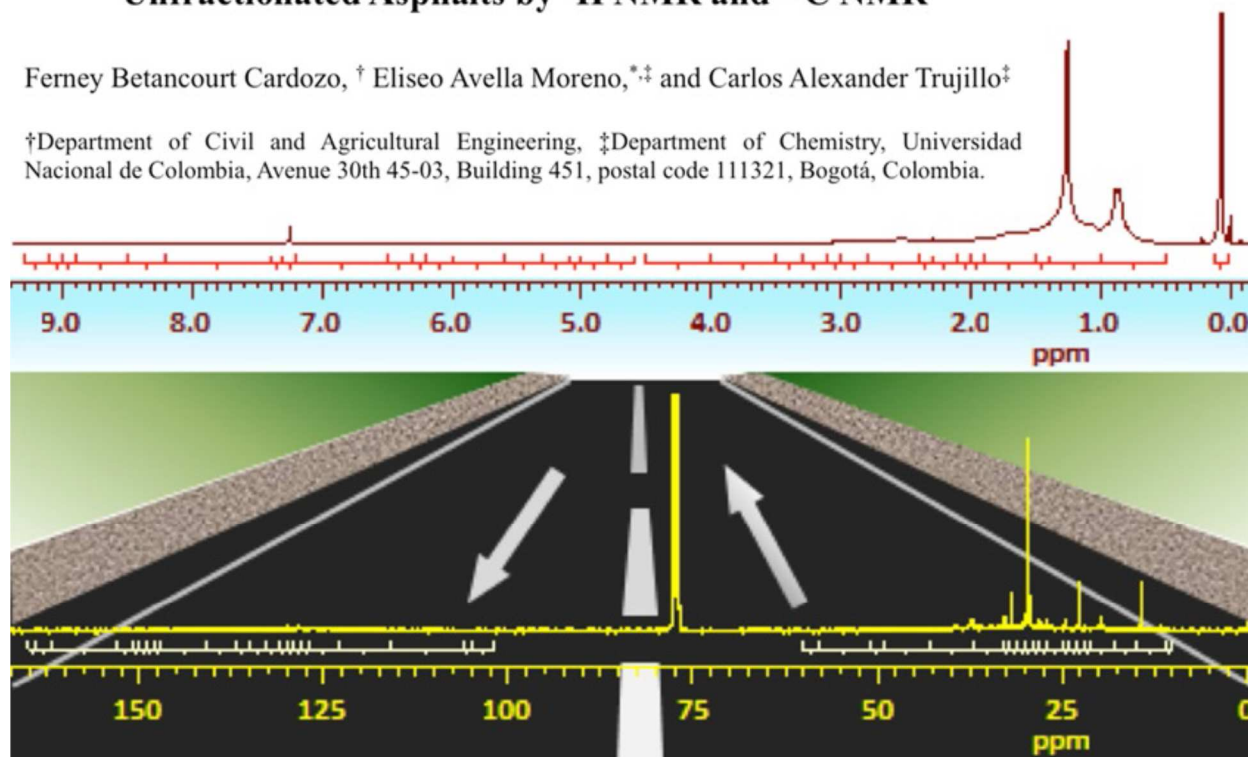
(88) Lindeman, L. P.; Adams, J. Q. Carbon-13 nuclear magnetic resonance spectrometry. Chemical shifts for the paraffins through C9. *Anal. Chem.* **1971,** *43*(10), 1245-1252.

(89) Spectral Database for organic compounds, SDBS. http://sdbs.db.aist.go.jp/sdbs/cgi-bin/cre_index.cgi (accesed Dec 1, 2014).

Structural Characterization of
Unfractionated Asphalts by ¹H NMR and ¹³C NMR

Ferney Betancourt Cardozo, [†] Eliseo Avella Moreno,[*,‡] and Carlos Alexander Trujillo[‡]

†Department of Civil and Agricultural Engineering, ‡Department of Chemistry, Universidad Nacional de Colombia, Avenue 30th 45-03, Building 451, postal code 111321, Bogotá, Colombia.

An improved methodology for the structural characterization of heavy fractions of petroleum by hydrogen-1 and carbon-13 nuclear magnetic resonance was applied to three fresh and unfractionated asphalts in solution. The results were compared with those generated by other two known characterization methods applied to the same NMR spectra. The comparison revealed inconsistencies in the traditional methods for the structural characterization of this type of materials. The improved methodology can be applied to unfractionated samples, and it provides a more detailed structural characterization of the asphalts than previously obtained. The new method provides a better correlation between physicochemical properties and the chemical structure of the complex mixtures of hydrocarbons.