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Investigation of Asphaltene Chemical Structural Modification Induced by Thermal Treatments

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In the conversion of heavy oil into valuable fuels by thermal processes, one of the main problems is the formation of soft coke-like substances that can cause equipment fouling and catalyst deactivation. Asphaltenes are present in large quantity in heavy crude oil and are known to be coke precursors. The objective of the present study was to obtain chemical structure information about the asphaltene molecules when they undergo a thermal treatment and to investigate the mechanism of coke formation. Asphaltenes were separated from two industrial thermal treated heavy crude oils and characterized by elemental analysis, NMR, FTIR, and FT-ICR MS. Analytical data were then compared with that obtained from asphaltene samples after thermal treatment at 400 °C. From complementary and comparative use of the different analytical techniques, we demonstrated that asphaltenes thermally treated at 400 °C tend to aromatize to form coke precursors. We found that the species rich in saturated rings and/or alkyl chains are less stable than the one containing aromatic rings; the main reaction in thermal treatment is the intramolecular cyclization/aromatization and not the cleavage of residual aliphatic chains. Moreover, asphaltene classes containing sulfur atoms present a lower stability than the other species.

Introduction

The worldwide current tendency in the oil refining industry is to convert the low-value heavy crude oil into more valuable fuels. These feedstocks are very difficult to process and to transform in light and middle distillates due to their high content of sulfur, nitrogen, and aromatics and large quantity of non-distillable hydrocarbons.^{1,2} One of the main problems in the catalytic hydrotreating process of heavy oil is the formation of soft coke-like substances, resulting in catalyst deactivation and unit operability trouble.^{3,4} This carbonaceous material usually deposits in the fractionable tower and fouls the transfer lines.⁵ To remove these sediments from the equipment, often chemical or mechanical treatments are needed, and this increases enormously the operation costs. The sediment formation becomes more critical with the increase in the operating temperature, forcing the refiners to operate at lower temperature, reducing the hydrocracking process conversion. Asphaltenes are well-known to be coke precursors, and they are present in large quantity in the heavy crude oil.^{6,7} They include the heaviest and the most polar fractions, contain condensed aromatic systems with alkyl and cycloalkyl and are enriched in heteroatoms (N, S, and O). To understand and control the coke

formation, asphaltene characterization is therefore of great interest. Asphaltenes are commonly separated from crude oil by SARA (saturates-aromatics-resins-asphaltenes) fractionation method^{8,9} using saturated hydrocarbons (e.g., heptane). Due to their compositional complexity, the chemical structure of asphaltenes is difficult to define. Different analytical techniques have been used to investigate their mean molecular structure, in particular the number of fused ring, the length of aliphatic chains, the common functional groups, and the molecular weight. Among these methods are vapor pressure osmometry (VPO),^{10,11} size-exclusion chromatography (SEC),^{12,13} ¹³C and ¹H nuclear magnetic resonance (NMR),¹⁴ Fourier transform infrared spectroscopy (FTIR),¹⁵ time-resolved fluorescence depolarization (TRFD),^{16,17} and Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS).^{18,19}

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The reported molecular weight of asphaltenes ranged from 500 to 100 000 g/mol.²⁰ These differences can be explained by considering some degree of aggregation in asphaltenes–solvent mixtures. Recent studies with TRFD have shown that these molecules have a single fused ring system of 4–10 rings, including a small number of aliphatic chains with a molecular weight in the range of 500–1000 g/mol.¹⁷ These data are in agreement with recent high-resolution ¹³C NMR spectra results,²¹ which confirm that average asphaltene molecules possess 4–10 rings.

¹H and ¹³C NMR have been used to examine the distribution of carbon and hydrogen according to different structural groups found in aliphatic and aromatic moieties.¹⁴ On the basis of NMR data, average molecular weights and elemental analysis measurements, number and type of aromatic, aliphatic carbons as well as hydrogens can be identified, and some structure parameters of the “average asphaltene molecule” can be estimated.

FTIR analysis has been used to define a series of structure indexes¹⁵ which, together with structural parameters deduced by NMR analysis, can be used to study the molecular modifications induced by thermal treatments, especially for highly carbonaceous samples that are more difficult to analyze by NMR.

Mass spectrometry is a powerful tool to analyze crude oils and petroleum derivatives. FT-ICR MS with a resolving power of $> 300\,000$ ($m/\Delta m > 300\,000$, Δm is the mass spectral peak full width at half height) allows high mass accuracy (< 1 ppm) for unambiguous assignments of elemental composition of thousands of components per mass spectrum. This technique has been successfully applied to analyze the complex asphaltene mixtures¹⁸ and has demonstrated the possibility to determine accurately the detailed classes (heteroatom content), type (number of rings plus double bonds), and alkylation pattern. The correlation between these parameters and the chemical and physical properties of oil or its derivatives is the main subject of the field known as Petroleomics.²²

All these analytical techniques can be joined together to provide insight into chemical structure information about the asphaltene molecules. This information could then be used to understand the structure–function relationship of these products and to investigate the mechanism of sediment formation. In the present paper the characterization of asphaltenes using different techniques and the corresponding information on their structural modification with respect to thermal treatments are reported. Two heavy crude oils from different Italian fields were treated in a thermal industrial plant, and their asphaltene fractions were collected and characterized by elemental analysis, NMR, FTIR, and FT-ICR MS analysis. The samples were then further heated and analyzed to obtain information on their chemical structure modification and to propose a mechanism of coke formation.

Materials and Methods

Asphaltene Samples Preparation. Asphaltenes were precipitated from the corresponding heavy crude oils treated in thermal industrial plant (samples 1 and 2) according to the following procedure: toluene (Sigma-Aldrich, HPLC grade)

was gently stirred for 30 min at room temperature with the oil samples (volume ratio 5:1). The mixture was filtered with a 0.5 μ m Millipore filter to separate the oil impurities. Toluene was then removed by rotavapor and the toluene-free crude oil was mixed with n-heptane (Sigma-Aldrich HPLC grade) (volume ratio 1:50) in order to precipitate asphaltenes. The mixture was stirred for 2 h and filtered with a 0.5 μ m Millipore filter. The asphaltenes collected on the filter were washed several times with n-heptane until the filtrate became colorless. The solid asphaltenes were dried in vacuum at room temperature with an oil-free pump to evaporate the solvent.

Thermal Treatments of Asphaltenes. Samples 1a and 2a were obtained by heating samples 1 and 2 at 400 °C for 3 h in argon atmosphere in a steel reactor equipped with a stirring system, temperature control, and vent. The thermal treated products were then suspended in toluene, with the mixture stirred for 30 min and filtered with a 0.5 μ m Millipore filter to separate the formed insoluble materials. Toluene was then removed by rotavapor. The solid residue was mixed with n-heptane (volume ratio 1:50), stirred gently for 30 min and the asphaltene fraction (sample 1a and 2a) recovered by filtration as previously described.

Elemental Analysis. The C, H, N, and S contents of the asphaltenes were determined in an elemental analyzer from ThermoQuest Instrument EA 1110. Each sample was analyzed in triplicate.

¹H and ¹³C NMR Analysis. ¹H and ¹³C NMR spectra were recorded after dissolution of the samples in deuterated chloroform (CDCl₃) on a Bruker Avance 400 NMR spectrometer operating at 400 MHz for ¹H and 100.6 MHz for ¹³C.

For the ¹H NMR spectra the following parameters were used: spectral width 6000 Hz, pulse flip angle 30°, relaxation delay 4 s., 128 scans. (CDCl₃ signal at 7.26 p).

For the ¹³C NMR spectra, the following parameters were used: spectral width 20.000 Hz, pulse flip angle 30°, relaxation delay 4 s., 20.000 scans (CDCl₃ signal at 77.7 ppm). For quantitative measurements, the ¹³C NMR spectra were acquired with full decoupling from proton but without NOE enhancement (inverse gated decoupling pulse sequence).

FT-IR Analysis. Asphaltenes were analyzed by diffuse reflectance (DRIFT) spectroscopy with a Nicolet Nexus 670 FTIR spectrometer; the samples were finely ground in an agate mortar with KBr powder (5% w/w ratio), and the so obtained mixtures were subsequently placed in the proper Smart Collector accessory for diffuse reflectance. Background spectrum was acquired using pure KBr powder as reference, and reflectance spectra were converted through a Kubelka–Munk function so that band intensity is linearly proportional to species concentration. All spectra were acquired in the 4000–400 cm^{−1} range with 64 scans and a resolution of 2 cm^{−1}.

FT-ICR MS Analysis. Asphaltene samples were dissolved in toluene and methanol 1:1 to a final concentration of 0.5 mg/mL. Acetic acid and ammonium hydroxide (solution 30%) have been added to a final concentration of 0.1% for positive and negative mode, respectively. Mass analyses were performed on a FT-ICR mass spectrometer (LTQ-FT ThermoFisher Scientific) with electrospray ionization technique (ESI). The FT-LTQ ultra system is a fully integrated hybrid mass spectrometer consisting of a linear ion trap mass spectrometer LTQ-XL, combined with a Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR MS). The FT-ICR MS is equipped with a 7 T actively shielded superconducting magnet. The whole instrument is equipped

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with atmospheric pressure ionization (API) sources; in this work ESI (positive and negative mode) has been used because of the high polarity and high content of heteroatoms in the asphaltene's samples.^{23–25} Chromatographic separation of asphaltenes and other oil-heavy and polar fractions into their single components is not possible because of the complexity and the high molecular weight of the sample. For this reason only direct mass spectrometry analysis with very high resolution can be used.

ESI analysis was carried out with a constant flow rate of 5 μ L/min with a syringe pump. The mass range of the analysis was 200–1000 m/z . Typical negative ion ESI conditions were: capillary voltage –40 V; tube lens voltage –81 V; capillary temperature 270 °C; source voltage 3.5 kV. Spectra have been recorded in profile mode, microscan 1, and max injection time 1000. A minimum of 50 scans were collected for each analysis. The resolving power was set on the instrument at 400 000 (average value at mass 400). Essentially all peaks with magnitude above a threshold of 3σ (standard deviation) of baseline noise have been assigned a molecular formula and considered in the data evaluation.

Data have been processed by the software Xcalibur (Thermo Fisher Scientific Company) after the selection of some restrictions of the range of elements according to elemental analysis results: 10–60 ^{12}C , 0–2 ^{13}C , 10–100 H, 0–6 N, 0–6 ^{32}S , 0–1 ^{34}S , and 0–6 O. These restrictions are required because of the huge number of possible different combinations of atoms that can be generated from a single accurate mass.²¹ First step of data evaluation has been done below 400 Da. At low masses the molecular formulas assignment is more reliable due to the lower number of possible combinations for a single mass. The lists of masses and molecular formulas were subsequently elaborated and distinguished with custom-built software (Isomass). If two or more elemental compositions were found within the mass tolerance of ± 2 ppm, then formulas endowed with the correspondent isotopes ^{13}C and ^{34}S for the sulfur-containing compounds at higher m/z values (respectively, 1.0078 and 1.9958 Da higher) have been regarded and the others skimmed off. The presence of isotopic matching pairs confirms unequivocally the elemental composition assignment.²³ Afterward, masses with relative intensities lower than 0.5% have been cut out. The consequent list of masses and molecular formulas has been elaborated with the software Isomass to pick out different classes of molecules according to the elements present in the formula.

To extend the assignments to higher masses (above 400 Da) the Kendrick mass defect (KMD)²⁷ has been used. Equations 1 and 2:

$$\text{Kendrick mass} = \text{IUPAC mass} \times (14.0000/14.01565) \quad (1)$$

$$\begin{aligned} \text{Kendrick mass defect (KMD)} \\ = \text{nominal Kendrick mass} - \text{Kendrick mass} \end{aligned} \quad (2)$$

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Table 1. Elemental Analysis of Asphaltenes Samples^a

asphaltenes	C (% w/w)	H (% w/w)	S (% w/w)	N (% w/w)	C/H
sample 1	86.88	5.92	1.06	2.08	1.22
sample 2	89.25	6.05	0.93	2.20	1.23
sample 1a	87.55	5.53	1.19	1.77	1.32
sample 2a	87.22	5.52	1.06	2.11	1.32

^a Relative standard deviation: C 1%; H 2%; N 2%; S 2.5%.

The nominal mass corresponds to the IUPAC mass without the decimal fraction. Every homologous series has a typical and constant KMD value. Through the Kendrick mass value classes identified below mass 400 have been extrapolated and extended to higher masses to obtain the final list of molecular formulas.

Ion classes were then classified and plotted according to the number of insaturation DBE (double bonds equivalents) and the relative intensities in the mass spectra.

Values of DBE (or RDB: rings plus double bonds) were determined from the molecular formula through the eq 3:

$$\text{DBE} = x - 1/2y + 1/2z + 1 \quad (3)$$

where x is the number of carbon atoms, y of hydrogen atoms, and z of nitrogen atoms.

Results and Discussion

Elemental Analysis. The elemental analysis data (% w/w) for the original asphaltenes (sample 1 and 2) and for the thermal treated asphaltenes (sample 1a and 2a) are reported in Table 1. C/H ratios are higher than those of standard asphaltenes because they come from an industrial thermal treatment. The data indicate no appreciable difference in carbon and hydrogen composition between samples 1 and 2. The asphaltene fractions recovered after thermal treatment present a higher ratio compared with originals.

These results show that asphaltene fractions undergo a chemical structure modification when they are heated at 400 °C. Higher C/H ratios indicate in fact an increase in aromaticity of samples 1a and 2a suggesting that the coke might be formed through successive transformations of asphaltenes in coke precursors.

^1H and ^{13}C NMR Analysis. Chemical characterization of asphaltenes by NMR spectroscopy can provide useful information.

Nowadays in the literature well-known equations (Dickinson's equations²⁸) are commonly used,¹⁴ which, on the basis of NMR integrals, provide average molecular parameters, such as the aromatic carbon fraction (f_a), the average number of carbon per alkyl side chain (n), the average percent of substitution of aromatic carbon (A_s) and the average number of aromatic rings per molecule (R_A). ^1H NMR spectrum of an asphaltene sample can be divided into four regions according to the different species of protons showed in the NMR spectrum:

Range 9 – 6.5 ppm: hydrogens on aromatic carbons

Range 4 – 2 ppm: hydrogens in α position with respect to the aromatic rings (H_α)

Range 2 – 1 ppm: hydrogens in β position with respect to the aromatic rings (H_β)

Range 1 – 0 ppm: hydrogens in γ position (terminal position) with respect to the aromatic rings (H_γ)

In Figure 1 the ^1H NMR spectrum of sample 1 has been reported where these four areas are shown.

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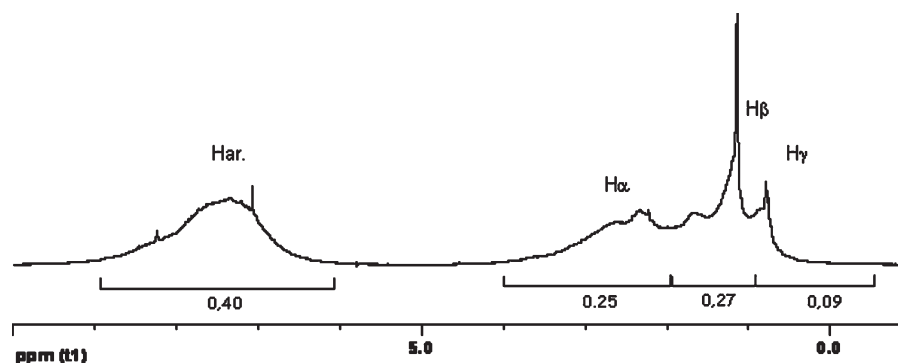


Figure 1. ^1H NMR spectrum of sample 1 in CDCl_3 .

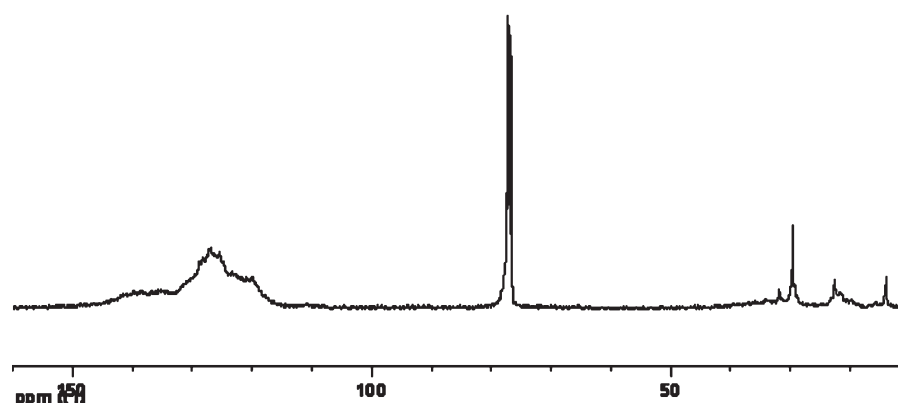


Figure 2. ^{13}C NMR spectrum of sample 1 in CDCl_3 .

The ^{13}C NMR spectrum of an asphaltene can also be divided into two regions:

Range 160–110: aromatic carbons (Car)

Range 60–10: aliphatic carbons (Cal)

As it is possible to see, these spectra are quite broad. Only in the ^{13}C NMR spectrum (Figure 2) some sharp peaks, peculiar of the presence of quite long aliphatic side chains at 31.8 (C_c), 29.6 (C_n), 22.6 (C_b) and 14.0 (CH_{3a}), are visible.

To apply the Dickinson's equations, some other analytical data, such as the atomic content of carbon (%C) and hydrogen (%H), are necessary. These data were obtained from elemental analysis (Table 1).

To calculate the average number of aromatic rings, we needed an average molecular weight, and we used the WAMW (weighted average molecular weight) as detected from FT-ICR MS spectra in negative mode at low resolution.

The equations used are the following:

$$f_a : \frac{\text{Car}}{\text{Car} + \text{Cal}} \quad (\text{aromatic carbon fraction}) \quad (4)$$

$$n : \frac{\text{H}\alpha + \text{H}\beta + \text{H}\gamma}{\text{H}\alpha} \quad (\text{average number of carbon per alkyl side chain}) \quad (5)$$

$$\%A_s : \frac{100 \times \text{C}_{1s}}{\text{C}_{1s} + \text{C}_{1u}} \quad (\text{percent of substitution of aromatic rings}) \quad (6)$$

where C_{1s} is the percent of substituted aromatic carbon, $\text{C}_{1s} = \frac{\text{C}\% \times \text{C}_{al}}{n}$ and C_{1u} is the percent of unsubstituted

aromatic carbon $\text{C}_{1u} = 12 \times \text{H}_{ar} \times \text{H}\%$,

$$R_A = [(\text{No. C}_A - \text{No. C}_1)/2] + 1$$

(number of aromatic rings per average molecule) (7)

where No. C_A is the number of aromatic carbons per average molecule and No. C_1 is the number of non-bridged aromatic carbon per average molecule ($\text{C}_1 = \text{C}_{1s} + \text{C}_{1u}$).

These eqs 4, 5, 6 have been applied on the four samples, using as input data the integrated values of the areas above-reported, obtained from the ^1H and ^{13}C NMR spectra. The structural parameters of the average molecule thus obtained have been reported in Table 2.

The value of average number of carbon per alkyl side chain (n) is low because asphaltene fractions 1 and 2 were collected from crude oils treated in a thermal industrial plant, which causes cleavage of long aliphatic chains.

Between the samples there are some small differences:

- (1) The fraction of aromatic carbons (f_a) is slightly higher in sample 2 than in 1.
- (2) The average number of carbons in the aliphatic chains (n) is slightly lower in sample 1.
- (3) The percent of substituted aromatic carbons ($\%A_s$) is higher in sample 1 than in 2 (22.8 vs 17.7).

All these experimental results lead us to the conclusion that in sample 1 the aliphatic chains are more numerous but shorter than in sample 2.

Comparing the samples before and after the heating process (see Table 2), we can see that:

- (1) The content of aromatic carbons (f_a) increases with the heating.

Table 2. Structural Parameters of the Average Molecule

structural parameters	sample			
	1	1a	2	2a
%H	5.92	5.53	6.05	5.52
%C	86.88	87.55	89.25	87.22
f_a	0.77	0.87	0.8	0.87
n	2.44	2.58	2.67	3.32
% A_s	22.8	13.2	17.7	10.1
R_A	7.2	9.3	7.1	8.5

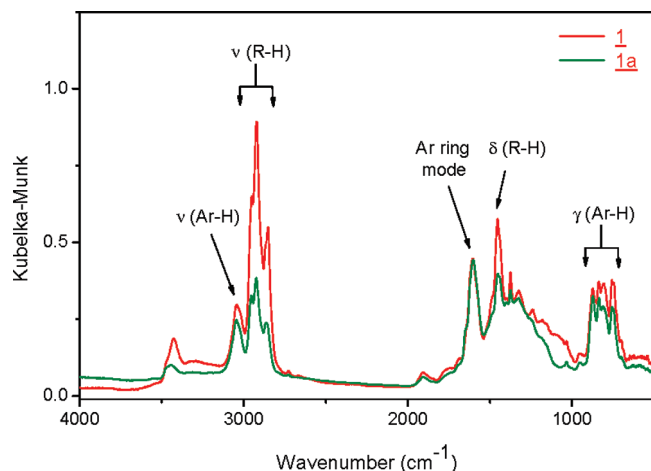


Figure 3. DRIFT spectrum of untreated and pyrolyzed asphaltene sample.

- (2) The average number of carbons in the aliphatic chains (n) is almost the same.
- (3) The percent of substituted aromatic carbons (% A_s) greatly decreases.
- (4) The number of aromatic rings per molecule (R_A) clearly increases.

As the average number of carbons per chain is almost the same but the percent of substituted aromatic carbons decreases, this means that the number of aliphatic chains also decreases. This change is accompanied by an increase in the content of aromatic carbons and, coherently, by an increase in the average number of aromatic rings.

The samples, due to the heating process, are therefore subjected to a sort of packaging process, and this conclusion, in agreement with what already reported,²⁹ seems to underline that the thermal treatment brings to highly packed structures a sort of coke precursors with less aliphatic chains and an higher number of aromatic rings.

FTIR. A typical DRIFT spectrum of an asphaltene (sample 1) is illustrated in Figure 3, in comparison with its asphaltenic fraction obtained upon thermal treatment at 400 °C for 3 h under Ar atmosphere.

According to deepened and detailed works on coals,³⁰ the main spectroscopic features are interpretable^{31,32} as follows: the aromatic units are characterized by a structured band centered at about 1600 cm⁻¹, ascribable to the ring breathing

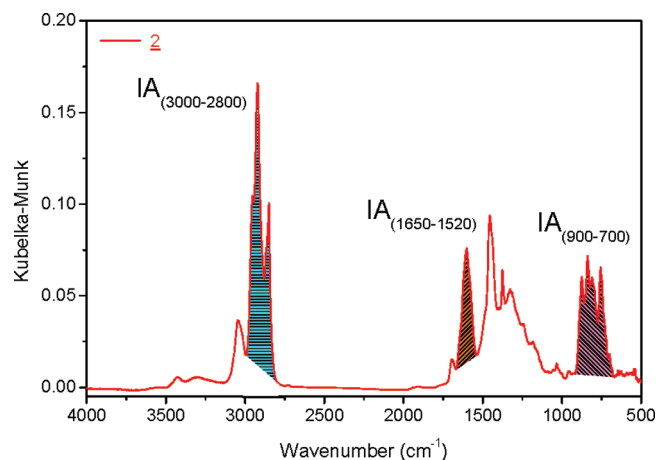


Figure 4. DRIFT bands used to determine the structure indexes.

mode. Moreover, the aromatic hydrogens can be identified by the Ar–H stretching bands at approximately 3070–3030 cm⁻¹ and by the corresponding out-of-plane deformations between 900 and 700 cm⁻¹. Vice versa, the aliphatic chains are characterized by the absorptions arising from R–H stretching modes between 3000 and 2800 cm⁻¹ and from R–H deformations at approximately 1460 and 1370 cm⁻¹, although the rocking modes of the methylenic units originate weak bands in the 770–720 cm⁻¹ range, overlapped and masked by the intense out-of-plane vibrations of the Ar–H groups.

The main spectroscopic modifications induced by pyrolysis are recognizable in a decrease in the relative intensity of the bands peculiar to aliphatic units (C–H stretches between 3000 and 2800 cm⁻¹ and corresponding bending at 1460 and 1370 cm⁻¹), together with a relative alteration of the Ar–H modes (stretches and deformations at 3070–3030 and 900–700 cm⁻¹, respectively) with respect to ring breathing band intensity at 1600 cm⁻¹. These changes are indicative of chemical structure modifications induced by thermal cracking, which is likely to proceed³³ through radical fragmentation with dealkylation and with naphthenic unit aromatization to highly polycondensed aromatic structures.

Similarly to coals and macerals,^{34,35} measuring directly from DRIFT spectra the integrated intensities (areas) of specific IR bands (Figure 4), it is possible to determine opportune structure indexes that allow to describe asphaltene compounds in terms of degree of aromaticity, of aliphaticity, and of condensation of the aromatic rings.

In particular:

- (1) The relative intensity of the aliphatic C–H stretching band with respect to the aromatic ring absorption (i.e., $I_1 = IA_{(3000-2800)}/IA_{(1650-1520)}$), represents the proportion of aliphatic to aromatic groups.
- (2) The intensity of the aliphatic C–H stretching band comparatively to the Ar–H out-of-plane deformations ($I_2 = IA_{(3000-2800)}/IA_{(900-700)}$) indicates the relative amount of aliphatic and aromatic hydrogens.
- (3) The area ratio between the bands peculiar to aryl ring breathing modes and to Ar–H out-of-plane deformations ($I_3 = IA_{(1650-1520)}/IA_{(900-700)}$) constitutes an index of the substitution and/or condensation degree of aromatic rings.

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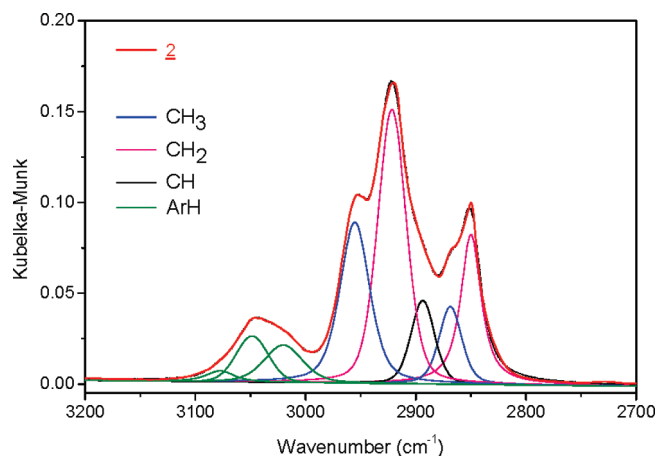


Figure 5. C–H stretching zone curve-fitting.

- (4) The “A” factor, defined as $IA_{(3000-2800)}/(IA_{(3000-2800)} + IA_{(1650-1520)})$, represents the relative fraction of aliphatic groups.

As clearly evident, such structural indexes are not independent and are therefore redundant; in particular, $A = I_1/(I_1 + 1)$ and $I_3 = I_2/I_1$. However, their explicitness renders the comparisons more immediate. Moreover, being simple relative intensities that do not take account of the extinction coefficients, these indexes do not coincide but are at least proportional to the relative amounts of the corresponding moieties; therefore, they allow estimating the relative variations between different samples. Regarding this, according to the literature,^{36,37} we verified experimentally that also for asphaltenes I_2 is linearly correlated to the aliphatic to aromatic hydrogen ratio determined by ^1H NMR.

A more detailed analysis of the C–H stretching zone between 3200 and 2700 cm^{-1} (Figure 5), clearly evidence the composite structure of such bands, and substantially the following main components can be individuated.^{30–32,37,38}

- (1) 3075, 3050, and 3020 cm^{-1} : aromatic C–H stretches;
- (2) 2956 and 2864 cm^{-1} : CH_3 asymmetric and symmetric stretches, respectively;
- (3) 2923 and 2848 cm^{-1} : CH_2 asymmetric and symmetric stretches, respectively;
- (4) 2900 cm^{-1} : C–H stretches.

Such components can be resolved by means of an opportune curve-fitting procedure,^{30,37} in order to discriminate the bands ascribable to the various aliphatic units and to the aromatic CH (Figure 5). For this purpose, the curve-fitting package of GRAMS/AI software (Thermo Galactic, USA) has been used, operating with a linear baseline in the 3200–2700 cm^{-1} range. The number and position of the single components to use in the fitting procedure have been evaluated by means of visual inspection, finding agreement with the data reported in literature for coals; mixed Gaussian and Lorentzian functions have been adopted for band shape, whereas bandwidths have been optimized during fitting iterations (as suggested by Maddams³⁹), setting up the values reported by Painter³⁷ as initial parameters.

Table 3. IR Structural Indexes

	I_1	I_2	I_3	A	CH_2/CH_3
	R–H/ Ar	R–H/ Ar–H	Ar/ Ar–H	R–H/ (R–H + Ar)	* ³⁵
asphaltene					
sample 1	4.31	2.06	0.48	0.81	1.68
sample 1a	1.53	1.06	0.69	0.60	1.00
sample 2	3.66	1.71	0.47	0.79	1.82
sample 2a	1.56	1.11	0.71	0.61	1.38

$$* (IA_{2923} + IA_{2848})/(IA_{2956} + IA_{2864})$$

On the basis of the intensities of the single components so resolved, it is therefore possible to define other structural indexes, such as the CH_2 to CH_3 ratio, indicative of the length and degree of ramification of the aliphatic chains. Concerning coals, in literature different alternative definitions are reported: Bustin³⁴ defined the CH_2/CH_3 ratio from the relationship IA_{2923}/IA_{2956} , instead Xuguang³⁵ considered the proportion $(IA_{2923} + IA_{2848})/(IA_{2956} + IA_{2864})$, while Painter³⁷ suggested using the symmetric stretching bands (2848 and 2864 cm^{-1}), in his opinion less influenced by the aromatic structure than the asymmetric modes. However, recently a linear correlation between the intensity ratio IA_{2923}/IA_{2956} and the proportion of methylenic to methylic units in alkyl-benzenes has been obtained, confirming the applicability of this relationship in characterizing the aliphatic chains of asphaltenes and resins.³⁶ Therefore, for every analyzed sample, the CH_2/CH_3 indexes have been calculated on the basis of all the above proposed relationships. However, the trends of the CH_2/CH_3 indexes were all together linearly correlated, and absolutely no significative discrepancy was observed. The Xuguang CH_2/CH_3 indexes are reported in Table 3 together with the other structure indexes previously described.

Comparing the data for the different untreated asphaltene samples 1 and 2, it is evident that sample 2 is characterized by a slightly lower portion of aliphatic groups ($I_1 = 3.66$ vs 4.31 and $A = 0.79$ vs 0.81) and of aliphatic hydrogens too ($I_2 = 1.71$ vs 2.06), by a slightly lower degree of substitution and/or condensation of aromatic rings ($I_3 = 0.47$ vs 0.48) and has longer and/or less branched aliphatic chains ($\text{CH}_2/\text{CH}_3 = 1.82$ vs 1.68). These evidence are substantially in agreement with the above-discussed NMR data.

The asphaltene fractions 1a and 2a obtained through the thermal treatment at 400 °C for 3 h in Ar atmosphere evidence a consistent structural modification with respect to untreated samples; in particular, pyrolysis induces a decrease in the aliphatic fraction (indexes I_1 , I_2 , and A) and an increase in degree of condensation of the aromatic rings (I_3), and results in more branched aliphatic chains (CH_2/CH_3).

FT-ICR MS. Samples 1-1a and 2-2a have been analyzed in ESI FT-ICR MS in negative and positive mode. Acidic groups are usually present in asphaltenes,⁴⁰ thus negative mode is used to ionize selectively acidic species such as carboxylic acids, phenols, and pyrrolic-type compounds. Positive mode is less applied for asphaltenes but has been carried out to ionize basic species containing nitrogen atoms, such as carbazoles, pyridines, and other compounds such as sulfoxides, which yield high signals in the mass spectra.⁴¹

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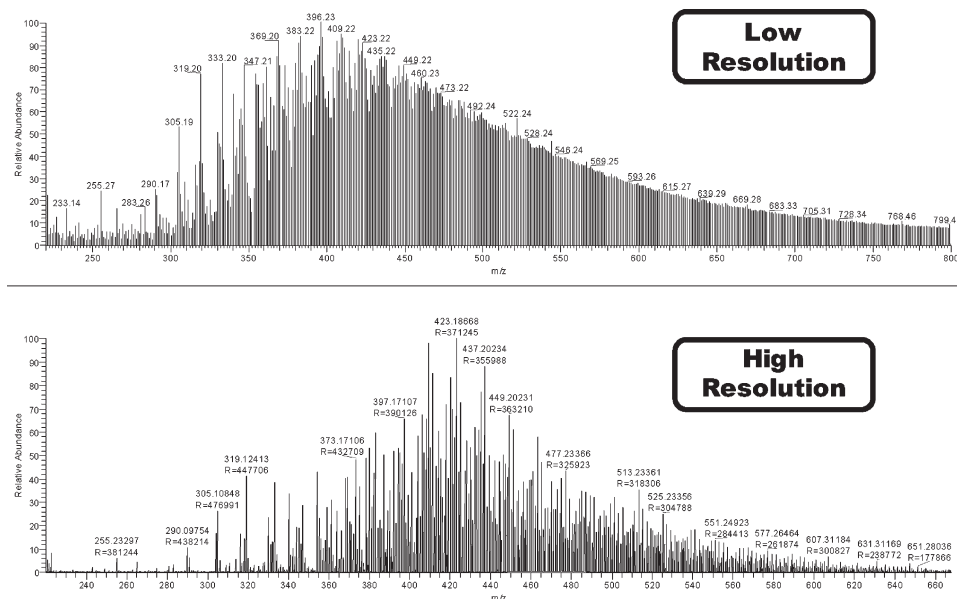


Figure 6. ESI negative mode sample 1a. Low- and high-resolution mass spectra.

A preliminary low-resolution analysis has been carried out to obtain the peaks distribution and the average-weighted molecular weight (WAMW). On the base of peaks distribution, the mass range 200–1000 Da has been used for the high-resolution acquisition (Figure 6 and Supporting Information Figures 17–19). Besides the WAMW values (1-1a: 494 and 476 Da; 2-2a: 426 and 442 Da) have been used in the NMR data calculation to provide the average molecular parameters.

Figure 7 illustrates expanded segments of mass spectra at around 450 Da for samples 1-1a and the molecular formula assignments (within the tolerance of 1.5 ppm) of the peaks above the threshold 3σ . Many of the species found in sample 1 are also present in sample 1a but with different intensities.

High-resolution mass spectra of positive and negative ESI mode for the sample 1 is shown in Figure 8. The spectra have an average molecular weight of approximately 400 Da. Peaks with higher relative abundances are included in the range 250–650 Da. The average number of peaks detected by the instrument varies around 10 000–15 000. This trend has been observed for all the four samples in both positive and negative mode.

ESI Positive Mode. Nitrogen-containing compounds are the main classes found in positive mode. A plot of relative abundances versus DBE values for these classes is reported in Figure 9. The two asphaltene samples show a similar behavior in terms of relative abundances before and after pyrolysis. The classes of nitrogen-containing compounds with higher relative abundances are N_2 , N_1 , N_3 , N_1O_1 , and N_2O_1 in all four samples. These classes are characterized by an increase in the DBE value after pyrolysis. (see Supporting Information Table 5). Other classes containing sulfur and oxygen (such as S_1 , S_2 , O_2) have been also identified but they have lower relative abundances.

Figure 10 plots the N_2 class that is the most abundant found in all four samples. The DBE distribution in the plot has initially a wide range with a maximum at around 13, and it becomes narrower after pyrolysis with a maximum at 18. The insert illustrates the carbon number distribution for a single value of DBE (17). The plot is similar for both

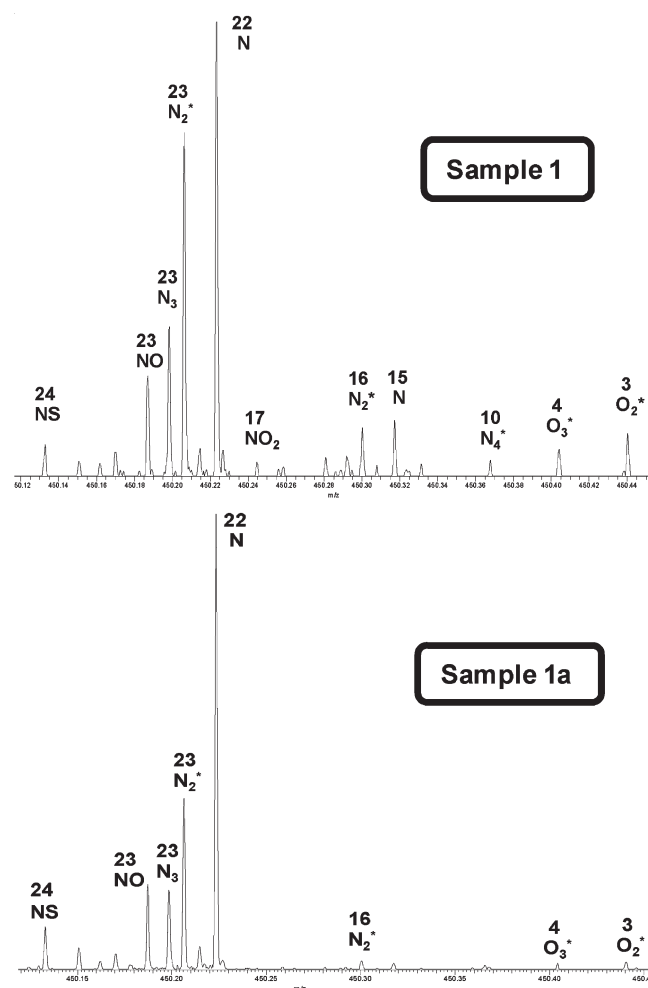


Figure 7. ESI negative mode sample 1-1a. Extended segment of mass spectra in the range 450.1–450.4 Da. Each identified peak has been labeled according to the heteroatom content and the value of DBE. The asterisks correspond to the presence of one ^{13}C in the molecular formula.

samples (1-1a) with a maximum at around 25–30 carbon atoms per molecule. From this data we can deduce that these

compounds undergo a cyclization/aromatization process and not a scission of the aliphatic side chains.

The total compounds average DBE is increased after thermal treatment for both the samples (1-2) (15.0–19.1 and 16.7–18.5, respectively, for samples 1-1a and 2-2a) in agreement with the increase in the fraction of aromatic carbons and the degree of condensation of the aromatic rings detected from NMR and FTIR analyses, respectively.

ESI Negative Mode. In ESI negative mode nitrogen- and oxygen-containing compounds are the majority (Figures 11 and 12), and they can be considered representative of the whole sample. The number of classes found in the four samples is almost the same (around 10–13 classes above 1% of relative abundance). Classes N_2 and N_1 are the most abundant in all the four samples and show an increased value of DBE after pyrolysis from 19 to 22. It is interesting to note that most of the nitrogen-containing classes shows an increase in DBE of about 2–3 units in the range 18–22 after thermal treatment, except for class N_4 that has a lower and almost constant DBE. Oxygen-containing classes behave in a different way: the O_2 class is characterized by the lowest DBE (about 2–3) and is not affected by the thermal treatment. On the other hand, the O_3 class shows in both samples (1 and 2) the most relevant variation of DBE after pyrolysis (shift forward of about 5 DBE units). Other classes with lower relative intensities that have been identified in samples 1-1a are: O_1S_1 , S_2 , N_2S_1 , O_2N_2 , O_2N_1 , O_3S_1 , O_4N_1 , O_1N_3 , and O_2S_1 . Some of them have been found with higher intensities in samples 2-2a and are included in the plot of Figure 12; the others have similar relative abundances to

those found in sample 1-1a (below 1%) (see Supporting Information Table 6).

Figure 13 reports the mass spectra of the class N_2 in sample 1. The peak distribution is centered at around 380 m/z and has a similar shape to the complete mass spectra (Figure 6) with a mass range between 290 and 600 amu.

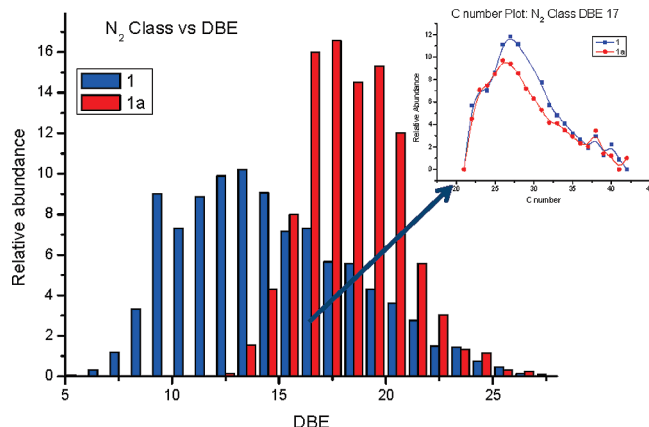


Figure 10. Sample 1-1a: Class N_2 distribution of DBE. The upper right plot is referred to the C number distribution of the molecular formulas with DBE 17.

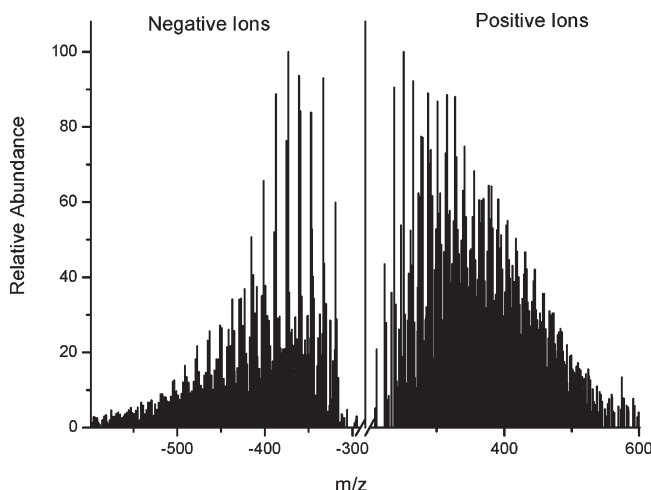


Figure 8. ESI FT-ICR high resolution spectra sample 1.

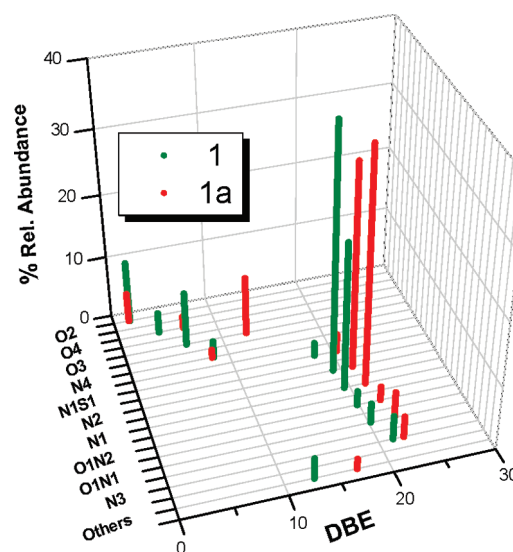


Figure 11. Main classes of compounds (with relative abundance > 1%) in samples 1-1a plotted according to DBE values and relative abundances.

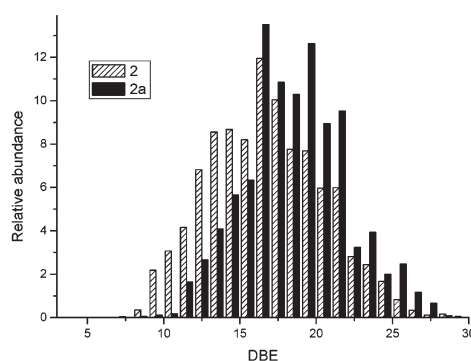
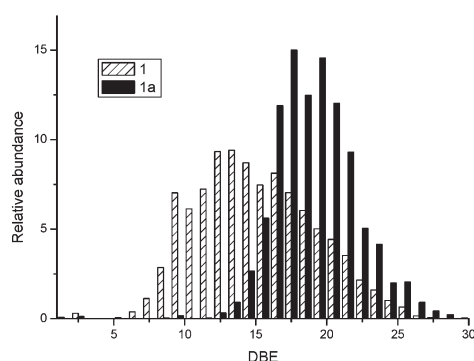


Figure 9. ESI positive mode samples 1-1a and 2-2a. Relative abundances vs DBE values of nitrogen-containing compounds.

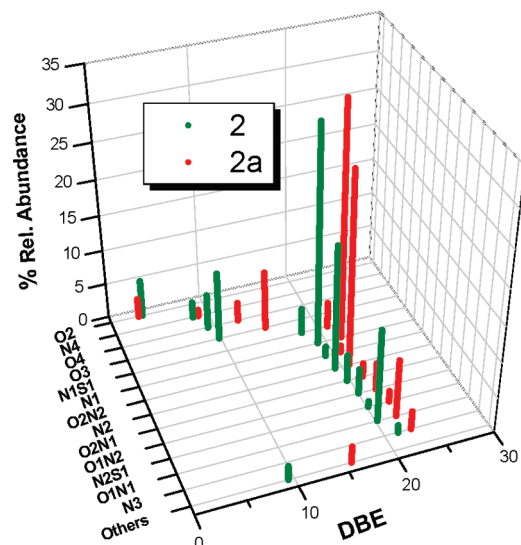


Figure 12. Main classes of compounds (with relative abundance > 1%) in samples 2-2a plotted according to DBE values and relative abundances.

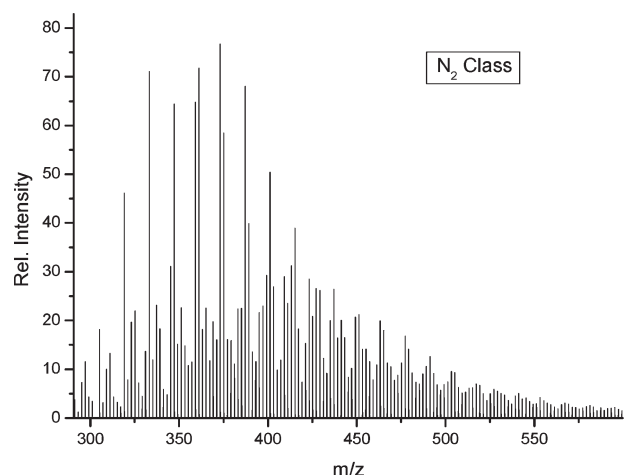


Figure 13. Mass spectra of N_2 class of sample 1.

The plots reported in Figures 14–16 present the Kendrick mass defect (KMD) versus the nominal mass. As described in the Materials and Methods section, KMD is calculated by subtracting the Kendrick mass from the nominal mass. Every homologue class has a constant value of DBE and KMD and gaps of 14 in the nominal mass.^{42,43} Furthermore, higher values of KMD correspond to lower values of DBE. Figure 14 shows that homologous series with higher KMD (low DBE) are less stable and disappear after thermal treatment. The length of the aliphatic chains is almost constant for both samples and is stretched similarly for different values of DBE and nominal masses. This trend, found for the macro classes O_1N_x (O_1N_1 and O_1N_2), has also been observed for most of the other nitrogen-containing classes, including the two most abundant N_1 , N_2 (see Supporting Information Figures 20–23).

From the obtained data it is possible to suppose that molecules with lower DBE have lower amount of aromatic

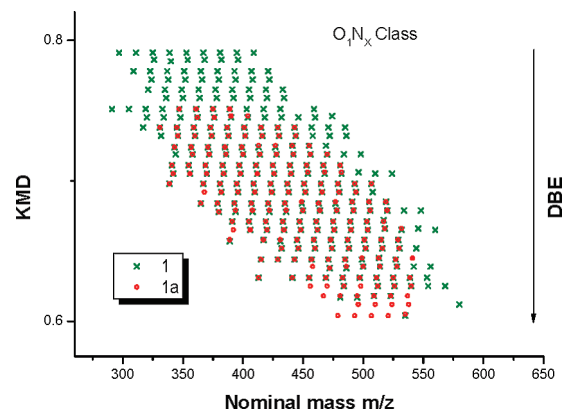


Figure 14. Compounds belonging to O_1N_x classes in samples 1-1a plotted according to the nominal mass and the Kendrick mass defect (KMD).

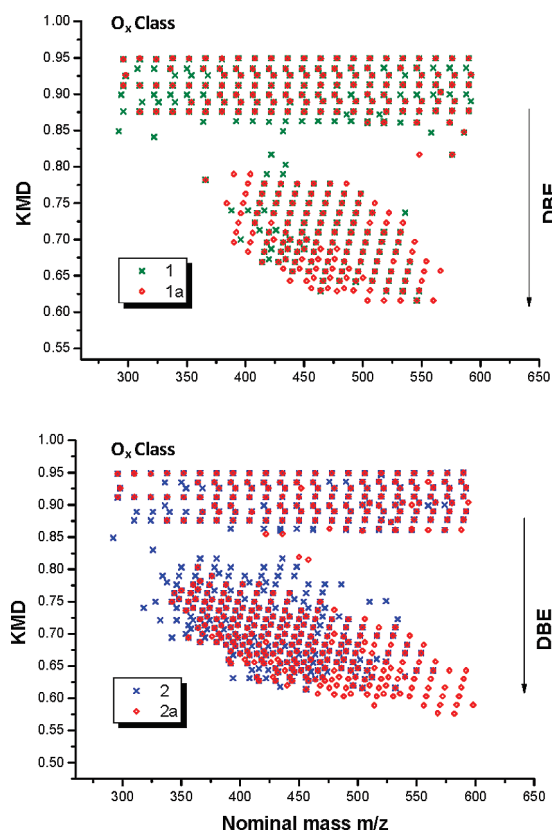


Figure 15. Compounds belonging to O_x classes (O_2 , O_3 , and O_4) in samples 1-1a and 2-2a plotted according to the nominal mass and the KMD.

rings and higher contents of naphthenic rings and/or aliphatic chains. Thus, they could form unstable radicals by thermal cracking that reconstitute into more aromatic molecules⁴⁴ without altering the molecular weight.

The plot (Figure 15) of oxygen-containing classes (macro class O_x) is quite different from all the other classes. Two main zones of series of homologues can be identified in both asphaltenes (1-2): the first zone in the higher part of the plot corresponds to lower values of DBE (2–4) and can be mostly associated to aliphatic molecules such as carboxylic acids included in the class O_2 . These series do not seem to be

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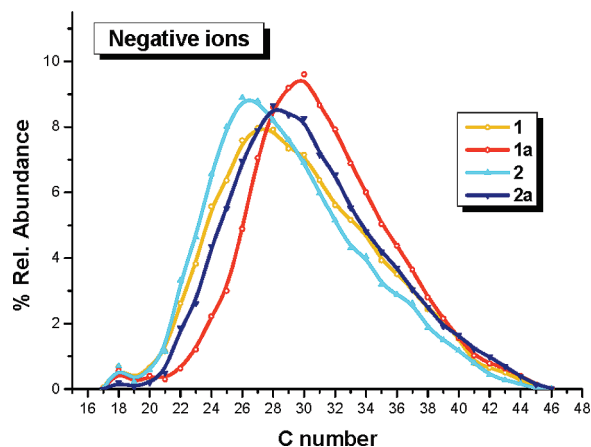


Figure 16. Relative abundances of the negative ions plotted according to the number of carbon atoms in the molecular formulas for the asphaltenes.

Table 4. ESI Negative Mode Average Results

sample	DBE			DBE		
	1	1a	common ions %	2	2a	common ions %
Total	15.56	19.24	68.24	16.67	19.91	77.88
N _x	18.97	21.23	76.00	18.73	21.18	86.10
O _x	3.86	8.66	80.14	7.96	11.99	76.09
O ₁ N _x	20.02	22.44	65.33	19.88	22.11	79.19
N _y O _z S _x	14.35	19.06	51.18	16.23	19.75	70.00

modified by the thermal treatment similarly as previously reported. The second zone in the lower part of the plot is related to higher unsaturated compounds (aromatic compounds) similar to those found previously in the other classes (nitrogen-containing classes). For these series of homologues the DBE increases after pyrolysis, whereas the length of the aliphatic chains is almost unaltered. The increase in DBE is more relevant in sample 1-1a than in sample 2-2a; besides, the aliphatic chains in the aromatic zone are longer in sample 2-2a than in sample 1-1a.

In Table 4 are reported the DBE values of the two samples both as total compounds and as macro classes, together with common ions (unchanged molecular formulas) detected in the spectra of the sample before and after thermal treatment. In the macro classes the index x varies in the range 1–4, while the indexes y and z can also assume a value of zero. DBE value has been calculated with respect to relative intensities. Sulfur atoms containing species (included in the macro class N_yO_zS_x) present a lower value of common ions in both samples (1-1a). The lower value of common ions can be related to their lower stability.⁴⁵

Figure 16 shows that the four samples are characterized by a similar distribution of carbon number centered at about 25–30 carbon atoms per molecule. The distribution is similar to the one that has been observed for the class N₂ in the ESI positive mode (Figure 10). The curves of the thermal treated samples are slightly shifted to higher values of carbon number.

Conclusions

The results of chemical analysis and detailed characterization of sample 1 and 2 indicate that the two asphaltenes are

compositionally different. Elemental analysis shows only slight differences in carbon and hydrogen contents. From NMR, DRIFT, and MS data it is, however, evident that asphaltene 2 is more aromatic than 1: the fraction of aromatic carbons and the DBE are slightly higher in sample 2 than in 1. Furthermore, the percent of substituted aromatic carbon is higher in sample 1.

Negative-ion electrospray confirms most of heteroatoms classes found in sample 1 are included also in asphaltene 2, but their relative abundance distributions are different. WAMW is slightly higher for sample 2, whereas DBE varies from 15.56 to 16.67. Since NMR and DRIFT demonstrate that asphaltene 2 is more aromatic than 1, its lower DBE value could indicate the presence of a higher number of saturated rings and/or alkyl chains in 1.

Elemental compositions of thermal treated asphaltenes in comparison with the original samples reveal an increment of the C/H ratios, suggesting an increase in aromaticity.

The presence of aromatization processes during the thermal treatments is supported by the analytical results obtained by FTIR, NMR, and FT-ICR MS.

On the basis of NMR measurements the content of aromatic carbons increases both in sample 1 and 2. The reduction of number of aromatic substituted carbons and the increase in number of aromatic rings support the hypothesis of intramolecular aromatization reactions.

FT-ICR MS confirms these results both in negative and in positive mode with a remarkable increase in the total DBE value. Similar behavior has been observed for the majority of the heteroatom classes detected.

This study based on detailed characterization by FTIR, NMR, and FT-ICR MS techniques of two asphaltene samples collected from industrial hydrotreating process and the corresponding compounds obtained after thermal treatment indicate the following:

- (1) Asphaltenes thermally treated at 400 °C tend to aromatize to form structures that can be considered coke precursors.
- (2) Asphaltenes characterized by higher content of naphthenic rings and/or aliphatic chains are less stable than the one with higher amount of aromatic rings.
- (3) Asphaltenes containing short residual alkyl chains when thermally treated undergo intramolecular cyclization/aromatization reactions and not the cleavage of aliphatic chains.
- (4) Asphaltenes containing sulfur atom species present the lowest stability.

The present study demonstrated that the complementary and comparative use of different analytical techniques can provide important information on the structure–function relationship of asphaltenes, and these results can be used by the refining industry to control and predict production performance and to prevent the coke formation problems in hydrocracking processes of heavy oil.

Acknowledgment. The authors thank Yue Xuan and Giorgio Vago of ThermoFisher Scientific for technical assistance in FT-ICR MS characterization.

Supporting Information Available: This material is available free of charge via the Internet at <http://pubs.acs.org>.

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