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# Structural Differences among the Asphaltenes in Colombian Light Crudes from the Colorado Oil Field

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**ABSTRACT:** The aim of this work was to demonstrate that the average chemical structure of the asphaltenes of a crude oil sample is unique compared with crudes of other wells from the Colorado Oil field, Colombia. Six crude oils extracted from several depths (from 2112 to 6178 ft) were studied; these crude oils have a very critical problem of deposition of paraffins and very low concentrations of asphaltenes (<1% w/w), although asphaltenes have been found with them in the organic deposits. To research this problem, first, we studied the chemical structure of asphaltenes; this information will be used in the future to understand the influence of asphaltene chemical structure on the crystallization of paraffins in waxy crude oils. The Colorado asphaltenes were characterized by nuclear magnetic resonance (NMR), mass spectrometry (MS), X-ray diffraction (XRD), and Raman spectroscopy to determine their main structural parameters. Average molecular parameters (AMPs) were analyzed using matrix plot, cluster analysis, and principal component analysis; it was demonstrated that the average molecular structures of asphaltenes differed from each other, and a cluster scatterplot suggests that there are four types of asphaltenes in the crude oils from the Colorado Oil field. The more extreme structural differences were between the asphaltenes of the crude oils obtained from the top sand and the bottom sand.



## 1. INTRODUCTION

Asphaltenes are the fraction of oil that is insoluble in *n*-heptane (n-$C_7$) and soluble in toluene. This fraction of the crude oil contains the hydrocarbon molecules that are the largest and most polar. The elucidation of the chemical structure of these molecules is a very complex and as yet unfinished task. These results have been interpreted according to the analytical method used, of which there are essentially two options. The first and more common option is to reduce the results to their average value and simplify all the complexity to a few AMPs: average molecular parameters (and/or to an average molecule). The second, and most modern option, is to try to identify as many of the molecules as are present in this fraction. It is accepted that these molecules mainly have aromatic backbones with attached paraffinic and naphthenic chains. In addition, a few percent comprises heteroatoms, mainly N, O, and S, that form the many different functional groups. The asphaltene molecular weight values range from 500 to 1000 g/mol, depending on the source.[1]

The molecular units of two samples, Boscan asphaltenes (Venezuela) from a marine source rock or type II kerogen and Duri asphaltenes (Indonesia) from a lacustrine source rock or type I kerogen, were determined by ruthenium-ion-catalyzed oxidation (RICO) and pyrolysis.[2] These samples have elemental compositions and chemical structures that are very different; the asphaltenes that extracted the paraffinic crude oil have low sulfur, while the Boscan asphaltenes from this aromatic and immature crude oil have high sulfur. When these samples are compared with other crude oils, i.e., from the Alberta tar sand and heavy oils and immature oils from China, in general, they all have *n*-alkyl groups attached to aromatic and naphthenic rings as side chains and bridges connecting aromatic and naphthenic rings, but the distributions show some variance based on differences in biotic source materials, source rocks, depositional environment, and diagenetic and thermal history.

The long polymethylene chains forming bridges between aromatic rings in the asphaltene structure allow folding into complex three-dimensional globular conformations having internal structures that form microporous units that allow adsorption and occlusion of other fractions present in the crude oil, such as the resins. To test this feature, asphaltenes from two crude oils were used: one from Congo (type I kerogen) and the other from Venezuela (type II kerogen).[3] A deuterated compound, n-$C_{20}D_{42}$, was used to simulate the adsorption/occlusion characteristics of asphaltenes in a toluene solution. Each of the asphaltenes and n-$C_{20}D_{42}$ were dissolved in toluene and precipitated by heptane, and then asphaltene-1 was obtained by centrifugation. After centrifugation, the supernatant was concentrated in a rotavapor system, and a quantitative analysis of the n-$C_{20}D_{42}$ was performed using GC. Then, the asphaltene-1 was dissolved in toluene and precipitated by heptane, again to obtain asphaltene-2. This process was conducted several times. The results from these simulation experiments indicated an abundance of microporous structural units inside the asphaltene structure, allowing the asphaltenes to adsorb/occlude the other fractions of the crude oil. The occlusions should occur inside the core of the asphaltene aggregates, while the adsorption occurs on the exterior surface of the asphaltene aggregates. The asphaltenes precipitated by *n*-$C_7$ promoted the occlusion of saturated hydrocarbons and alkyl aromatics having a high content of heteroatoms, contributing to the stabilization of the asphaltene aggregates.[4]

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Table 1. Characteristics of the Colorado Oil Field Wells and Their Crude Oils

| Well | Oil Sand | Depth (ft) | Bottomhole temp (°C) | Production by sand (% vol) | API Gravity | Asphaltene conc (ppm) |
|---|---|---|---|---|---|---|
| Col-B1 | B | 2112 | 40 | 100 | 36.0 | 2270 |
| Col-C1 | C | 5540 | 60 | 100 | 39.0 | 1500 |
| Col-BC1 | B−C | 4802 | 59 | 21 and 79 | 36.5 | 440 |
| Col-BC2 | B−C | 5600 | 62 | 53 and 47 | 39.0 | 90 |
| Col-CE1 | C−E | 5900 | 65 | 68 and 32 | 39.0 | 850 |
| Col-CE2 | C−E | 6178 | 66 | 71 and 29 | 38.2 | 750 |

The asphaltenes from crude oil deposits at different depths of the production strings of sucker pump rods were characterized by synchrotron radiation-based microanalysis.[5] Samples from the Mosteller 1 well were obtained at 22.9, 68.6, 114.3, 160.0, 205.7, 251.4, and 297.1 m. The results showed that three different types of asphaltene aggregates are present in the same deposit and are dominated by nonpolar, polar, and mixed polar/nonpolar compounds. The nonpolar aggregates (Type I) are of the waxy type, and their molecules have long aliphatic chains, aromatic rings, and aliphatic thiols. The polar aggregates (Type II) have molecules with aromatic rings, sulfur, nitrogen, oxygen, some aliphatic chains, and water associated with salts. The profile of the solid deposits, from the deepest to the shallowest, shows: (a) increasing amounts of deposits; (b) decreasing concentrations of inorganic components; (c) sulfur-containing compounds shifting their relative abundances from predominantly reduced to oxidized forms; (d) increasing carbon content and the H/C atomic ratio; and decreasing atomic ratios of S/C and N/C; (e) the distribution of the *n*-alkanes mixture (wax components) shifting from higher to lower molecular weight; (f) some metals (V, Ba, Ti, and Cr) being only detected in the deepest samples; (g) some elements (Ca, Fe, Ni, Cu, Pb, and Br) being present in all samples along the depth profile.

Asphaltenes from unstable oil and deposits have a higher polarity than those of stable crude oil, although they showed no significant differences in their elemental compositions and functional groups.[6] These results suggest that the presence of asphaltenes having lower polarity could increase the stability of crude oil. Additionally, asphaltenes with high aromaticity, such as those separated from deposits, have high density, have low H/C ratios, and are more difficult to dissolve.[7]

Asphaltenes from light crudes have been shown to be different from those obtained from heavy crude oils. Normally, the paraffinic crude oils have small amounts of asphaltenes that exceed one or two percent only in a few cases. However, despite their low content of asphaltenes, some petroleums have severe blockage problems in wells and pipelines due to the coprecipitation of asphaltenes with paraffins. This is the situation in the Colorado oil field, Colombia. This oil field has serious problems caused by blockages in the production tubing. Most of the deposits have been found to contain paraffins as well as asphaltenes.[8]

Precipitation of paraffins has been attributed mainly to the cooling of the crude oil. This can affect the production process and pipeline transport, especially in offshore wells. Also, experimental evidence indicating that asphaltenes could be strong promoters of paraffins precipitation has been found. Nevertheless, these studies have been mainly conducted with mixtures of synthetic hydrocarbons, while many other studies have used pure or mixed paraffins dissolved in pure or mixed aliphatic solvents. Despite the wide range of publications and scientific articles on this subject, there is still no consensus or agreement that may lead to a generalized explanation of the effect produced by asphaltenes on the precipitation of paraffins.[8]

Studies of the influence of asphaltenes on wax precipitation have been conducted with different results. Asphaltenes with different degrees of aromaticity and stability, from operationally unstable crude oils, from stable crude oils, and from deposit crude oils, have been used to evaluate the effect of these asphaltenes on the waxes in solution and flocculation experiments. The test oil was a highly waxy crude oil to which commercial wax was added. They concluded that the flocculated asphaltenes serve as nucleation centers and increase the crystallization point. Asphaltenes from stable crudes (with lower aromaticity and higher H/C ratio) are more easily solubilized than those extracted from unstable crude oil and from deposits.[9] In another study of the effect of asphaltene polarity on the rheological properties of waxes, three fractions extracted from the crude oil of the Zuata field in Venezuela were added into a synthetic oil with previously dissolved waxes at 5% w/w. They found that the asphaltenes fraction with the lowest polarity decreased the gel point by 4 °C, and increased the yield point up to 110 kPa when compared with the sample of oil without asphaltenes.[10]

Asphaltenes function as an additive that modifies the wax crystals and alters their morphology.[11] Mixtures of alkanes ($C_{10}$ to $C_{14}$) and methylnaphthalene-type solvents, and two commercial waxes and asphaltenes (H/C at 1.41) from a highly waxy crude oil were used in different proportions. The mixtures prepared with asphaltenes at concentrations lower than 0.2% w/w and wax concentrations up to 10% w/w showed that the precipitation temperature of the crude oil decreased by nearly 2 °C. They also noted that, with high concentrations of asphaltenes, the gel point temperature was affected by as much as 3 °C and the yield stress by up to 1200 Pa. In contrast, the asphaltenes that are occluded in the wax deposit do not affect wax precipitation.[12]

Unfortunately, these studies using synthetic crude might not show the true effect of the asphaltene concentration on the precipitation of paraffins because of various chemical and physical interactions that are not included in the experiments conducted with this type of synthetic crude. In the present work, complete characterization of the asphaltenes from six waxy oils from one Colombian oil field was made, and the objective was to determine the AMPs of the asphaltenes from Colorado crude oils; understanding the effect of their chemical structure during the crystallization of paraffins in a light crude oil is a future research topic.

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** To have a wide range of the Colorado crude oils, six samples from several depths were selected from different wells and from sands B and C, as well as mixtures of sands B−C and C−E, whose characteristics are presented in Table 1. The Colorado field is



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located in the Middle Magdalena (Colombia) basin; its geology is characterized by a main fault, the Colorado major fault (Figure 1) with

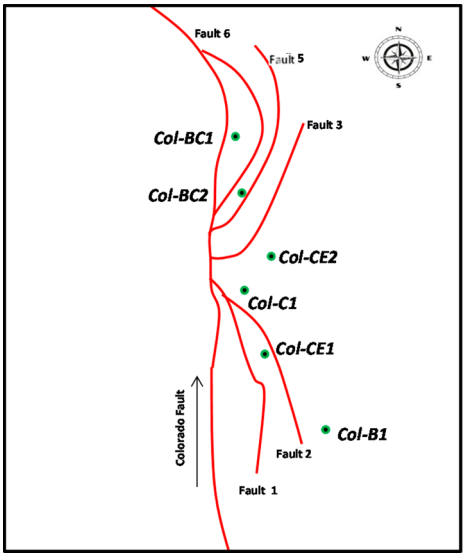


**Figure 1.** Map of the Colorado oil field.

a series of reverse faults with curved planes that are associated with the main fault; two faults in the southern section of the field and three faults in the northern section form semicircular blocks.[13] The largest producer of hydrocarbons is the "Mugrosa" formation (B and C sands), and the lowest producer is the "Esmeraldas" formation (sand E). The Mugrosa formation is characterized by fine-grained sandstones with interbedded mudstones that have accumulated in a meandering type of geological environment. The field has proven reserves of 128 million barrels of oil with an API gravity that is between 34° and 42°.

**2.2. Extraction and Characterization of Asphaltenes.** Asphaltenes were obtained from the six crude oils, as characterized in Table 1, according to the ASTM - method. Briefly, the asphaltenes were precipitated by first preparing a 20:1 solution of *n*-heptane/crude oil that was refluxed for 2 h at the temperature 120 °C, allowed to stand for 24 h, and then filtered. Subsequently, the asphaltene solution was put into a Soxhlet extraction unit until the solvent was transparent. Next, toluene was added to the Soxhlet extraction unit to dissolve and to remove the asphaltenes from the thimble. This was continued until the solvent was colorless. Finally, the toluene was removed in a rotavapor system.

*2.2.1. Physicochemical Characterization.* The methodology used to calculate the AMPs of the asphaltenes were based on a combination of elemental analysis, matrix assisted laser desorption and ionization−time of flight (MALDI-TOF) mass spectrometry and $^{1}H$ and $^{13}C$−nuclear magnetic resonance.[14] In summary, the elemental analysis was conducted using a Thermo Scientific Flash 2000 elemental analyzer. The MALDI-TOF spectra were acquired using a Bruker Reflex II MALDI-TOF mass spectrometer equipped with a Nd:YAG laser emitting at the third harmonic, 355 nm, with a repetition rate of 500 Hz, and a pulse width of 3.5 ns. The TOF-MS analyzer was operated in the reflector mode and was equipped with a microchannel plate detector. The reflection plates were polarized at 25 kV to obtain a potential gradient according to the kinetic energy of the ions, allowing the best reflection properties and refocusing the ions close to the detector. The asphaltenes were dissolved in a saturated solution of

**Table 2. Average Molecular Parameters of Colorado Asphaltenes**

| Parameter | Method | Col-B1 | Col-BC1 | Col-BC2 | Col-CE1 | Col-CE2 | Col-C1 |
|---|---|---|---|---|---|---|---|
| H | EA and MS[b] | 48.4 | 46.1 | 47.5 | 45.3 | 41.4 | 45.1 |
| C | EA and MS[b] | 41.1 | 39.9 | 40.1 | 38.4 | 37.2 | 39.0 |
| $C_{al}$ | NMR[a] | 18.1 | 18.9 | 21.6 | 18.6 | 14.6 | 19.1 |
| $C_{ar}$ | NMR[a] | 23 | 21 | 18.5 | 19.8 | 22.5 | 19.9 |
| $H_{ar}$ | NMR[a] | 6.5 | 3.9 | 2.7 | 5.2 | 5.4 | 5.4 |
| n | NMR[a] | 3.9 | 3.9 | 6.7 | 3.8 | 4 | 3.2 |
| $C_{ar\text{-}alk}$ | NMR[a] | 5.3 | 8.5 | 8.1 | 5.6 | 6.1 | 5.6 |
| $C_{ar\text{-}CH3}$ | NMR[a] | 1 | 0.7 | 0.7 | 0.6 | 0.8 | 0.8 |
| $C_{ar\text{-}n}$ | NMR[a] | 3.1 | 2.3 | 2 | 2.5 | 2.7 | 2.3 |
| $C_{ar\text{-}H}$ | NMR[a] | 6.5 | 3.9 | 2.7 | 5.2 | 5.4 | 5.4 |
| $C_p$ | NMR[a] | 15.8 | 15.4 | 13.4 | 13.9 | 15 | 14 |
| $C_i$ | NMR[a] | 7.1 | 5.5 | 5.1 | 5.9 | 7.6 | 5.9 |
| $C_{aa}$ | NMR[a] | 5.5 | 3.7 | 3.3 | 4.3 | 5.5 | 4.1 |
| $C_{aaa}$ | NMR[a] | 1.6 | 1.9 | 1.8 | 1.6 | 2.1 | 1.8 |
| $C_s$ | NMR[a] | 9.6 | 13.3 | 16.1 | 14.2 | 11.7 | 15.5 |
| $C_n$ | NMR[a] | 8.5 | 5.6 | 5.5 | 4.4 | 2.9 | 3.6 |
| $R_a$ | NMR[a] | 5 | 4 | 4 | 4 | 5 | 4 |
| $f_a$ | NMR[a] | 0.56 | 0.53 | 0.46 | 0.52 | 0.61 | 0.51 |
| Φ | NMR[a] | 0.31 | 0.26 | 0.28 | 0.30 | 0.34 | 0.30 |
| $C_p/C_{ar}$ | NMR[a] | 0.69 | 0.74 | 0.72 | 0.7 | 0.66 | 0.7 |
| $T_{ar}$ | NMR[a] | 0.27 | 0.44 | 0.47 | 0.31 | 0.31 | 0.32 |
| MW (g/mol) | MS[b] | 589.3 | 573.2 | 584.1 | 547.5 | 561.3 | 585.6 |
| La (Å) | RAMAN[c] | 16.5 | 14.7 | | 13.6 | 19.4 | |
| Lc (Å) | XRD[d] | 26.1 | 8.5 | | 8.5 | 28.3 | |

[a]References 14 and 16−18. [b]Reference 15. [c]Reference 19. [d]Reference 20. H: total number of hydrogens. C: total numbers of carbons. Cal: number of aliphatic carbons. Car: number of aromatic carbons. Har: number of aromatic hydrogens. n: average length of aliphatic chains. Caralk: number of aromatic carbons attached to alkyls. CarCH3: number of aromatic carbons with attached methyl groups. Carn: number of aromatic carbons attached to naphthenic groups. CarH: number of protonated aromatic carbons. Caa: number of kata-condensed aromatic carbons or a bridge of two aromatic rings. Caaa: number of pericondensed aromatic carbons or a bridge of three aromatic rings. Cs: number of saturated carbons. Cn: number of naphthenic carbons. Ra: aromatic ring number. Fa: aromaticity factor. Φ: aromatic condensation index. $C_p/C_{ar}$: the ratio of aromatic carbons to aliphatic carbons. MW: average molecular weight. La: average size of the asphaltene molecule. Lc: average height of the asphaltene cluster.



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anthracene in toluene at approximately 3 wt %. An aliquot of 4 μL of this solution was deposited in a MS holder, and the solvent was removed with a current of air. This procedure was repeated three times to concentrate the sample. Afterward, the holder with asphaltenes was introduced into the spectrometer for measurement.

The $^{1}H$ and $^{13}C$ NMR asphaltenes spectra were obtained with a Bruker Avance III spectrometer operating at 400.16 and 100.63 MHz, respectively. The $^{1}H$ NMR samples were 4 wt % solutions in $CDCl_3$ (99.8% D), and the measurements were performed with 30° pulses (Bruker zg30 pulse sequence), a sweep width of 49000 Hz, 32K data points, and a delay time between scans of 10 s. Tetramethylsilane (TMS) was used as a reference, and 16 scans were averaged for each spectrum. The $^{13}C$ NMR samples were 10 wt % solutions in $CDCl_3$ (99.8% D) using $Cr(acac)_3$ as the paramagnetic relaxation reagent at a 0.05 M concentration, and the measurements were performed with 30° pulses (Bruker zgig30 pulse sequence), a sweep width of 22400 Hz, 32K data points, and a delay time between scans of 20 s. The zgig30 pulse sequence suppresses the Overhauser effect and the C to H coupling with an inverse gated decoupling sequence and composite pulse decoupling (CPD). Tetramethylsilane (TMS) was used as reference, and 2000 scans were averaged for each spectrum. In both cases, the $^{1}H$ and $^{13}C$ NMR, phase and baseline values of the resulting spectra were manually adjusted and corrected using a very large expansion of the frequency axis.

## 3. DISCUSSION AND RESULTS

**3.1. Characterization of Asphaltenes.** Table 2 shows the AMPs of the Colorado asphaltenes. These parameters were calculated from the elemental analysis and molecular spectroscopy data. The methodology used has been reported in these references: MS,[15] NMR,[14,16−18] Raman,[19] and XRD.[20] It is important to note that, as their names indicate, these are the average values of some wide ranging molecular properties. They provide general trends and are useful for comparisons among samples that are subject to diverse studies or processes.[21]

The average molecular weight values ranged between 547.5 and 589.3 g/mol, with the lowest for Col-CE1 and the highest for Col-B1. Among the asphaltenes, there were differences observed in the amounts and distributions of the carbon and hydrogen atoms. Paraffinic carbons ($C_s$), which belong to the aliphatic carbons ($C_{al}$), were in greater proportion than naphthenic carbons ($C_n$); the average length of the aliphatic chains (n) varied between 3 and 7, and the aromaticity factor ($f_a$), defined as the relationship between aromatic carbons ($C_{ar}$) and total carbons ($C = C_{ar} + C_{al}$), varied between 0.46 and 0.61. When the analysis of the crude oil asphaltenes is sorted by sand origin, those produced from sand B had relatively more aromatics than those produced from sand C (that is deeper); the asphaltenes that were extracted from the crude oil mixtures of sands C and E had relatively more aromatics than those of sand C. Therefore, it can be inferred that the asphaltenes from oil produced from sand E (the deepest sand of the field) had the most aromatics. There was no correlation between the aromaticity factor, the crude oil API, or the asphaltene concentration. However, it is noted that the crude oil mixture B−C had lower concentrations of asphaltenes than those from only B or C. This mixture had an effect on the precipitation of asphaltenes, and it is likely that they are more productive deposits.

The number of aromatic rings ($R_a$) varied between 4 and 5, and their ratios of peripheral to aromatic carbons ($C_p/C_{ar}$) varied between 0.74 and 0.63. It was observed that as this value increased, there were lower numbers of rings in the asphaltene molecules; that is, they were less complex. This result is consistent with the condensation ratio Φ (2.6−3.4); that is, with larger Φ ratios the internal carbon abundance would increase and there would be more rings.

The average heights of the asphaltene clusters (Lc) increased with the number of aromatic rings in the asphaltene molecules ($R_a$) because of their planar shape, which facilitates the pi−pi type of interaction and its formation. In contrast, the increasing number of carbons ($C_{al}$) in the aliphatic chain in the asphaltene molecules is responsible for steric repulsion, and, as a consequence, the thickness is reduced. Asphaltenes of crude Col-CE2 had the largest-sized molecules (La) and the greatest height of the aggregates (Lc), which confirms it as the most aromatic of the Colorado field asphaltenes that have been analyzed in this investigation.

The Colorado oil field has the same geological formation with different sands, while the biotic source materials, source rocks, and depositional environments are similar. These sands had different diagenetic and thermal histories during the migration and accumulation of hydrocarbons.[21] For this reason, their crude oils are different, and their asphaltenes also have different structural characteristics.

**3.2. Matrix Plot.** This procedure creates a matrix of plots for three or more numeric variables. The diagonal of the matrix contains box-and-whisker plots for each variable. The off-diagonal positions contain two-variable scatterplots for all pairs of variables. The procedure is very useful for obtaining an initial look at multivariate data. From the plot, one can often detect relationships among the variables, the presence of outliers, and other interesting features of the data. The Scatterplot Matrix (Figure 3) shows a rectangular matrix of plots. Each data variable defines a row and a column. For example, variable 1 (CarH) is shown in the first row and first column, variable 2 (n) is shown in the second row and second column, etc. [Statgraphics. StatPoint, Inc. Rev. 1/10/2005].

Figure 2 shows the relative content of carbons of nine AMPs selected from Table 2. It is easily seen that there are significant

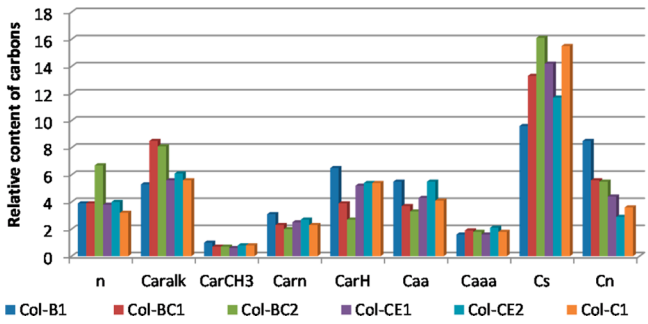


**Figure 2.** Comparison of the average parameters of Colorado asphaltenes.

differences in the relative amount of carbon atoms. These results showed that differences in the chemical composition of the asphaltenes may be easily detected by means of the methodology used in this work and it is able to distinguish their chemical differences with high accuracy, thus showing that it is a valuable tool in their characterization. They were chosen because they are the most representative of the aliphatic and aromatic parts of the molecules that are present in the asphaltenes. They were n, Cs, Cn, Caralk, CarCH3, Carn, CarH, Caaa, and Caa. They were used to describe the chemical structural differences of the asphaltenes of the crude oils from the Colorado field. A matrix plot (Figure 3) was used to assess


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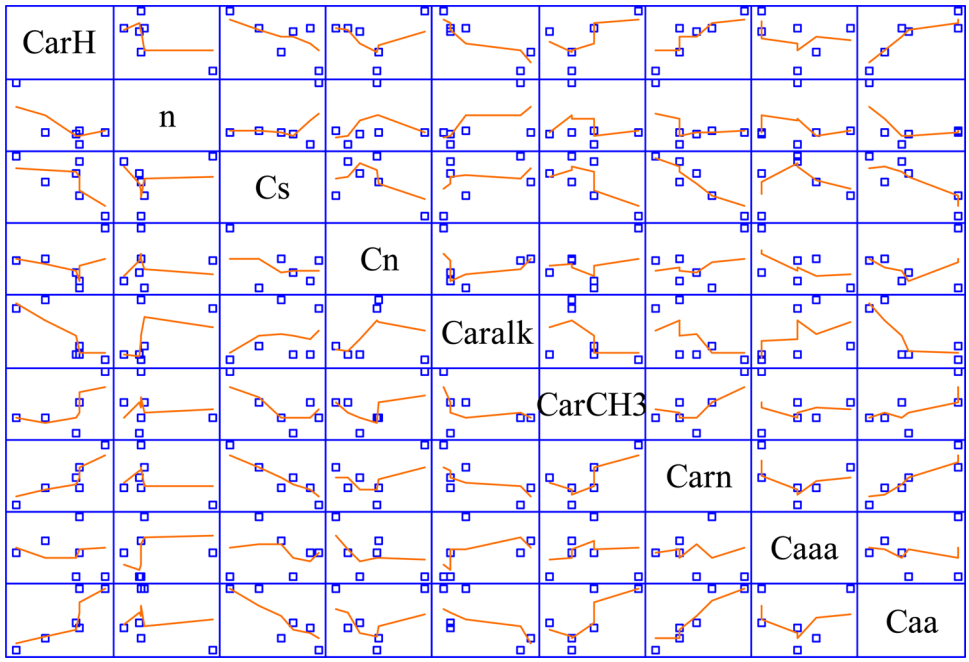


**Figure 3.** Matrix plot of the AMPs of the asphaltenes from crude oils: Colorado oil field.

the relationship among several pairs of variables at the same time. In general, this graph shows that there were no relationships between the several pairs of the nine AMPs used. This matrix confirms the independence of the variables used in this work. Because the whiskers are not linear, this indicates that all of the variables are useful to confirm the differences of the chemical structures of the six asphaltenes.

**3.3. Cluster Analysis.** The Cluster analysis procedure is designed to group observations or variables into clusters based upon their similarities [Statgraphics. StatPoint, Inc. Rev. 1/10/2005]. In this case, these are the chemical structural similarities obtained from the EA, MS, and NMR analyses. The raw data for this procedure may be in either of two forms:

(1) n rows or cases, each containing the values of p quantitative variables (n, Cs, Cn, Caralk, CarCH3, Carn, CarH, Caaa, and Caa, from Table 2).
(2) n rows and n columns, if clustering observations, or p rows and p columns, if clustering variables, all containing a measure of the "distance" between the pairs of items.

When raw data is input, the procedure will calculate the distances between the observations or variables. A number of different algorithms are provided for generating clusters. Some of the algorithms are agglomerative, beginning with separate clusters for each observation or variable and then joining clusters together based upon their similarity. The results of the analysis are displayed in several ways, including a dendrogram, a membership table, and an icicle plot.

The Cluster analysis procedure was used to identify those asphaltenes that have chemical structural similarities. The conditions used to derive the clusters were:

- Clustering Method: Farthest Neighbor (Single Linkage).
- Distance Metric: Squared Euclidean.
- Clustering: observations.
- Standardized: yes.
- Variables (from Table 2): n, Cs, Cn, Caralk, CarCH3, Carn, CarH, Caaa, Caa.

The results of this analysis are presented in Figure 4. The first and the farthest cluster was the joining of BC1 and BC2, at

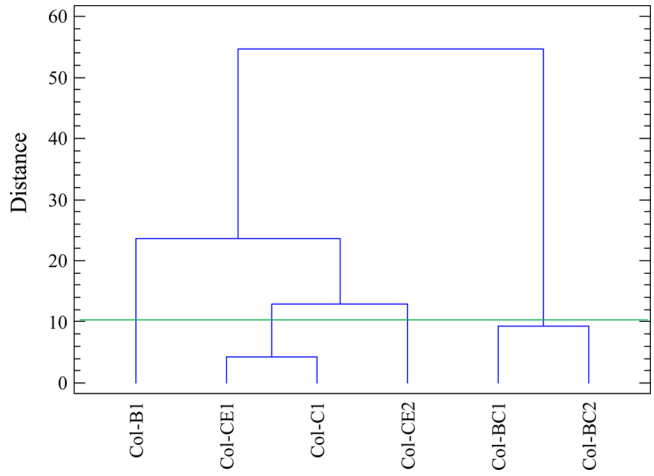


**Figure 4.** Cluster Scatterplot. Variables: n, Cs, Cn, Caralk, CarCH3, Carn, CarH, Caaa, Caa.

a distance of approximately 55 with the single cluster, B1. Next, CE2 was joined to the former cluster. At the fourth step, CE2 was joined to cluster CE1-C1. The general shape of the cluster scatterplot suggests grouping the asphaltenes into four groups: BC1-BC2, B1, CE2, and C1-CE1.

**3.4. Principal Component Analysis.** The Principal components procedure is designed to identify $k$ principal components from a set of $p$ quantitative variables, $X$ (n, Cs, Cn, Caralk, CarCH3, Carn, CarH, Caaa, Caa). The principal components are defined as the set of orthogonal linear combinations of $X$ that have the greatest variance. When the variables are highly correlated, the first few principal components may be sufficient to describe most of the variability present. [Statgraphics. StatPoint, Inc. – Rev. 6/28/2005]


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Table 3 shows the analysis summary. This table summarizes the variance attributable to each principal component. In this case, three components have been extracted because they had eigenvalues that were greater than or equal to 1.0, and together, they account for 90.9% of the variability in the original data.

**Table 3. Summary of PCA of Colorado Asphaltenes**

| Number Component | eigenvalue | Percent of Variance | Cumulative Percentage |
|---|---|---|---|
| 1 | 5.211 | 57.904 | 57.904 |
| 2 | 1.737 | 19.300 | 77.204 |
| 3 | 1.233 | 13.707 | 90.911 |
| 4 | 0.466 | 5.184 | 96.095 |
| 5 | 0.351 | 3.905 | 100.000 |
| 6 | $2.8 \times 10^{-16}$ | 0.000 | 100.000 |
| 7 | $5.0 \times 10^{-17}$ | 0.000 | 100.000 |
| 8 | 0.0 | 0.000 | 100.000 |
| 9 | 0.0 | 0.000 | 100.000 |

Figure 5 presents the principal plane as defined by the first two eigenvectors representing more than 77% of the total data variability. The vector lengths of all variables are similar, indicating that all of the AMPs used in the PCA define the chemical structures of the asphaltenes that were studied. Component 1 was affected positively for the AMPs related to aliphatic chains n, Caralk, and Cs and negatively by aromatic AMPs CarCH3, Carn, Caa, and CarH. Component 2 was affected positively by Cn and negatively by Caaa. This plane also shows that there are three very different asphaltenes: B1, CE2, and BC2.

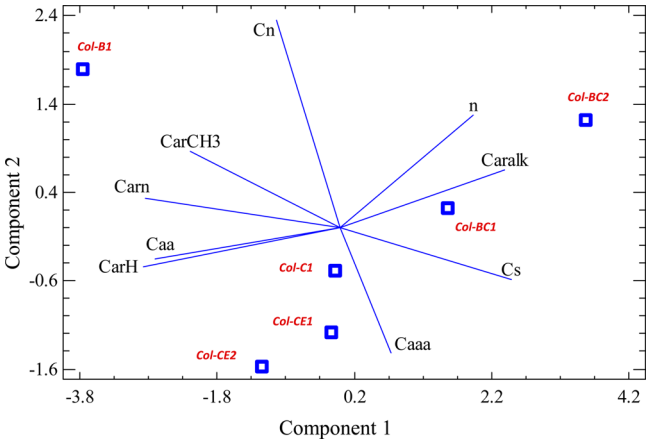


**Figure 5.** PCA of the AMPs of Colorado asphaltenes, principal plane.

The analysis shows that the asphaltenes from B1 have molecules with chemical structures mainly having aromatic backbones with kata (Caa) and protonated (CarH) carbons, and that the predominant aliphatic chains are the naphthenic type (Cn). The asphaltenes from CE2 had predominately the pericondensed (Caaa), the protonated aromatic (CarH) carbons, and alkyl groups having saturated chains (Cs). Asphaltenes from BC2 had the predominant structure of the aliphatic region (Cs) with long chains (n), and their aromatic carbons are highly substituted with alkyl groups (Caralk).

## 4. CONCLUSIONS

The results of the Matrix Plot, Cluster, and Principal Component Analyses using the independent variables n, Cs, Cn, Caralk, CarCH3, Carn, CarH, Caaa, and Caa demonstrated that the average molecular structures of the asphaltenes of the various crude oils from the Colorado oil field are different from each other. The more extreme structural differences of the asphaltenes were between the crude oils obtained from the top sand B (2112 feet) and the bottom sand CE (6178 feet). Asphaltenes from B1 mainly contained molecules with chemical structures with aromatic backbones with kata (Caa) and protonated (CarH) carbons, and the predominant aliphatic chains were of the naphthenic type (Cn). The asphaltenes from CE2 had predominately the pericondensed (Caaa) and protonated aromatic (CarH) carbons, and alkyl groups with saturated chains (Cs). Asphaltenes from BC2 had the predominant structure of an aliphatic part (Cs) with long chains (n), and their aromatic carbons are highly substituted with alkyl groups (Caralk). The general shape of the cluster scatterplot suggests grouping the asphaltenes into four groups: BC1-BC2, B1, CE2, and C1-CE1. The Colorado oil field has the same geological formation with different sands, while the biotic source materials, source rocks, and depositional environments are similar. These sands had different diagenetic and thermal histories during the migration and accumulation of hydrocarbons.[22] For this reason, their crude oils are different, and their asphaltenes also have different structural characteristics.

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### Notes

The authors declare no competing financial interest.

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