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Effect of Average Molecular Parameters of Asphaltenes on the Rheological Properties of Crude Oils from Colorado Oil Field

Emiliano Ariza,*[,†] Arlex Chaves-Guerrero,[‡] and Daniel Molina V.[§]

[†]Escuela de Ingeniería de Petróleos, [‡]Escuela de Ingeniería Química, and [§]Laboratorio de Resonancia Magnética Nuclear, Universidad Industrial de Santander, Bucaramanga, Colombia

ABSTRACT: In our previous articles (Energy & Fuels **2017**, *31*, 133−139 and Energy & Fuels **2017**, *31*, 8997−9005), it was presented that the asphaltenes of the Colorado field have different chemical structures, and these change the properties of crystallization of the paraffins. In this paper, we present a new way to understand the effects of the chemical structure of the asphaltenes on crude oil rheology, which includes correlating the average molecular parameters (AMPs) and the concentration of the asphaltenes with rheological properties using chemometric methods such as the partial least squares method. The asphaltenes were separated from six crude oil samples (average °API of 38) and were characterized using nuclear magnetic resonance to determine their main molecular parameters. Rheological properties including viscosity, yield stress, and gel temperature were experimentally determined for each of the crude oil samples and their respective maltenes. The results of a multivariate analysis show that the AMPs of the asphaltenes that cause the greatest effects are the ratio of peripheral aromatic carbons to aromatic carbons (C_p/C_{ar}) and pericondensed aromatic carbons (C_{aaa}), which increase the gel temperature among maltenes and crude oils. The concentration of the asphaltenes (C_{oasf}) contributes to decreasing this property. An increase in the yield stress is mainly caused by the aliphatic chains of the asphaltenes (n) and the molecular weight (M_w), whereas C_{oasf} causes decrease on the yield stress. Finally, the change in viscosity at 20 °C is increased by C_p/C_{ar} and is decreased by C_{oasf} and paraffinic carbons (C_s).

1. INTRODUCTION

Crude oil is a very complex mixture of hydrocarbon families, and to facilitate detailed studies, it has been divided into four fractions[1] based on solubility and polarity,[2] namely, saturated, aromatic, resin, and asphaltenes (SARA). Paraffin (C_{18}+) and asphaltene fractions can precipitate due to changes in pressure, temperature, and composition, forming solid deposits during the production and transport of petroleum.

The precipitation of paraffin is mainly caused by the cooling of crude oil and occurs when the crystallization temperature (or wax appearance temperature, WAT) is reached. The WAT is defined as the temperature at a given pressure at which there is at least 0.1% by weight of solid paraffin within the crude.[3] Once the first crystals of paraffin appear, nucleation begins, followed by a stage of growth. Depending on the hydrodynamic conditions (flow rate, surface characteristics, flow direction), accumulation of this organic material can occur on pipe walls.

In several studies, researchers have shown that at temperatures above the point of crystallization, the rheological behavior of waxy oils is Newtonian,[4,5] whereas at temperatures below the crystallization temperature, the rheological behavior becomes complex. For example, Wardhaugh[4] noted that the precipitation of waxy crystals and colloidal asphaltene particles generates a broad spectrum of rheological behaviors such as yield stress, shear thinning, and time dependencies in conditions of steady shear flow. The time-dependent behavior of waxy oils is generated principally by the formation of a thermoreversible gel that consists of paraffin crystals, with a complex morphology, that interact and form a network. This gel forms owing to the precipitation of orthorhombic wax crystallites and, during the flocculation, form a highly porous and rigid structure full of entrapped oil whose formation process is extremely dependent on the thermal history, shear history, and of the content of asphaltenes.[6] Based on the time-dependent rheological behavior observed in gelled waxy oils, the gel temperature has been defined as the temperature at which solid-like behavior dominates liquid-like behavior.[6] Accordingly, the gel temperature is obtained using the oscillatory rheological test to obtain the temperature at which the storage modulus (G') is equal to the loss modulus (G'').

This has raised the possibility that the quantity and composition of asphaltenes have a substantial effect on the precipitation of paraffin. Several investigations have aimed to verify this theory using real waxy crude oil or model waxy oil. The model oils are obtained from aliphatic or aromatic hydrocarbons or mixtures of these, to which dissolved paraffins and asphaltenes are added. The asphaltenes originate from crude oils or from deposits in oil storage tanks or from production pipelines.

For example, Venkatesan et al.[6] searched the effect of the asphaltenes on the gelation of waxy oils using the value of yield stress and the change of the gelation temperature as points of comparison. For this, they used synthetic oil composed of a mixture of pure paraffin (5% w/w) and asphaltenes dissolved in toluene and mineral oil. The asphaltenes used were from crude oil from the Zuata field in Venezuela, which were separated into three polarity-based fractions, and they found that the fraction of asphaltenes with less polarity decreased the gel point to 4 °C and increased the yield stress value to 110 kPa compared to samples without asphaltenes.

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Furthermore, Kriz and Andersen[7] focused on verifying whether there is a relationship between the type of asphaltenes or its state of aggregation (dissolved or solid aggregates in the crude oil) and the crystallization of paraffin. To develop their study, they used deasphalted paraffinic crude that was obtained from the North Sea, as well as three kinds of asphaltenes that were obtained from a stable oil, an organic deposit, and unstable oil. Initially, to the crude oil they added the same amount of each type of asphaltenes (0.01% w/w). They observed that the WAT value was 10 °C higher than the value of WAT for an asphaltene-free oil, indicating that asphaltenes directly influence wax crystallization. However, for concentrations of asphaltenes greater than 0.01% w/w, the WAT value decreases significantly, suggesting that the effect on the crystallization of paraffin depends more on the degree of dispersion or flocculation of the asphaltenes than on their origin. At a lower concentration, they are well-dispersed or well-dissolved in the crude and may interact with the paraffin, but at higher critical concentrations, the equilibrium is broken, causing flocculation and increasing the concentration of solids in the oil. The flocculated asphaltenes increase the dynamic viscosity but depress the yield stress.

Also, Oh et al.[8] studied the influence of asphaltenes at temperatures below the pour point of seven oil models. These were prepared using several proportions of two types of waxes, asphaltenes (0.1 and 0.01% w/w), kerosene, toluene, and different mineral oils. The asphaltenes were collected from the production line of a well in the Rangely field (Colorado, USA). They found that, at each concentration of asphaltene, as the temperature decreased below the pour point, the yield stress of the model oil increased. However, the inclusion of asphaltenes reduced the yield stress (which agrees with results presented by Kriz and Andersen[7]) because asphaltenes obstruct the formation of continuous and consistent gel networks.

The effects of asphaltenes on wax crystallization behavior was studied. The impact of the asphaltenes on the WAT, gelation temperature, and yield stress was evaluated using optical microscopy and oscillatory rheological measurements to obtain structural information about the waxy gel. The authors used model oils that were made by blending wax with a continuous carbon distribution of C_{20} to C_{47}, asphaltenes extracted from Shengli crude, and a combination of Norpar 12 and 1-methylnaphthalene as a solvent. They observed that there was a contradiction between their study and previous work regarding the effect of asphaltenes on WAT, leading them to conclude that the chemical nature of the asphaltenes has a significant effect. This conclusion is based on previous observations of Venkatesan et al.[6] and the aliphatic character of the Shengli asphaltenes used. Additionally, they observed that the amount of wax relative to asphaltenes is important for the value of the yield stress and that the network begins to degrade beyond of the threshold of asphaltene concentration.

The former study was extended by Tinsley et al.[10] to assess the effect of asphaltenes on the effectiveness of three polymer additives, polyethylene butene (PEB), poly(ethylene-*co*-vinyl acetate) (EVA), and poly(maleic anhydride amide-*co*-α-olefin) (MAC16−18 and MAC Et-22), to prevent gelation problems when using the same model oil as in the previous study.[9] In general, they found that the effect of asphaltenes on the gel temperature and yield stress value depends on the polymer that was aggregated in the model oil. They observed that the asphaltenes do not affect the gelation temperature for PEB and MAC16−18 but do affect the temperature when asphaltenes are aggregated in model oil with MAC Et-22. Concerning the value of yield stress, they observed that the concentration of asphaltenes had approximately the same effect for model oils both with and without the polymer.

Another problem in the oil industry is the precipitation of asphaltenes during the mixing of incompatible crude oils. Lei et al.[11] addressed this problem, evaluating the transition kinetics of asphaltenes from dispersion to aggregation and characterized the effect of the dispersed and aggregated asphaltenes on wax crystallization. They concluded that the asphaltene transition does not appreciably change the WAT from dispersed to aggregated. However, it affects the amount of precipitated wax. To explain this observation, they used two arguments: (i) First, the flocculated asphaltenes become paraffin nucleation sites for wax crystal growth, as proposed by García.[12] (ii) Second, dispersion of the asphaltenes caused a steric hindrance for the crystallization of saturated wax molecules greater than that with the same amount of aggregated asphaltenes, as proposed by Kriz and Andersen.[7] They propose that the aggregated asphaltenes can serve as crystallyzation seeds for growing wax molecules, promoting their precipitation, weakening the strength of the network, and delaying the gelation process of crude oil. In contrast, the dispersed asphaltenes can serve as the connecting points between wax crystals, accelerating the gelation and increasing the gel strength of crude oil.[11]

Alcazar-Vara and Buenrostro-Gonzalez[13] studied three Mexican crudes that during production and transport have organic precipitation problems. They observed that the asphaltenes significantly affect the solid−liquid equilibrium and rheological behavior of crude oil. Their experimental results showed that the pour point and gel temperatures increase linearly as the wax/asphaltene ratio increases, despite their compositions of saturates, aromatics, and resins being very similar. In another study by the same researchers,[14] they prepared model oils using asphaltenes that were extracted from two Mexican wells (which displayed severe precipitation) and blended at several concentrations (0, 0.03, and 0.05% w/w) to commercial paraffin. They observed that if the concentration of asphaltenes increases the WAT temperature decreases by approximately 2 °C. However, they did not find a significant effect of the chemical characteristics of the asphaltenes on the value of WAT. In contrast, they found a strong effect of the concentration and chemical nature of asphaltenes on the pour point temperature. Additionally, they observed that the viscosity decreases with asphaltenes with a higher aromaticity factor (f_a), whereas the gel temperature dropped with the asphaltenes with a lower aromaticity factor, and the opposite occurred for the pour point. On the other hand, the asphaltenes with greater f_a inhibited and disturbed the formation of wax crystals and are promoters of a less stable gel structure.

Zhao et al.[15] studied several variables that affect the paraffin gelation process, such as thermal and shear history, asphaltene content, and chemical additives. Additionally, they proposed a model to predict the waxy oil yield stress value of a formed gel, which is an important criterion in the strategic implementation of flow assurance. They used model oils with asphaltenes A or B at concentrations up to 0.08% w/w, as well as macrowax and microcrystalline wax. They found that the yield stress and surface tension decreased when the concentration of asphaltenes increased. The effect of the concentration of asphaltenes on decreasing the yield stress was attributed to heterogeneous nucleation, adsorption, or steric hindrance, whereas that additive presumably suppressed the crystal growth

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Table 1. Characteristic Crude Oils from the Colorado Field

well	oil sand	depth (ft)	bottom hole temperature (°C)	production by sand (vol %)	API gravity	asphaltene concentration (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

process via adsorption or a cocrystallization mechanism. Finally, they proved that a modified Eyring model could represent the value of the yield stress as a function of the cooling rate for a waxy oil during the static gelation process.

As can be noted from the previous discussion, there are a large number of studies and publications about the effects of asphaltenes on the precipitation of paraffin and, therefore, on the rheological behavior of waxy crude oils. However, few relate the molecular chemical structure of asphaltenes to the behavior of these properties.

This paper focuses on evaluating the effects of the average molecular parameters of six asphaltenes on the rheological properties of paraffinic crudes. For this, different spectroscopic techniques were used for evaluating the average molecular parameters of asphaltenes that were related to changes in the rheological properties of deasphalted oils (maltenes) and their respective whole oils. The dependent variables include changes in gel temperature (ΔT_{gel}), changes in yield strength ($\Delta\tau_o$), and change in viscosity ($\Delta\mu$). The independent variables include the molecular weight (M_w), the concentration of asphaltenes (C_{oasf}), and the average molecular parameters (AMPs): pericondensed aromatic carbon number (C_{aaa}), average length of aliphatic asphaltenes chains (n), the ratio of peripheral carbons to aromatic carbons (C_p/C_{ar}), the aromaticity factor (f_a), paraffinic carbon number (C_s), naphthenic carbon number (C_n), molecular weight (M_w), and the concentration of asphaltenes (C_{oasf}).

2. EXPERIMENTAL SECTION

2.1. Materials. The paraffinic crude oils used in this study were produced from the Colorado field, Colombia. The principal producing formation in this field is the Mugrosa Formation (sands B and C) and, to a lesser extent, the Esmeraldas Formation, which we refer to as sand E. The field produces waxy oil with an average °API between 34 and 42°.[16,17] The Colorado field has historically had problems related to the precipitation of paraffin deposits that obstruct oil flow, resulting in the abandonment of more than 70% of the wells. Asphaltenes have been found in the deposits, which indicates that this fraction from waxy oils is contributing to the problem.

For this work, six samples of waxy oils were collected from sands B and C and blends of B with C and C with E (Table 1).

2.2. Extraction of Asphaltenes and Maltenes. Asphaltenes were extracted from the Colorado crude oils following the ASTM D6560-12 standard method. In summary, were mixed *n*-heptane (J.T. Baker, 99.3%) with crude oils in a 20:1 ratio. After the samples were refluxed for 1 h at 98 °C, they were left to rest for 24 h and were then filtered. Afterward, the filtered asphaltenes were refluxed in a Soxhlet extractor until the *n*-heptane was clear. The solvent was removed, and toluene (J.T. Baker, 99.90%) was then added to the Soxhlet flask to dissolve the asphaltenes until the solution in the Soxhlet siphon was colorless. The toluene was removed by rotoevaporation.

2.3. Characterization of Asphaltenes and Maltenes. The ^{1}H and ^{13}C NMR spectra of the asphaltenes and maltenes were acquired with a Bruker Avance III spectrometer at resonance frequencies of 400.16 and 100.63 MHz, respectively. The samples for ^{1}H NMR were ran as 4 w/w% solutions in $CDCl_3$ (Merck, 99.8% D, 0.03 vol % tetramethylsilane), and the spectra were performed with 30° pulses (Bruker zg30 pulse sequence), a sweep width of 49000 Hz, a delay time of 10 s, and after 16 scans, they were recorded with 32000 data points. The samples for ^{13}C NMR were ran as 10 w/w% solutions in $CDCl_3$ using $Cr(acac)_3$ (Merck) at 0.05 M concentration. The spectra were obtained with 30° pulses (Bruker zgig30 pulse sequence), a sweep width of 22400 Hz, a delay time of 20 s, and after 2000 scans, they were recorded with 32000 data points.[16,17]

For each spectrum, the phase and baseline were manually adjusted. For both ^{1}H and ^{13}C NMR, tetramethylsilane was used as the reference scale, and the integration areas chosen were standardized.[19,20] The parts per million ranges chosen for the NMR spectra were based on the methodology proposed by Poveda and Molina.[21] For each sample, spectra processing was repeated five times to obtain an average of the integration areas.

2.4. Rheological Tests. Rheological tests were performed in an Anton Paar rheometer model MCR-302 with a parallel plate geometry that had a 50 mm diameter and a Peltier temperature control system; this procedure was performed based on Venkatesan et al.[6] The gel temperature was determined by placing the sample under constant oscillatory stress (τ) of low amplitude (0.1 Pa) and a frequency of 0.1 Hz. The initial temperature was 70 °C, and the cooling rate was 1 °C/min to 0 °C. The gel temperature was estimated as the temperature where the loss moduli (G'') was equal to the storage moduli (G') (Figure 1). The repeatability of this test was ±1.5 °C.

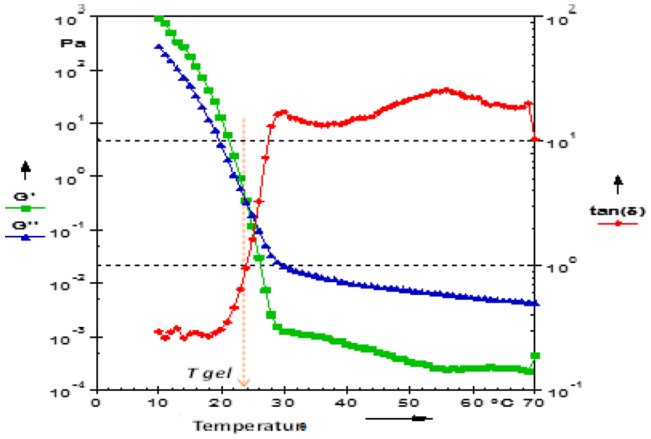

Figure 1. Determination of gel temperature for maltenes of crude Col-CE1.

When the gel temperature test was finished, the sample was left to rest for 10 min at a lower temperature (0 °C) than the gel temperature of the studied samples, and then the loss and storage moduli were determined again using a logarithmic stress ramp from 10^{-1} to 10^4 Pa at a constant temperature. These curves allowed estimations of both the yield stress (τ_o) as that stress at which the storage modulus drops dramatically[18] (Figure 2). The repeatability of yield stress test was ±2 Pa.

The viscosity measurements were made for a temperature range that corresponded to that of the bottom hole down to 0 °C. For these measurements, a cooling rate of 1 °C/min and a shear rate of 10 s^{-1} were used. However, to compare this property between different crude

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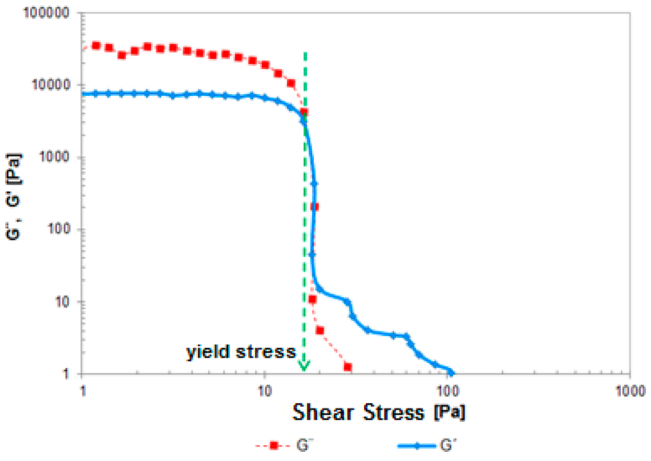

Figure 2. Determination of yield stress for maltenes of crude Col-CE1.

oils, the values of viscosity at a temperature of 20 °C were obtained, at which a viscoelastic behavior is present. The repeatability for measuring the viscosity with the rheometer was ±2.0 cP.

3. RESULTS AND DISCUSSION

3.1. Characterization of Asphaltenes. Table 2 shows the results of the characterization of asphaltenes for the six crude

Table 2. Average Molecular Parameters of Colorado Field Asphaltenes[a]

AMPs	Col-B1	Col-BC1	Col-BC2	Col-CE1	Col-CE2	Col-C1
C_{al}	18.1	18.9	21.6	18.6	14.6	19.1
C_{ar}	23	21	18.5	19.8	22.5	19.9
n	3.9	3.9	6.7	3.8	4	3.2
C_{aaa}	1.6	1.9	1.8	1.6	2.1	1.8
C_s	9.6	13.3	16.1	14.2	11.7	15.5
C_n	8.5	5.6	5.5	4.4	2.9	3.6
f_a	0.56	0.53	0.46	0.52	0.61	0.51
C_p/C_{ar}	0.69	0.74	0.72	0.7	0.66	0.70
M_w (g/mol)	589	573	584	547	561	585

[a] C_{al}, aliphatic carbon number; C_{ar}, aromatic carbon number; n, average length of aliphatic chains; C_{aaa}, pericondensed aromatic carbon number; C_s, paraffinic carbon number; C_n, naphthenic carbon number; f_a, aromaticity factor; C_p/C_{ar}, ratio of peripheral aromatic carbons to aromatic carbons; M_w, average molecular weight.

oils. Aromatic carbons (C_{ar}) are more abundant than aliphatic carbons (C_{al}), and paraffinic carbons (C_s) are more abundant than naphthenic carbons (C_n); these are common results in typical asphaltenes. The average chain length (n) varies between 3.2 and 6.7 and the aromaticity factor (f_a) between 0.46 and 0.61. Asphaltene molecules extracted from crude oil produced from sand B contain more aromatic carbons than those produced from sand C (which is deeper), and those extracted from crude oil mixtures of sand C and E contain more than those of sand C. Therefore, it can be inferred that asphaltenes from oil produced by sand E (the deepest sand in the field) contain the most aromatics.

3.2. Characterization of Maltenes. NMR results show (Figures 3 and 4) variation in the content of aromatic and aliphatic carbons (C_{ar}, C_{al}) as well as the content of aliphatic and aromatic protons (H_{al}, H_{ar}) between maltenes and between asphaltenes of crude oils.

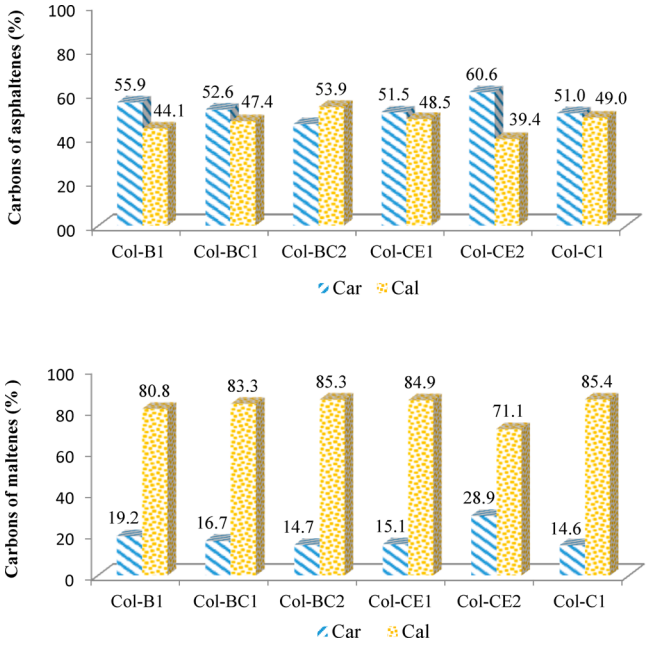

Figure 3. Comparison of carbon distributions by ^{13}C NMR for asphaltene and maltene fractions from Colorado field crude oils.

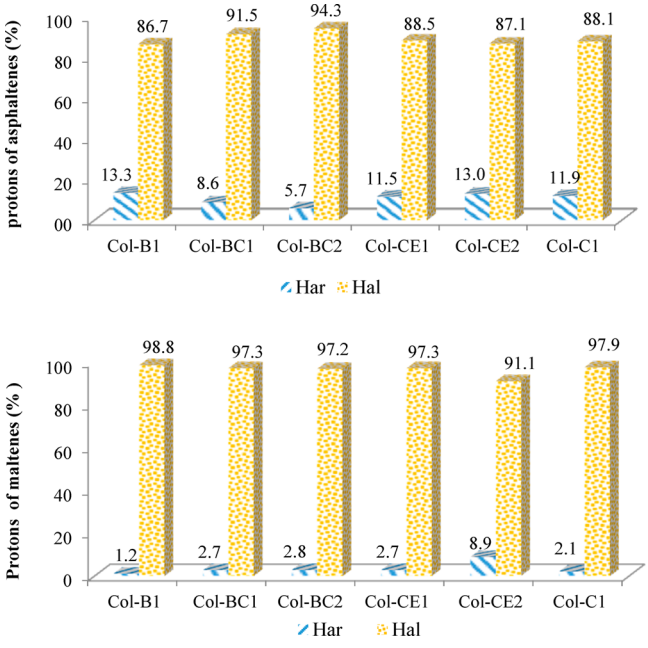

Figure 4. Comparison of proton distributions by ^{1}H NMR for asphaltene and maltene fractions from Colorado field crude oils.

The average proportion of aromatic carbons in the crude maltenes is 18.8%, whereas the proportion of aliphatic carbons is 81.8% (Figure 3). Carbons from sand B producing wells have an aliphatic content higher than that of sand C, but in the mixtures, changes in the composition were observed. For example, Col-CE2 (E and C sand mixture) has a high content of aromatic carbons.

Aliphatic protons (H_{al}) of the maltenes is 96.6%, whereas it is 3.4% in the aromatic protons (H_{ar}) (Figure 4). Variation between wells was observed, with the highest percentage of maltenes in well Col-B1 and the lowest percentage in well Col-CE2.

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A correlation between AMPs of asphaltenes and rheological properties was obtained with the goal of determining the relationship between the chemical structure of the asphaltenes and the paraffin crystallization phenomenon. Data analysis started with 18 AMPs and the concentration of the asphaltenes. For this purpose, a correlation analysis between variables was made with multiple linear regression. The p value was calculated for each correlation coefficient to know whether or not two variables are significantly related to each other (if the p value is less than 0.05, a statistically significant linear correlation exists at the 5% significance level). The collinear variables mask the result; therefore, it was necessary to reduce the number of independent variables to correlate with the dependent variables (gel temperature, yield stress, and viscosity); finally, 10 independent variables were selected, nine parameters (Table 2), and the concentration of asphaltenes (C_{oasf}) is presented in Table 1. The molecular parameters selected were as follows: pericondensed aromatic carbon number (C_{aaa}), the average length of aliphatic asphaltene chains (n), the ratio of peripheral aromatic carbons to aromatic carbons (C_p/C_{ar}), the aromaticity factor (f_a), paraffinic carbon number (C_s), naphthenic carbon number (C_n), molecular weight (M_w).

The changes in flow properties during paraffin crystallization were considered as dependent or response variables. These include the change in gel temperature ($\Delta T_{gel} = T_{gel,crude} - T_{gel,maltenes}$), the change in yield stress ($\Delta\tau_o = \tau_{o,crude} - \tau_{o,maltenes}$), and the change in viscosity ($\Delta\mu = \mu_{crude} - \mu_{maltenes}$). Each of the physical properties was measured for both crudes and maltenes, and the differences in their values represent the effect of the asphaltenes, presented in Table 3.

Table 3. Change in Rheological Properties Due to the Asphaltenes

well	asphaltenes (ppm)	ΔT_{gel} (°C)	$\Delta\tau_o$ (Pa)	$\Delta\mu$ (cP) at 20 °C
COL-BC2	90	40	34	30
COL-BC1	440	34	8	49
COL-CE2	750	1	13	−9
COL-CE1	850	−5	−6	−148
COL-C1	1500	−2	−34	−288
COL-B1	2270	−20	−23	−72

Multivariate partial least squares regression analysis was performed to determine a correlation between the structural parameters of asphaltenes (AMPs) and the changes on rheological properties due to the asphaltenes. Various models were obtained, and to select the best, cross-validation was performed (leave one out) until the model got a p value <0.05 and an R^2 close to 1.0 (100%). To explain the effect and importance of each AMP, the standardized regression coefficients of the parameters were taken with its sign and magnitude. A greater magnitude indicated a greater impact on the rheological properties; a negative sign means that if the value of the AMP increases, the value of the property decreases. In contrast, the value increases if the sign is positive.

3.3. Effect of Asphaltenes on Gel Temperature. The difference between crude oil and maltene gel temperatures can be separated into three descriptive groups (Table 3). The first group (promoter) is characterized by the significant increases of 40 °C (Col-BC2) and 34 °C (Col-BC1); the second group (neutral) shows small changes, such as 1 °C for Col-CE2, −5 °C in Col-CE1, and −2 °C in Col-C1; and the third group (depressant), including Col-B1, showed a change of −20 °C.

The results of the multivariate analysis (Figure 5) show the depressant effects of asphaltenes at high concentrations (C_{oasf})

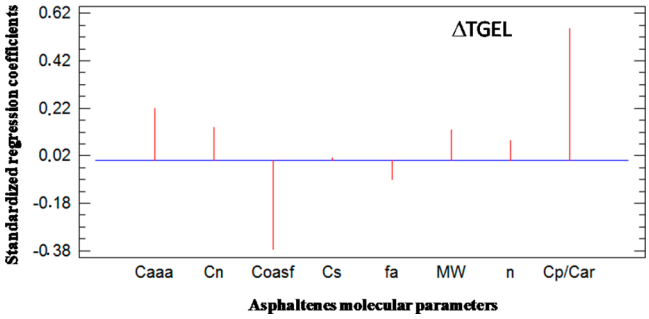

Figure 5. Multivariate analysis of asphaltenes: effect on the change in gel temperature.

and a minor effect from the aromaticity factor (f_a). In contrast, asphaltene parameters C_p/C_{ar} and C_{aaa} favor an increase in the value of the gel temperature.

A plausible explanation for this behavior is that asphaltenes with a high concentration of aromatic carbons intercalate between the paraffins, obstructing the contact between the crystals that are forming and those that are growing. Therefore, they lower the temperature, facilitating a viscous rheological behavior over a wide temperature range. Namely, considering that once the gel temperature is reached, the dominant rheological behavior is viscoelastic. On the other hand, these results allow us to infer that a higher concentration of polycondensed aromatic rings (C_{aaa}), naphthenic carbons (C_n), and a high value of C_p/C_{ar} favor the formation of crystal lattices, increasing the value of the gel temperature.

Our results are analogous with those of Alcazar-Vara et al.,[13] who also concluded that highly aromatic asphaltenes are depressors of the gel temperature. In their study, Alcazar-Vara et al. observed that with a small increase in the concentration of asphaltenes (0.03 to 0.05% w/w) in a solution of decane *o*-xylene and 5% w/w of commercial paraffin, a decrease of approximately 14 °C in the gel temperature was present when asphaltenes with a higher aromaticity factor (f_a = 0.67) were used. This indicated that the chemical structure of asphaltenes plays an important role in the behavior of the gel temperature. Unfortunately, the authors did not describe the effects of the other structural parameters of asphaltenes, so it is necessary to note that not only the aromaticity factor impacts the gel temperature. In addition, these results partially agree with observations by Venkatesan et al.,[6] who found that an increase in asphaltene concentration decreases the value of the gel temperature, but for those of minor polarity, the parameter is difficult to correlate to aromaticity (f_a).

3.4. Effect of Asphaltenes on Yield Stress Value. Experimental measurements showed that the value of the yield stress of the crude oil concerning its maltenes may increase or decrease, as shown in Table 3. Specifically, it was found that the variation of $\Delta\tau_o$ is positive ($\tau_{o,oil} > \tau_{o,maltenes}$) and has a magnitude of 34 Pa for well Col-BC2 and 13 Pa for well Col-CE2. In contrast, it is negative (yield stress depressants) and has a magnitude of 6 Pa in well Col-CE1, 34 Pa in well Col-C1, and 23 Pa in well Col-B1.

Results for the multivariate analysis of the effect of asphaltenes on the change in yield stress ($\Delta\tau_o$) are presented

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in Figure 6. The results show that C_{oasf} and C_s (concentration of paraffinic carbons) are depressors on the yield stress value.

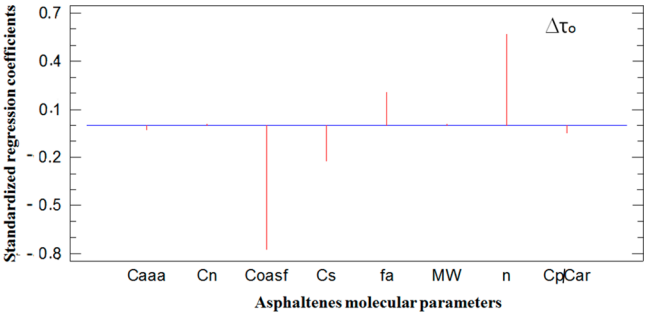

Figure 6. Multivariate analysis of asphaltenes: effect on the change in yield stress.

Therefore, the presence of asphaltenes with these structural characteristics contributes to the weakening of the interactions between paraffin crystals, facilitating their breakup when shear stress is applied (i.e., flow conditions).

On the other hand, asphaltene molecules with long aliphatic chains (n) that intertwine with the alkanes of the maltenes make the breaking and deformation of the crystals more difficult because of greater attraction forces. For this reason, the increase in the value of yield stress between maltenes and crudes is favored, meaning that a higher initial effort is required for the flow of the oil to occur mainly caused by the presence of maltenes.

Venkatesan et al.,[6] Tinsley et al.,[9,10] and Alcazar-Vara et al.[13,14] reported that an increase in the concentration of asphaltenes decreases the magnitude of the yield stress of model wax oils, but our results show that the C_{oasf} has the opposite effect and agrees with those of Kriz and Andersen[7] who observed that the yield stress could also increase at low concentrations of asphaltenes and later decrease as the concentration of asphaltenes increased.

Alcazar-Vara et al.[13,14] concluded that asphaltenes with a high aromaticity factor and more polar character have a depressant effect on yield stress. Venkatesan[6] concluded that asphaltenes with a less polar character are more effective as yield stress depressants.

Results presented in this work show that the effects of asphaltenes on yield stress are influenced by other structural parameters of these species in addition to the concentration and the degree of aromaticity.

3.5. Effect of the Asphaltenes on the Viscosity. The behavior of viscosity as a function of temperature for crude oils and their respective maltenes has two patterns that are shown in Figure 7. In the Col-BC1 and Col-BC2 crudes, which are oil mixtures from sands B and C (Figure 7a), the average difference in viscosity is 4 cP at temperatures above the crystallization temperature (average 60 °C). When the sample approaches temperatures below the crystallization temperature, it shows a gradual increase in viscosity with a similar trend for the two crude oils and with a value higher than that of their respective maltenes. In crude Col-BC1, the viscosity changes from 4 to 75 cP over a temperature range of 60 to 20 °C; a similar behavior was observed for crude Col-BC2. In these crudes, the asphaltenes contribute to the increase in oil viscosity at temperatures lower than the crystallization temperature.

The second group (Figure 7b) includes crudes produced by B, C, and mixtures from the C and E sands, in which the

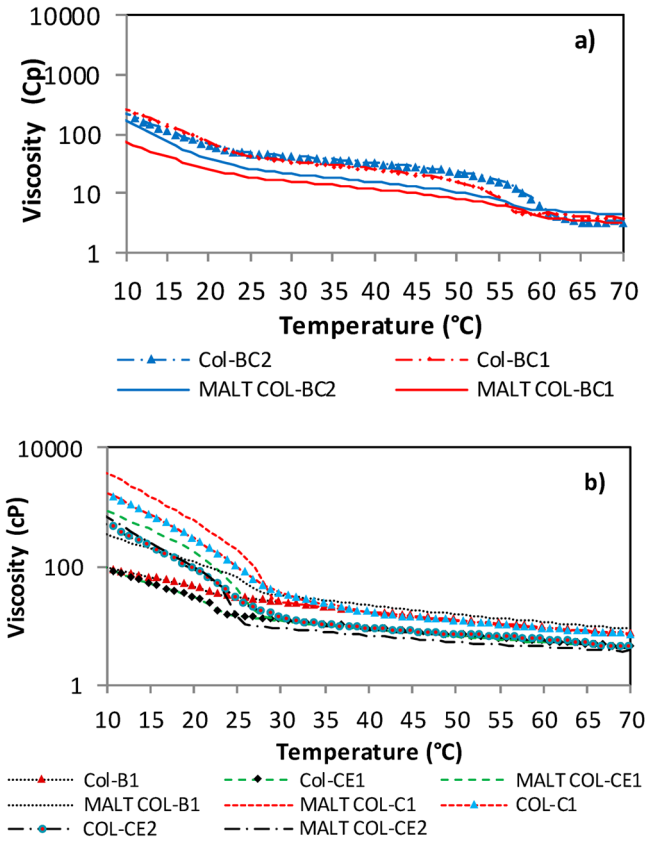

Figure 7. Maltenes and crude oil viscosity: (a) Col-BC1 and Col-BC2. (b) Col-B1, Col-C1, Col-CE1, and Col-CE2.

crystallization temperature is low (average 29 °C). Between 70 °C and the crystallization temperature, the viscosity of crude oils and their maltenes is greater for Col-B1 and Col-C1, which have the highest concentrations of asphaltenes of the crude oils. The viscosity increase in this temperature range is from 9 to 40 cP. In general, at temperatures below the wax temperature appearance, a considerable increase occurs for this group, which is higher for maltenes of Col-C1, showing a change from 40 cP at 29 °C to 587 cP at 20 °C. Maltenes in this group have a viscosity higher than that of crudes, so the asphaltenes have a viscosity depressant character.

To observe the isothermal viscosity behavior between maltenes and crudes, a base temperature of 20 °C was used because it is the lowest average ambient temperature of the Colorado field. It is noted that crudes with low asphaltene content (Col-BC1 and Col-BC2) showed a slight increase in viscosity difference ($\Delta\mu$) of 30 to 49 cP (Table 3). For others, the change was negative; that is, the maltenes have viscosities higher than those of the crudes, and the values are very different. For the Col-CE2, it was −9 cP; for Col-CE1, it was −148 cP; for Col-C1, it was −288 cP, and for Col-B1, which was the oil with the highest concentration of asphaltenes (2270 ppm), the change in viscosity was −72 cP.

Multivariate analysis (Figure 8) shows that the factors that contribute to the decrease the viscosity of the crudes and maltenes are the asphaltene concentration (C_{oasf}) and the paraffinic carbons (C_s). In contrast, $\Delta\mu$ between crude oil and its maltenes increases with the concentration of naphthenic carbons (C_n), the aromaticity factor (f_a), the length of the aliphatic chains (n), and the C_p/C_{ar} ratio.

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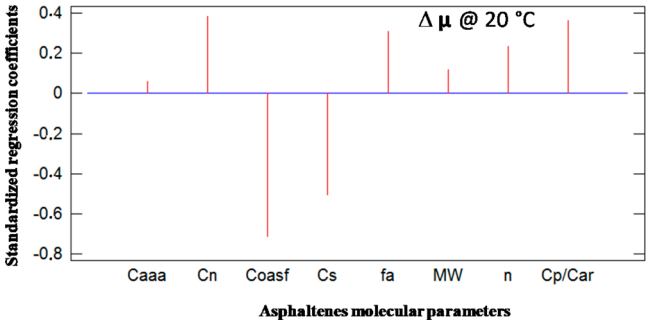

Figure 8. Multivariate analysis of asphaltenes: effect on the change in viscosity.

It seems contradictory that an increase in the concentration of asphaltenes decreases the viscosity of the paraffinic crudes oils considering that in heavy crude oils it has been determined that high concentration of asphaltenes is responsible for the higher viscosity. Luo and Gu[22] performed viscosity measurements against asphaltene concentration in heavy crude oils at different temperatures. They found that at low asphaltene volumetric fractions ($\varphi \leq 5$ vol %), the viscosity of the crudes increases smoothly and linearly with the concentration of asphaltenes with low temperature dependence. The reason is that when the colloidal suspension is diluted, there is no appreciable interaction between the asphaltenes. This slow increase in viscosity by effect of the asphaltenes is due to the long-range hydrodynamic interactions (perturbations of the flow around the particles) between the asphaltene particles and the maltenes.[23] Moreover, when the asphaltene volume fraction becomes higher, the short-range interparticle interactions become more efficient, increasing the value of the viscosity as the concentration increases.

In paraffinic crude oils, the ratio content of paraffins to asphaltenes is much greater than that in heavy crude oils. For example, Alcazar-Vara et al.[23] observed that the amount of asphaltenes has a depressant effect on the viscosity of crude oil (light) models at temperatures that are lower than or equal to the pour point. They used two commercial paraffin waxes named A and B, which are differentiated by the length of their chains where the wax A has a carbon distribution of C_{28} to C_{38} and that of wax B from C_{22} to C_{45}. They used two asphaltenes named AsphPC (f_a = 0.67) and Asphlri (f_a = 0.50) with concentrations of 0, 0.03, and 0.05 wt %.

Additionally, Venkatesan et al.[6] observed that the paraffin crystals formed in the absence of asphaltenes have a longer and thinner form than those formed in the presence of asphaltenes. The wax crystals formed from long chains of alkanes (paraffinic hydrocarbons) in the absence of asphaltenes were rodlike in shape, whereas those crystals formed in the presence of asphaltenes were more globular in shape. This observation is important because it has been found that particles of rounded shape[24] tend to generate a lower viscosity in the suspension than elongated particles, which is consistent with the decrease in viscosity with the incorporation of asphaltenes to the maltenes found in the multifactorial analysis of the present research. The change in the shape of the crystal is explained by Venkatesan et al., proposing that the asphaltenes are like nucleation centers on which the paraffin crystals are grouped. Consequently, the contacts between the wax crystals are minor in the presence of asphaltenes, resulting in a weak network.

4. CONCLUSIONS

In the Colorado field, there are wells that produce oil from sands B, C, and E; however, mixtures of crude oil from these sands are also produced. In the case of Col-BC1 and Col-BC2 (they produce crude mixtures of sands B and C), the rheological properties of the crude have a different behavior than that of the crude ones produced by single sand. Therefore, it can be inferred that the composition final changes the content and chemical structure relationship of the crude fractions (saturated, aromatic, resins, and asphaltenes) and therefore the influence on these properties. Also, it was demonstrated that the average molecular structure of asphaltenes changes between crudes within the same field. Similarly, changes between carbons and protons of the maltenes that were associated with the crude oils were observed.

The changes on the rheological properties of Colorado crude oils depend on both the concentration and the chemical structure of the asphaltenes. Multivariate analysis shows that an increase in the concentration of asphaltenes from the oils tends to decrease the gel temperature, the yield stress, and the viscosity. Meanwhile, the aromaticity factor contributes to increasing the viscosity and the yield stress and decreases the gel temperature. However, the other structural parameters of the asphaltenes, such as C_{aaa}, n, C_s, C_n, and C_p/C_{ar}, also have an impact on the results. Finally, this work confirms that the chemical structure of asphaltenes influences the rheological properties of the crude. However, further research must be done to determine the effect of the physicochemical and structural characteristics of the paraffins and their interaction with asphaltenes.

AUTHOR INFORMATION

Corresponding Author

*E-mail: earizal@uis.edu.co.

ORCID

Daniel Molina V.: 0000-0002-7897-2526

Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Hammami, A.; Ratulowski, J. *Asphaltenes, Heavy Oils, and Petroleomics*; Springer: New York, 2007.
(2) Aske, N. Ph.D. Thesis; Department of Chemical Engineering, Norwegian University of Science and Technology, Trondheim, Norway, 2000; pp 1−51.
(3) Ball, R.; Jones, J. *Open Thermodyn. J.* **2009**, *3*, 34−37.
(4) Wardhaugh, L. T.; Boger, D. V.; Tonner, S. P. Rheology of Waxy Crude Oils *International Meeting on Petroleum Engineering*, Tianjin, China, November 1-4, 1988; 10.2118/17625-MS.
(5) Dimitriou, C. J. *The Rheological Complexity of Waxy Crude Oils: Yielding, Thixotropy and Shear Heterogeneities*, Ph.D. Thesis, Massachusetts Institute of Technology, 2008.
(6) Venkatesan, R.; Östlund, J. A.; Chawla, H.; Wattana, P.; Nydén, M.; Fogler, H. S. *Energy Fuels* **2003**, *17*, 1630−1640.
(7) Kriz, P.; Andersen, S. I. *Energy Fuels* **2005**, *19*, 948−953.
(8) Oh, K.; Deo, M. *Energy Fuels* **2009**, *23*, 1289−1293.

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Energy Fuels 2018, 32, 6557−6564

(9) Tinsley, J. F.; Jahnke, J. P.; Dettman, H. D.; Prud'home, R. K. *Energy Fuels* **2009**, *23*, 2056−2064.
(10) Tinsley, J. F.; Jahnke, J. P.; Adamson, D. H.; Guo, X.; Amin, D.; Kriegel, R.; Saini, R.; Dettman, H. D.; Prud'home, R. K. *Energy Fuels* **2009**, *23*, 2065−2074.
(11) Lei, Y.; Han, S.; Zhang, J.; Bao, Y.; Yao, Z.; Xu, Y. N. *Energy Fuels* **2014**, *28*, 2314−2321.
(12) García, M. D. C. *Energy Fuels* **2000**, *14*, 1043−1048.
(13) Alcazar-Vara, L. A.; Buenrostro-Gonzalez, E. *Fuel Process. Technol.* **2011**, *92*, 2366−2374.
(14) Alcazar-Vara, L. A.; Buenrostro-Gonzalez, E. *J. Therm. Anal. Calorim.* **2012**, *107*, 1321−1329.
(15) Zhao, Y.; Kumar, L.; Paso, K.; Safieva, J.; Sariman, M. Z. B.; Sjoblom, J. *Energy Fuels* **2012**, *26*, 6323−6331.
(16) Molina V., D.; Ariza Leon, E.; Chaves-Guerrero, A. *Energy Fuels* **2017**, *31*, 8997−9005.
(17) Molina V., D.; Ariza, E.; Poveda, J. C. *Energy Fuels* **2017**, *31*, 133−139.
(18) Andrade, D. E. V.; da Cruz, A. C. B.; Franco, A. T.; Negrão, C. O. R. *Rheol. Acta* **2015**, *54*, 149−157.
(19) Qian, K.; Edwards, K.; Siskin, M.; Olmstead, W.; Mennito, A.; Dechert, G.; Hoosain, N. *Energy Fuels* **2007**, *21*, 1042−1047.
(20) Speight, J. G. *Petroleum Chemistry and Refining*; Taylor and Francis: Washington, DC, 1998; pp 103−120.
(21) Poveda, J.; Molina, D. J. *J. Pet. Sci. Eng.* **2012**, *84*−*85*, 1−7.
(22) Luo, P.; Gu, Y. *Fuel* **2007**, *86*, 1069−1078.
(23) Alcazar-Vara, L. A.; Garcia-Martinez, J. A.; Buenrostro-Gonzalez, E. *Fuel* **2012**, *93*, 200−212.
(24) Barnes, H. A. *A Handbook of Elementary Rheology*; University of Wales Institute of Non-Newtonian Fluid Mechanics: Cardiff, 2000.

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