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Assessment of Asphaltene Stability in Crude Oils Using Conventional Techniques

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Fundamental physicochemical factors involved in asphaltene precipitation under ambient conditions are studied in an effort to correlate them with the precipitation behavior observed in the oilfields. Asphaltene stabilization was evaluated by flocculation onset determination in titration experiments. The reversibility of asphaltene precipitation at ambient conditions was also explored with the proposed titration technique. It was found that the flocculation onsets of recombined long distillation residua are usually lower than the ones of the original samples. This finding suggests an irreversible nature of the process; this irreversibility is particularly observed for crude oils deemed stable from their field production records. Physicochemical characterization of crude oil hydrocarbon group-types was carried out and their influence on asphaltene stability was evaluated. Stable crude oils are characterized by possessing asphaltenes with lower density and lower aromaticity, compared with asphaltenes from unstable crude oils. Their resins show a higher stabilizing activity than the ones from unstable crude oils, and their maltenes also exhibit higher asphaltene stabilization effectiveness. Flocculation onsets of stable crude oils are higher than the flocculation onsets of unstable oils, at the same asphaltene content in the sample to be titrated. On the basis of this finding, a simple method is proposed for the evaluation of the possible risk of asphaltene precipitation in the oilfields.

Introduction

The addition of *n*-heptane or other alkanes to crude oils originates the selective precipitation of the most aromatic and highest molecular weight compounds present in the crude oils.[1] The crude oil fraction that precipitates under such conditions is known as asphaltenes, being a complex mixture of a wide array of different molecular types.[2] This fraction is well-known for its tendency to precipitate during production and refining operations, causing significant losses to the oil industry every year.[3–5] For this reason, prevention or minimization of asphaltene precipitation is a major goal for many oil corporations. However, despite the great research effort carried out over many years, the main causes of asphaltene deposition have not been completely unveiled.

It is currently accepted that crude oils are colloidal systems. In such systems, asphaltenes, together with resins, compose the disperse phase, while maltenes are the continuous phase.[6] Then, asphaltene precipitation depends on the colloidal stability of these complex systems.[7] Among the causes that originate this phenomenon, it has been found that composition plays a major role.[8–10] In particular, the characteristics of the disperse phase[8] and the peptizing power of the resins[10,11] are considered fundamental factors for the stabilization of asphaltenes in crude oil. Recent studies have also emphasized the importance of the nature of asphaltenes in determining the relative stability of crude oils and related materials.[12–16]

During field production operations, asphaltene precipitation is induced when pressure drops close to the bubble point value.[17] However, under laboratory conditions, the asphaltene precipitation tendency is usually

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(1) Mullins, O. C. *Anal. Chem.* **1990**, *62*, 508.
(2) Bestougeff, M. A.; Byramjee, R. J. In *Chemical Constitution of Asphaltenes, Asphaltenes and Asphalts*; Yen T. F., Chilingarian G. V., Eds.; Elsevier: The Netherlands, 1994.
(3) Leontariris, K. J. *Oil Gas J.* **1998**, *Sept. 01*, 122.
(4) Taylor, S. E. *Fuel* **1992**, *71*, 1338.
(5) Galoppini, M.; Tambini, M. *SPE European Production Operations Conference and Exhibition*, Aberdeen, U.K., 1994, SPE 27622.
(6) Andersen, S. I.; Birdi, K. S. J. *J. Colloid Interface Sci.* **1991**, *142*, 497.
(7) Laux, H.; Rahimian, I.; Butz, T. *Fuel Process. Technol.* **1997**, *53*, 69.
(8) Hatke, von A.; Rahimian, I.; Neumann, H. J. *Erdöel Erdgas Kohle* **1993**, *109*, 73.
(9) Loeber, L.; Muller, G.; Morel, J.; Sutton, O. *Fuel* **1998**, *77*, 1443.
(10) Taylor, S. E. *Fuel* **1998**, *77*, 821.
(11) Koots, J. A.; Speight, J. G. *Fuel* **1975**, *54*, 179.
(12) Wiehe, I. A.; Liang, K. S. *Fluid Phase Equilib.* **1996**, *117*, 201.
(13) Buckley, J. S. *Fuel Sci. Technol. Int.* **1996**, *14*, 55.
(14) Carbognani, L.; Orea, M.; Fonseca, M. *Energy Fuels* **1999**, *13*, 351.
(15) Carbognani, L.; Espidel, J.; Izquierdo, A. In *Asphaltene and Asphalts, 2. Developments in Petroleum Science*; Yen, T. F., Chilingarian, G. V., Eds.; Elsevier: The Netherlands, 2000.
(16) Rogel, E.; León, O.; Espidel, J.; González, J. *SPE Production Facilities*, May 2001, SPE72050.
(17) De Boer, R. B.; Leerlooyer, K.; Eigner, M. R. P.; Van Bergen, A. R. D. *1992 SPE European Conference*, Cannes, France, 1992, SPE 24987.

measured using titration techniques by adding a non-solvent. Tests carry out at high pressure and temperature are expensive, time consuming, and nonroutinely used. In titration experiments, the incipient precipitation or flocculation onset is usually caused by adding *n*-heptane or *n*-pentane to the sample.[18−21] Titration techniques applied to dead oils proved to be useful for the selection of asphaltene precipitation inhibitors to be used in field operations.[18,22−26] Even though their use is widespread, it is not clear which is the relationship between the results obtained using these methods and the asphaltene precipitation behavior observed in the oilfield. In an earlier study, a relationship between the change in pressure and the change in volume fraction of *n*-heptane was reported based on thermodynamic characteristics of the crude oil.[17] However, this relationship is specific for each crude oil and depends on the evaluation of its thermodynamic characteristics at high pressure and temperature. Therefore, it is highly desirable to find a direct correlation that does not require live crude oil samples.

The main goal of the present work is to contribute to the understanding of the key chemical factors that affect the asphaltene precipitation. To this end, studied samples include crude oils that have shown operational problems because of asphaltene precipitation, as well as some crude oils without asphaltene deposition problems during their production record. First, the effect of the separation procedures on the reversibility of the asphaltene precipitation at ambient conditions is studied and correlated with the crude oil characteristics. Second, flocculation onset measurements by a titration method are used to evaluate the influence of different hydrocarbon group types on asphaltene stabilization. Third, physicochemical characterization of such hydrocarbon types was carried out to test the influence of chemical properties on asphaltene stability. The relationship between these measurements and the precipitation behavior observed at the oil field was explored. Several relationships presented in the literature, as well as some proposed by the authors, were tested to investigate their applicability to the set of the crude oils studied in the present work. As a result, an empirical equation was developed to evaluate possible asphaltene precipitation risks by means of dead crude oil titration.

This work constitutes an effort to systematically evaluate the essential chemical factors involved in the asphaltene precipitation at laboratory conditions and how these factors can be related to the precipitation behavior observed at the oil field.

(18) Bouts, M. N.; Wiersma, R. J.; Muijs, H. M.; Samuel, A. J. *JPT* **1995**, *Sept.*, 782.

(19) Hammami, A.; Chang-Yen, D.; Nighswander, J. A. *Fuel Sci. Technol. Int.* **1995**, *13*, 1167.

(20) Clarke, P. F; Pruden, B. B. *Fuel* **1997**, *76*, 607.

(21) León, O.; Rogel, E.; Urbina, A.; Andújar, A.; Lucas, A. *Langmuir* **1999**, *15*, 7553.

(22) Lambert, D. C. Europe Patent 304,233, 1988.

(23) Garcia, M. C. *2001 SPE International Symposium on Oilfield Chemistry*, Houston, Texas, 2001, SPE 65009.

(24) Thomas, D. C.; Becker, H. L.; Del Real Soria, R. A. *SPE Production Facilities* **1995**, *May*, 119.

(25) Groffe, P.; Volle, J. L.; Ziada, A. *1995 European Formation Damage Conference*, The Hague, Netherlands, 1995, SPE 030128.

(26) Carbognani, L.; Contreras, E.; Guimerans, R.; León, O.; Flores, E.; Moya, S. *2001 SPE International Symposium on Oilfield Chemistry*, Houston, Texas, 2001, SPE64993.

Experimental Methods

Crude Oil Characterization. A total of sixteen crude oils were studied in the present work. Of these, eight were stable crude oils and eight were unstable crude oils. The unstable crude oils have shown operational problems due to asphaltene deposition at the wellbore. On the other hand, stable crude oils have shown no asphaltene deposition problems during all their years of production. These crudes come from the main two Venezuelan production areas, i.e., eastern and western basins. In general, unstable crude oils are medium or light oils produced from very deep reservoirs. The main characteristics of the studied crude oils are presented in Table 1. The relative amounts of naphtha fraction (C13-) and the long distillation residue (C13+) were determined either by gas chromatography simulated distillation[27] or by physical distillation.[28] The later technique provides preparative amounts of both materials for further characterization. The amount of saturated and aromatic hydrocarbons present in the isolated naphtha fraction was determined by gas chromatography following an in-house methodology based on a published report.[29] The SARA composition (saturates, aromatics, resins and asphaltenes) of the C13+ fraction was determined by thin-layer chromatography (TLC-FID) with a Iatroscan flame ionization detector.[30] The total SARA composition of the studied crudes was obtained from the combination of the results just described. The asphaltene contents for the whole crudes were also determined following the IP-143/90 method.[31]

Asphaltenes, Resins, and Oils. The asphaltenes were isolated from crude oils according to the method described in IP143/90.[31] Mixtures of coprecipitated asphaltenes plus resins were obtained as follows (asphaltenes/resins): 30 g of crude oil was mixed with 900 cm³ of *n*-heptane and the mixture was left in a closed flask for 48 h. Then, the mixture asphaltene/resin/*n*-heptane was filtered and the resulting solid was dried in a vacuum oven at 55 °C and 130 mmHg. Remaining oils were recovered in all cases from the filtered solution by distillation carried out in a rotary evaporator, followed by evaporation to dryness inside a vacuum oven kept at the above-mentioned conditions. Fractions workup removes naphtha fractions, providing a preparative method for long residual fractions recovery (C13+ or 220 °C+).

NMR Characterization of Asphaltenes and Asphaltene/Resins. Aromaticity values were determined by means of ¹³C NMR spectroscopy. Asphaltene and asphaltene/resins samples were dissolved in a 1:1 ratio mixture of CD_2Cl_2/CS_2 containing CrACAC relaxation agent to reduce the relaxation times of the sample. All the spectra were obtained on a Brucker ACP 400 spectrometer, operating at a frequency of 100.62 MHz for carbons. Experimental conditions were as follows: (i) relaxation delay: 6 s; (ii) number of scans: 10 000; (iii) 5 μs 90° pulse. An inverse gate decoupling pulse sequence was used to obtain the quantitative NMR spectra. Aromaticity (fa) was calculated as the ratio of the aromatic carbon integral (185.0−91.64 ppm) over the total carbon spectrum integral [(185.0−91.64 ppm) + (46.8−2.0 ppm)].

Density Measurements of Asphaltenes and Asphaltene/Resins. The density of the asphaltenes and asphaltene/resin mixtures was measured using a standard glass pycno-

(27) Standard D-5307-97. Standard Test Method for Determination of Boiling Range Distribution of Crude Petroleum by Gas Chromatography. Annual Book ASTM Standards, 05.03.

(28) Standard D-2892-01. Standard Test Method for Distillation of Crude Petroleum (15-Theoretical Plate Column). Annual Book ASTM Standards, 05.01.

(29) Green, L. E.; Matt, E. Technical paper 100. Hewlett-Packard: Avondale, 1982.

(30) Sol, B.; Romero, E.; Carbognani, L.; Sánchez, V.; Sucre, L. *Revista Técnica de Intevep* **1984**, *4*, 127.

(31) IP-143/90 *IP Standards for Petroleum and its Products;* Institute of Petroleum, London, 1993.

Table 1. Chemical and Physical Properties of Crude Oils

crude oils	fraction[a]	amount (wt %)	API gravity	hydrocarbon SARA group-types[b] (wt %)				asphaltenes[c] (wt %)
				S	A	R	A	
Unstable Crude Oils								
U2	TC	100.0	22.4	43.21	35.30	16.68	4.99	9.7
	C13+	86.0	-	36.90	37.90	19.40	5.80	-
U16	TC	100.0	22.2	45.31	33.29	17.55	3.85	-
	C13+	82.0	-	37.50	36.40	21.40	4.70	
U94	TC	100.0	25.7	49.43	37.62	8.61	4.43	4.7
	C13+	82.0	-	50.20	32.10	11.80	5.60	-
U16L	TC	100.0	26.8	49.68	37.78	9.28	3.34	5.4
	C13+	83.6	-	51.10	36.20	9.70	3.00	-
U91	TC	100.0	22.8	48.61	34.35	11.65	5.38	6.0
	C13+	81.5	-	43.60	35.50	14.30	6.60	-
U98	TC	100.0	25.6	48.83	37.40	9.51	4.26	5.8
	C13+	82.0	-	44.30	38.90	11.60	5.20	-
U100	TC	100.0	25.0	54.54	35.35	8.23	1.87	3.6
	C13+	81.5	-	45.60	34.20	17.00	3.20	-
U103	TC	100.0	26.3	55.41	36.77	6.89	0.94	1.5
	C13+	85.0	- -	51.90	38.90	8.10	1.10	-
Stable Crude Oils								
S4	TC	100.0	27.2	49.41	38.23	10.44	1.92	3.5
	C13+	83.5	-	44.70	40.50	12.50	2.30	-
S29	TC	100.0	18.3	39.62	38.71	16.83	4.93	8.5
	C13+	85.0	-	32.30	42.20	19.80	5.80	-
S27	TC	100.0	24.1	42.94	36.35	12.96	7.74	11.0
	C13+	87.0	-	37.90	38.30	14.90	8.90	-
S24S	TC	100.0	26.1	49.53	41.33	2.54	6.15	1.2
	C13+	82.0	-	44.60	44.80	3.10	7.50	-
S23	TC	100.0	26.7	51.79	29.93	15.83	2.46	3.9
	C13+	82.0	-	47.30	30.40	19.30	3.00	-
S22	TC	100.0	25.1	54.73	30.41	12.78	2.08	4.2
	C13+	77.0	-	47.70	33.00	16.60	2.70	-
S20	TC	100.0	16.3	32.45	41.50	21.12	4.93	5.0
	C13+	88.0	-	26.10	44.30	24.00	5.60	-
S277	TC	100.0	14.0	26.13	45.30	22.57	6.01	-
	C13+	91.0	-	21.10	47.50	24.80	6.60	-

[a] TC: Total crude oil; saturates/aromatics data included for TC were calculated from the combined results of naphthas aromatics content plus the C13+ SARA analysis. [b] SARA by TLC/FID.[30] (Results reported on a $C_{13}+$ (>220 °C basis). [c] IP-143/90.[31]

meter. *n*-Heptane was used as displacing fluid. The pycnometer has a capacity of 10 cm³. The procedure was as follows: 0.50 to 0.55 g of the sample was placed in the pycnometer and weighed to the nearest 0.1 mg. Then 9 to 9.5 cm³ of *n*-heptane was added, and trapped air bubbles are eliminated by ultrasonication. The pycnometer was filled with *n*-heptane and thermostated by immersion in a water bath maintained at 25 °C. The stopper was pressed firmly in place, and the pycnometer was removed, dried, and weighed. The density of the sample was calculated from its mass and the mass of *n*-heptane displaced by the sample. The determinations were found to be accurate to the second decimal figure. Absolute deviations were ±0.02 g/cm³. Details on density measurement and data for other asphaltenes have been published elsehwere.[32,33]

Preparation of Recombined Long Distillation Residua (C13+). On the basis of the original crude oil composition (Table 1), recombined crude oil long distillation residua were prepared. Preparatively isolated oils (>220 °C saturates plus aromatic hydrocarbons) were added to asphaltene/resins obtained previously and the mixture was treated with sonication for 8 h. Closed vessels were employed in order to avoid ambient oxidation.

Flocculation Onset Measurements. In this work, flocculation points were determined for different samples: original crude oils, asphaltenes, asphaltene/resin mixtures, long distillation residua (C13+), and recombined long distillation residua (C13+). Onset typical repeatabilities were ±0.5 mL of *n*-heptane titrant.

The flocculation points for original crude oils were determined by a titration method. *n*-heptane is added at a constant rate (1 cm³/min) to a solution 20% w/vol of the different samples in toluene, under intensive stirring. No differences were observed when the *n*-heptane flowrate varied within the range 0.5−2.0 mL/min. The titration is monitored by means of a Guided Wave NIR spectrophotometer at the wavelength of 768 nm. The flocculation point is defined as the amount of *n*-heptane needed to obtain the maximum of the light intensity, which corresponds to the beginning of aggregation and coagulation of colloids. Comparison of the flocculation points of original crudes and their corresponding straight run long distillation residua (C13+) were performed both under these conditions.

Experiments carried out with straight run long distillation residua (C13+) and/or recombined residua (C13+) were performed on 3% w/vol sample solution in toluene because of serious limitations in the amount of recombined samples. For asphaltenes and asphaltene/resin mixtures, the flocculation onset was determined in toluene solutions prepared mixing 30 mg of sample and enough toluene to reach 10 cm³ of solution. Temperature, stirring speed, and time of sample preparation were the same in all titrations. The titration rate was 1 cm³/min of *n*-heptane for crude oils, asphaltene/maltene mixtures and recombined crude oils. For asphaltenes and mixtures asphaltene/resin, a titration rate of 2 cm³/min was used. In the latter case, it was found that a titration rate of 1 or 2 cm³/min of *n*-heptane produces the same flocculation onset, but better detectability was observed at the highest titration rate. Therefore, for these samples the higher titration rate was selected.

Results and Discussion

The Effect of Separation Procedures on the Reversibility of Asphaltene Precipitation. The reversibility of asphaltene precipitation is a controversial

(32) Carbognani, L. *Energy Fuels* **2001**, *15*, 1013.
(33) Rogel, E.; Carbognani, L. *Energy Fuels* **2003**, *17* (2), 378.
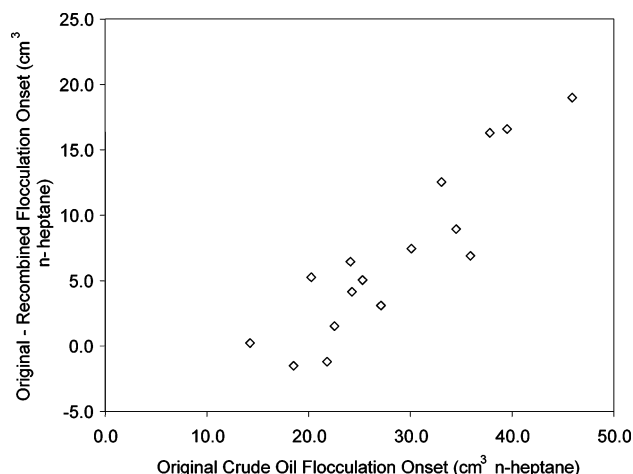
Figure 1. Difference between the flocculation onset of the original crude oil and the flocculation onset of the recombined crude oil as a function of the original crude oil flocculation onset.

matter. Both, the reversibility[34,35] and the irreversibility[36,37] of this phenomenon have been reported for different crude oil samples. Moreover, there is evidence that indicates that the reversibility depends on the precipitation and redissolution conditions.[36] In fact, some results have shown hysteresis between precipitation and dissolution of asphaltenes indicating some irreversibility for the process.[37]

Flocculation onset differences between original and recombined crude oils were investigated. Since the preparative isolation procedures described in the Experimental Section allowed us to obtain long distillation residual components (C13+ or 220 °C+), a first aspect has to be verified, i.e., if titration of whole crudes is equivalent or differs from the titration of long distillation residua. In this work it was verified that, for all the studied cases, flocculation onsets of whole crudes are equivalent to the values for their respective long distillation residua, within the experimental error (±0.5 mL). According to this finding, it seems that in the studied crude oils the C13-fraction does not influence the stability of the asphaltenes measured by the flocculation onset method. It could also be that the relative asphaltene increase in the residue is balanced by a solvent enriched in longer alkanes (less precipitation ability). These results suggest that small changes in SARA distributions do not affect stability to a noticeable degree. In fact, in the following sections, it will be shown that the composition of the crude oils represented by traditional colloidal indexes does not correlate with the stabilities of such crude oils in the oilfield.

Having found the above results, the flocculation onsets for both the original crude and the recombined long distillation residua were compared. Figure 1 shows the difference between the flocculation onset of the original crude oils and the recombined long distillation residua as a function of the flocculation onset of the original crude oil. The magnitude of the differences

shown in Figure 1 reveals that the asphaltene precipitation is generally irreversible at the studied conditions. In other words, the precipitated asphaltenes cannot be reincorporated in the bulk of the maltene phase to reach its original state and for this reason, the flocculation onsets of the recombined long residua are usually lower. This means that the recombined long distillation residua are less stable at ambient conditions that the original crude oils. Among the factors that have been cited as causes of this behavior are the following: chemical changes in the asphaltenes such as oxidation, polymerization and molecular rearrangements;[38,39]and a very slow process of asphaltene redispersion.[24]

However, it seems that these changes do not affect unstable crude oils as much as they affect stable crude oils. In fact, Figure 1 also reveals that the higher the original flocculation onset, the higher is the difference between original crude and recombined long residue stability. In other words, the difference in the onsets is higher for the crude oils that are originally more stable at ambient conditions according to flocculation onset measurements. It is speculated that for crude oils with lower flocculation onsets the cited changes had already occurred in the past and, therefore, the original crude oils exhibit low flocculation onsets that remain practically unaltered by the precipitation, isolation, and redissolution processes.

Physicochemical Factors and the Operational Stability of Crude Oils. The three ensuing sections within the discussion of results will address compositional parameters of oils, asphaltenes, and resins that were observed to influence the operational stability of crude oils.

Crude Oil Composition and Asphaltene Properties. Table 1 shows the SARA composition of the crude oils. Recently, it was reported that one of the main differences between stable and unstable crude lies in the noticeable difference of their saturates and aromatics contents.[15] It is also generally accepted that a high ratio of resins to asphaltenes is indicative of low asphaltene precipitation risk.[11,40]

In the present study, the compositional factors mentioned are examined using different colloidal stability indexes.[9] In a bitumen, the different constituents follow a colloidal law, expressed by[9]

$$CI = (\text{dispersed constituents})/$$
$$(\text{flocculated constituents}) \quad (1)$$

For bitumens, a higher colloidal index means higher stability of the asphaltenes. It is supposed that the dispersion power of the maltenes is reflected by these ratios and, as a consequence, a relationship between the stability of the crude oils and these indexes would be expected.

Figure 2 presents three different colloidal indexes calculated[9] for the studied crude oils and also for their long residues (C13+). These indexes were, respectively,

(34) Buckley, J. S. *5th North American Chemical Congress, Symposium on Chemistry of Asphaltenes*, 1997.

(35) Mohamed, R. S.; Loh, A. C: S.; Delgado, C. C.; Almeida, V. R. *Pet. Sci. Technol.* **1999**, *17*, 877.

(36) Rassamdana, H.; Dabir, B.; Nematy, M.; Farhani, M.; Sahimi, M. *AICHE J.* **1996**, *42*, 10.

(37) Andersen, S. I. *Fuel Sci. Technol. Int.* **1992**, *10*, 1743.

(38) Andersen, S. I.; Stenby, E. H. *Fuel Sci. Technol. Int.* **1996**, *14*, 261.

(39) Carbognani, L.; Espidel, J.; Carbognani, N.; Albujas, L., Rosquete, L.; Parra, L.; Mota, J.; Espidel, A.; Querales, N. *Pet. Sci. Technol.* **2000**, *18*, 671.

(40) Speight, J. G.; Wernick, D. L.; Gould, K. A.; Overfield, R. E.; Rao, B. M. L. *Rev. Inst. Fr. Pet.* **1985**, *40*, 51.
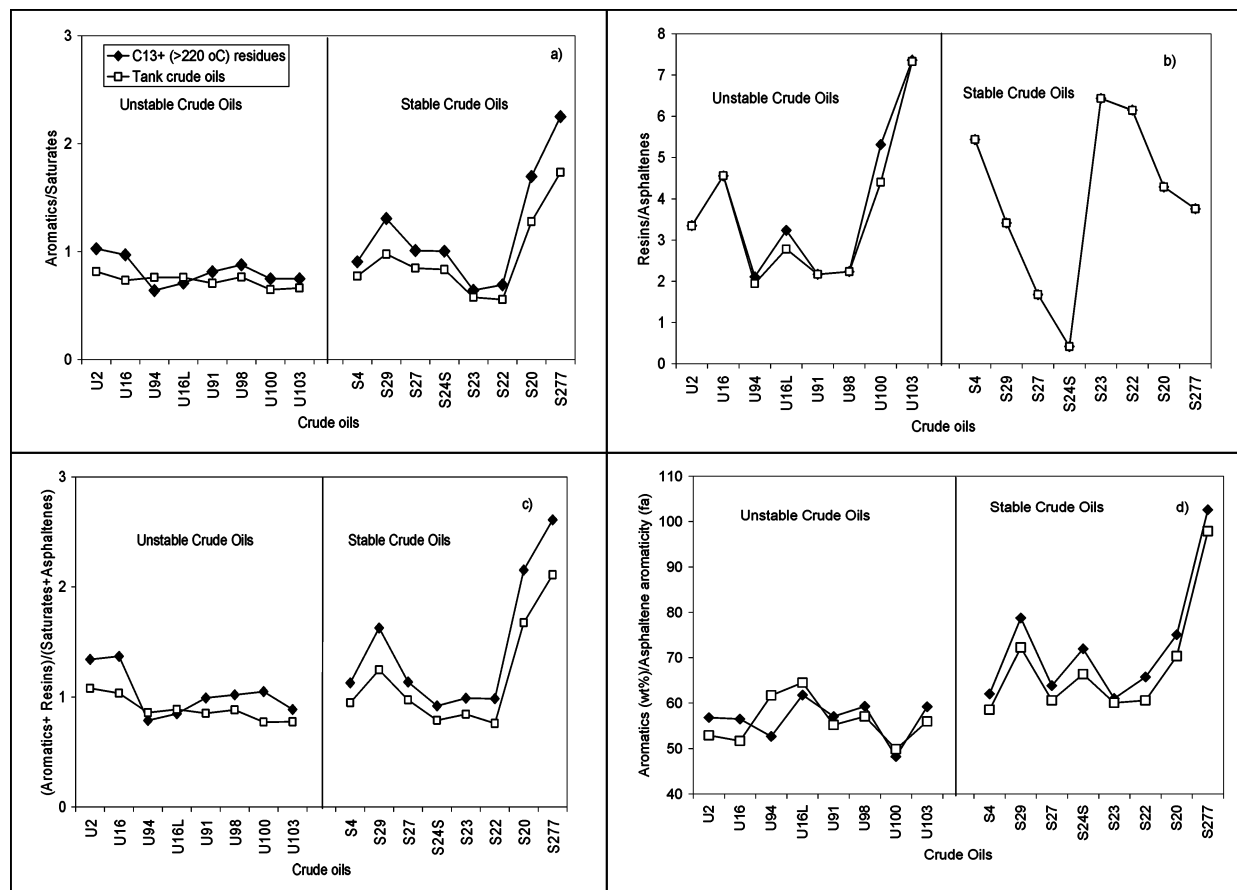
Figure 2. Calculated indexes for the studied crude oils: (a) aromatics/saturates, (b) resins/asphaltenes, and (c) (resins + aromatics)/ (asphaltenes + saturates); (d) wt % aromatics/asphaltene aromaticity. Tie lines were plotted only for better observation of the results.

(a) aromatics/saturates, (b) resins/asphaltenes, and (c) (resins + aromatics)/ (asphaltenes + saturates). According to Figure 2, there is not a clear relationship between composition and stability of the studied crude oils at the oilfield. In fact, contrary to expectations, this figure suggests that a high ratio of dispersed-constituents/ flocculated-constituents is not a key factor in determining the asphaltene stability for the studied crude oils. This finding indicates that other aspects linked to the chemical characteristics of the constituents can also play an important role in asphaltene stability and will be also examined in the next sections.

Recently, a new index has been suggested that incorporates compositional and chemical aspects: solvent properties of the media and molecular characteristics of the asphaltenes.[15] This index is defined as the ratio of the aromatics content of the oil to the aromaticity (fa) of the respective asphaltene. Figure 2d shows the values of these factors plotted for the studied crude oils. As can be seen in this figure, this index works better than the previous ones for grouping stable and unstable crude oils. It is also worth noting that grouping is better observed when the data for the long residua (C13+) were plotted. The separation between stable and unstable crude oils in this figure can be easily explained: low aromatics contents are simultaneously found with high asphaltene aromaticity for unstable crude oils which means that these crudes contain low-soluble asphaltenes in a poor solvent medium. The opposite behavior is observed for the stable ones.

Asphaltene and Resin Properties. According to previous studies,[14-16] chemical characteristics of the asphaltenes play a major role in their stability within crude oils. In particular, it has been found that asphaltenes from unstable crude oils or deposits show higher aromaticity and a lower hydrogen-to-carbon ratio than asphaltenes extracted from stable crude oils.[14-16,32] It has also been reported that the relative interaction energy measured for all fractions from saturates to coke correlates inversely with the H/C ratio and directly with the molecular weight.[12] A high interaction energy corresponds to a low solubility.

Density measurement is the simplest way to estimate the cohesive forces and, therefore, the interaction energies of a particular material. The density is also a measurement of the molecular packing of the solid, and in the case of aromatic compounds, this packing strongly depends on the structural molecular topology of the molecules.[41] For instance, it has been found that the asphaltene density varies linearly with the hydrogen-to-carbon ratio.[42]

In the present study, it was found that the density and the aromaticity increase simultaneously. Asphaltenes from unstable crude oils generally show higher aromaticity and higher density than the asphaltenes from stable crude oils. The less dense and less aromatic samples correspond to asphaltene/resins mixtures.

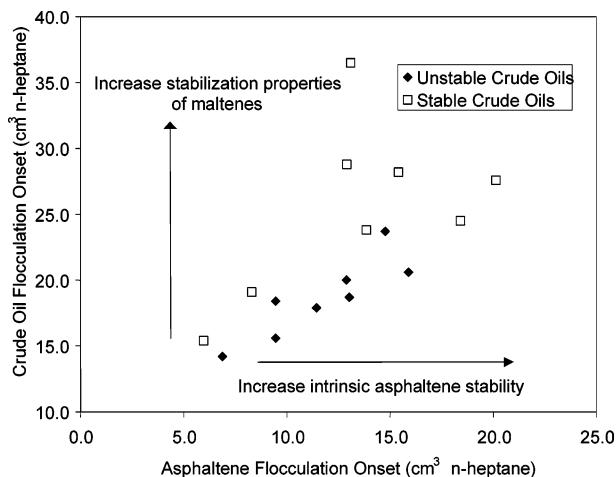(41) Satou, M.,;Nakamura, T.; Hattori, H.; Chiba, T. *Fuel* **2000**, *79*, 1057.

Figure 3. Flocculation onsets of the studied crude oils as a function of the flocculation onsets of the asphaltenes extracted from them.

According to these results, it is possible to suppose that the asphaltenes with higher densities also show the higher cohesive energies and, therefore, the lower solubility in the crude oil, generating unstable crude oils. In fact, it was observed that the measured flocculation onsets for the asphaltenes and asphaltene/resin mixtures grossly decrease as the density of the sample increases. However, the high dispersion found for these data also indicates that other factors such as molecular weight of the material might play important roles in the solubility.[12]

The influence of the intrinsic stability of the asphaltenes on operationally observed stability of crude oils is evaluated in Figure 3. This figure shows the flocculation onsets of the studied crude oils as a function of the flocculation onsets of their isolated asphaltenes. As might be expected, there is a correlation between both measurements. In general terms, the higher the flocculation onset of the asphaltene, the higher is the flocculation onset of the crude oil. Figure 3 also reveals that for the same asphaltene stability, the operationally stable crude oils show higher flocculation onsets than those crude oils classified as unstable. In fact, both kinds of crude oils are separated in different regions in Figure 3. The differences in the flocculation onsets for crude oils containing asphaltenes of the same stability can be attributed to the different asphaltene stabilization properties of the maltenes of these crude oils. Then, Figure 3 can be interpreted in terms of asphaltene stability and stabilization properties of the maltenes. The increase in the crude oil stability along the *x*-axis arises because of the increase in the intrinsic asphaltene stability, while the increase in the crude oil stability along the *y*-axis is a consequence of the increase in the stabilizing properties of the maltenes. These results are important because reveal that the stability of any crude oil has two components: the intrinsic stability of the asphaltenes and the peptizing activity of the maltenes presented in the crude oil. In other words, a crude oil can be unstable because its asphaltenes are highly unstable and/or its maltenes are not good stabilizing agents.

Asphaltene Stabilizer Power of the Resins. The asphaltene stabilizing properties of the resins are very
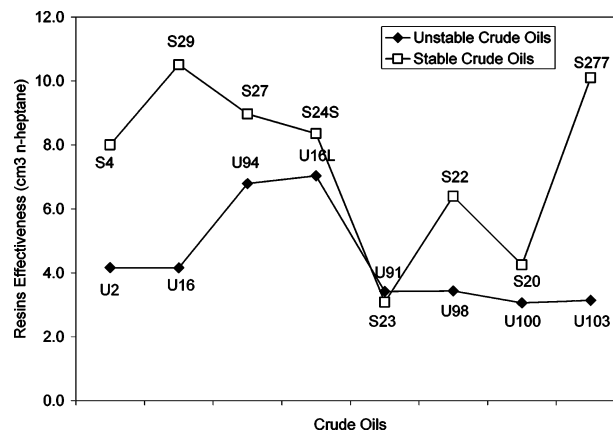

Figure 4. Effectiveness of the resins as asphaltene stabilizing agents. Tie lines were plotted only for better observation of the results.

well-known, although the mechanisms of such behavior continue to be a matter of discussion.[43] In the present paper, the asphaltene stabilizing effectiveness of the resins that coprecipitated with asphaltenes is examined using flocculation onset measurements. The effectiveness is defined as the difference between the flocculation onset of the asphaltene/resin mixtures and the flocculation onset of the corresponding asphaltenes. In the past, this kind of measurement has been successfully used to evaluate the effectiveness of different amphiphiles as asphaltene stabilizers.[16,44−46] Figure 4 shows the comparison of the effectiveness of the resins to stabilize their corresponding asphaltenes (asphaltenes and resins isolated from the same crude oil). Some resins from stable crude oils show higher effectiveness in comparison with the resins from unstable crude oils. However, there is a noticeable overlapping between the results that precludes sound conclusions.

To estimate the relative contribution of the asphaltenes and resins to the stability of the crude oil, a plot of the effectiveness of the resins and the asphaltene stability as a function of the stability of the crude oils is shown in Figure 5. This plot reveals that the effectiveness of the resins to stabilize asphaltenes of the same stability is higher for the resins from stable crude oils in comparison to the resins from unstable crude oils. The decrease in asphaltene stability for stable crude oils was observed to occur simultaneously with the increase of the effectiveness of their resins. This means that stable crude oils contain (a) stable asphaltenes and/or (b) resins with a high effectiveness as stabilizers.

Operational Stability and Flocculation Onset of Crude Oils. Flocculation onset measurements have usually been employed to determine the stability of crude oils at ambient conditions,[16] and also to evaluate the effectiveness of commercial inhibitors of asphaltene precipitation.[18,22−26] However, although this technique is widely used, the relationship between its results (obtained at ambient conditions) and the stability of the

(42) Laux, V. H.; Rahimian, I. *Erdöl Erdgas Kohle* **2000**, *116*, 15.
(43) Andersen, S. I.; Speight, J. G. *Pet. Sci. Technol.* **2001**, *19*, 1.
(44) León, O.; Contreras, E.; Rogel, E. *Colloids Surf. A: Physicochemical and Engineering Aspects* **2001**, *189*, 123.
(45) León, O.; Contreras, E.; Rogel, E.; Dambakli, G.; Acevedo, S.; Espidel, J. *Energy Fuels* **2001**, *15*, 1038.
(46) León, O.; Contreras, E.; Rogel, E.; Dambakli, G.; Acevedo, S.; Carbognani, L.; Espidel, J. *Langmuir* **2002**, *18*, 5106.
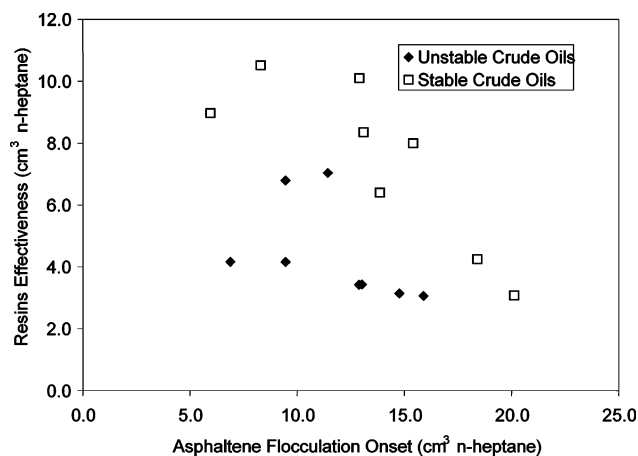
Figure 5. Effectiveness of the resins as a function of the flocculation onset of the asphaltenes.

Figure 6. Measured flocculation onset of the crude oils as a function of the asphaltene content in the solution to be titrated.

crude oil at reservoir conditions (high pressure and high temperature) has not been proven. As a matter of fact, the usefulness of flocculation onset techniques is a subject of controversy.

One of the objectives of the present work is to find a correlation between flocculation onset measurements and operational stability. However, titration results from this work showed that flocculation onsets of crude oils do not directly reflect their stability behavior at oil fields. In spite of the fact that some stable crudes showed larger flocculation onsets, there is a noticeable overlap between them and the unstable ones that invalidated the desired correlation.

Asphaltene contents vary widely for the studied crude oils as can be seen in Table 1. In principle, the asphaltene content does not have any influence on the flocculation onset as has been reported earlier. From the thermodynamic point of view, the beginning of the flocculation depends on the asphaltene solubility and not on its concentration.[47] However, the experimental detection of this phenomenon depends of the sensibility of the employed equipment, and usually this sensibility is a function of the concentration of the solute to be detected. Then, it is possible to expect that a higher content of asphaltenes of the same solubility would be detected earlier.

On the basis of the former assumption, the effect of the asphaltene concentration on the onset measurements was evaluated. The asphaltene content of the crude oil solutions in toluene was calculated using the determined asphaltene content (IP-143/90)[31] and the density of the crude oil at 25 °C calculated from the determined API Gravity (Table 1).[48] Figure 6 shows the flocculation onsets as a function of the asphaltene content on the crude oil solutions in toluene. In this plot, stable and unstable crude oils are grouped in different regions. For the same asphaltene content, the flocculation onset is higher for stable crude oils than for unstable crude oils. This difference can be explained by the variations in asphaltene solubility caused by the compositional parameters discussed in previous sections. On the basis of the fact that stable and unstable
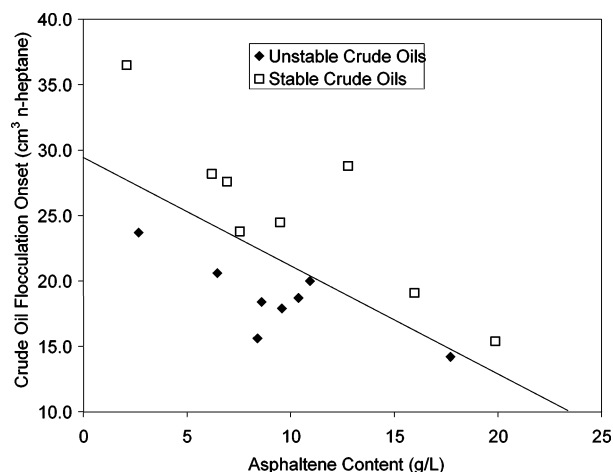
crude oils can be neatly grouped within two sets (Figure 6), it is possible to establish an empirical relationship that allows the prediction of asphaltene precipitation risk in the oil field. The line that separates the two sets in Figure 6 is

$$FL = -0.78 \times A + 29.8 \qquad (2)$$

where FL is the flocculation onset limit of the crude oil obtained by titration of a 20% V/V crude oil solution in toluene and A is the IP-143[31] asphaltene content (g/L) in this solution. If the experimental flocculation onset is lower than FL, the crude oil has a high asphaltene precipitation risk. Experimental flocculation onsets higher than FL mean that the crude oil is stable. Values near to FL should be taken with precaution and,- obviously required a deeper study.

It is important to point out that the above correlation is valid only for the equipment and the conditions used to determine flocculation points in the present work. The use of different experimental settings would require new calibrations with representative crude oil samples in order to obtain a useful correlation. These constraints are imposed by diverse detectabilities achievable by different experimental setups.

Conclusions

The flocculation onset titration technique of dead crude oils is a useful method for predicting the operational stability of crude oils. It was also ascertained to be an ancillary technique for the study of chemical factors that affect asphaltene precipitation.

Stable crude oils have asphaltenes with lower density and lower aromaticity than asphaltenes from unstable crude oils. Their resins show higher activity for stabilization of asphaltenes with the same flocculation onset, compared to resins from unstable crude oils. In general, the maltenes from stable crude oils also exhibit higher asphaltene stabilization effectiveness compared to maltenes from unstable crude oils.

The flocculation onset measurements of recombined long residua reveal that asphaltene precipitation is irreversible for the majority of the studied crude oils. The irreversibility proved to be higher for those crude oils that originally exhibit the higher flocculation onsets.

(47) Cimino, R.; Correra, S., Sacomani, P. A. *1995 SPE International Symposium on Oilfield Chemistry*, San Antonio, Texas, 1995, SPE 28993.

(48) *Petroleum Measurement Tables. Volume Correction Factors*, Volume IV, ASTM D1250-80, ASTM, 1980.

The flocculation onset of stable crude oils is higher than those from unstable crude oils, measured at the same asphaltene content in the sample to be titrated. On the basis of this fact, an empirical equation was found for predicting asphaltene precipitation risks using information extracted from dead crude oil samples.