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Investigation of Asphaltene Stability in the Iranian Crude Oils

A. R. Solaimany Nazar[*], *L. Bayandory*

Chemical Engineering Department, School of Engineering, University of Isfahan, Isfahan, Iran.

Abstract

The influence of different factors on the asphaltene stability in three iranian crude oils was evaluated. Compositional studies and structural characterization of resins and asphaltenes were carried out in order to study a possible relationship between these properties and asphaltene deposition behavior. Low hydrogen to carbon ratios and high aromaticities were the main characteristics of the asphaltenes from more unstable crude oils. According to these results, the stability behavior of asphaltenes was influenced strongly by their structural characteristics. Colloidal stability indexes such as the (aromatic+resins)/(asphaltene+saturates) ratio and (aromatics+resins)/ asphaltene ratio do not play a key role in the asphaltene stability for the studied crude oils.

Keywords: *Asphaltene, Crude oil, Stability, Structural Characterization, Flocculation*

Introduction

Asphaltene is defined as the fraction of a crude oil which is soluble in toluene but insoluble in light saturated oils such as pentane or heptane and comprises the heaviest components of the oil [1]. Asphaltene deposition is a serious problem frequently faced in the oil industry throughout the world and generates a large cost increase [2]. Severe formation damage in the porous media, wellbore and production pipelines plugging, and coking difficulties in refining processes usually arise due to the occurance of this phenomenon [3]. Minimizing asphaltene precipitation is a major goal for many crude oil corporations; however, the main causes of asphaltene deposition are not completely understood at present.

Crude oils are colloidal systems having a disperse phase composed of asphaltenes and resins. The precipitation of asphaltenes depends on the colloidal stability of these complex systems [4]. Among the different factors that influence the stability of crude oils, composition plays a main role. In general, the presence of similar weight percentages of saturates, aromatics, and asphaltenes are considered signs of similar asphaltene stability [5]. It has been pointed out that the nature and content of asphaltenes together with the nature and content of the dispersion medium are the main factors that determine the relative stability of crude oils and related materials [6-7].

In this article two different aspects related to the asphaltene deposition problem were studied, namely, composition of crude oils

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[*] - Corresponding author: E-mail: asolaimany@eng.ui.ac.ir

and the chemical and structural characterization of asphaltene and resins. In particular, interest is focused on the characterization of the asphaltene fraction and its relation to the stability of the crude oil. The aim of this work is to improve the understanding of the relation between the stability of crude oils and their chemical characteristics as a first step towards the development of new tools for the prediction and prevention of asphaltene deposition.

Experimental

Materials

Crude oils: Three dead crude oil samples from three different iranian south reservoirs were used in this study. These samples, which were collected from Ahwaz Bangestan, Maroon, and Mansoori fields, have been labeled oils A through C. Each of the oils is unstable with precipitation problems. The obtained crudes were stored in the dark, in air. The chemically pure grade toluene and n-heptane were used as the solvent and precipitant for all samples respectively.

Preparation and characterization of asphaltenes

Asphaltene samples were extracted from each oil sample according to the most common and widely used method described in IP143/90 or ASTM D3272-90[8].

Measurements

Crude oils characterizations

Crude oils from different sources exhibit a wide range of physical and chemical properties. To predict the behavior of any crude oil with regard to, for instance, emulsion stability knowledge of these properties is of utmost important. In the following section some of the main characterizing techniques used in this paper are described.

SARA Separation

Traditionally chromatographic techniques have been extensively used for hydrocarbon group type determination like, for instance the SARA separation. To establish the relationship between the composition and the stability behavior of the crude oils, the main constituents of the crude oils, saturates, aromatics, resins and asphaltenes were determined following the procedure that had already been used by Carbognani [9]. Resins were obtained through chromatographic fractionation of the deasphalted oil. Silica was used as a packing material, and the different fractions were sequentially eluted with hexane (saturates), toluene (aromatics) and a 10% methanol/toluene mixture (resins). Solvents were removed by distillation and resins were further dried under vacuum.

X-ray diffraction

The X-ray diffraction measurements are made on finely ground powders of extracted asphaltene samples with a Philips Xpert-MPD automated diffractometer, using the K_α(=1.54 $^\circ$A) wavelength. The sample measured was in neat phase with the diffraction angle range scanned from 2° to 100°. The X-ray patterns for three samples appear in Figure 1. Structural parameters, such as simple aromaticity of asphaltene, are calculated from the X-ray diffraction measurements of these oils. The aromaticity f_a was determined by calculating the areas A of the peaks for the γ and the grapheme bands using the following formula reported in the literature [10-11]:

$$f_a = \frac{C_A}{C_A + C_S} = \frac{A_{graphene}}{A_{graphene} + A_\gamma}$$

where C_A and C_S are the number of saturated and aromatic carbon atoms per structural unit. For more details, see references [10-12].

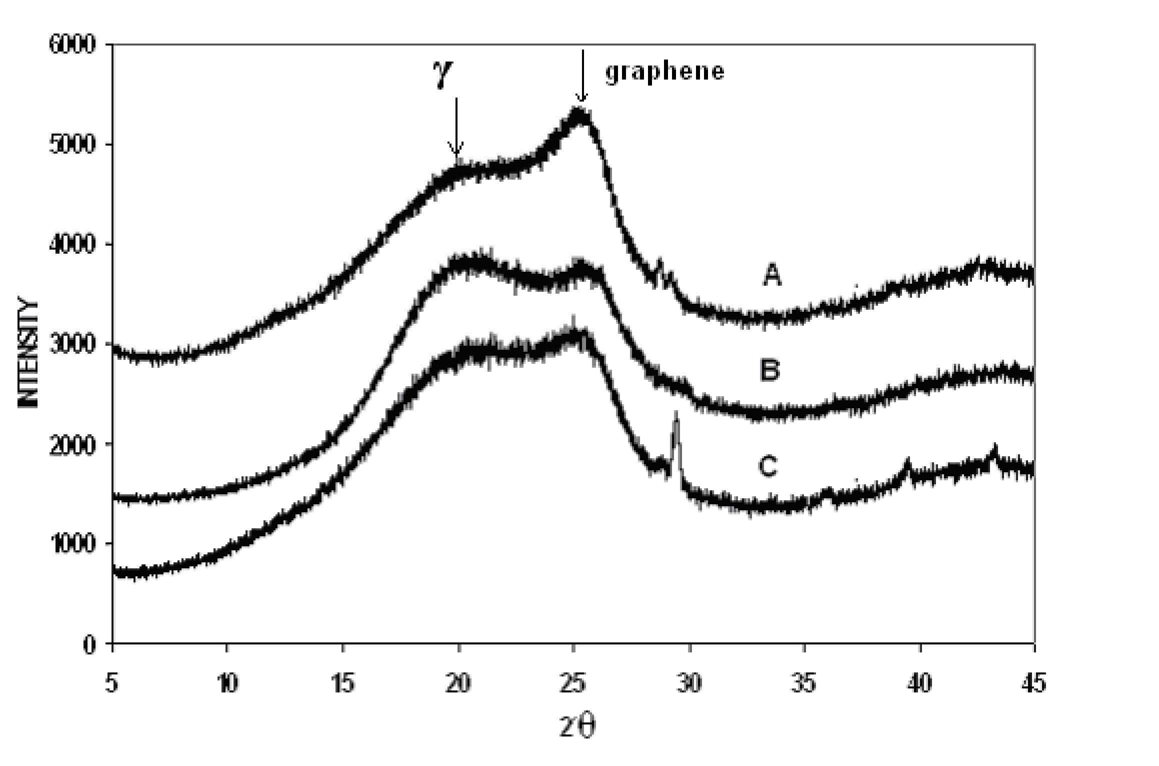

Figure 1. X-ray diffraction pattern of three Iranian crude asphaltenes.

Elemental composition analysis

The elemental composition of asphaltenes and resins was determined using a CHL-O-Rapid Model of Foss Heraes elemental analyser, ASTM D5292 standard [13].

Spot test

Spot measurements were determined with ASTM D4740-95 [14] on three samples of crude oils. The spot test is a useful and simple method for the initial identification of stable crude oil.

Flocculation onset

A number of methods are used to estimate the point at which asphaltene flocculation or precipitation starts. A useful way to evaluate the relative stability of crude oils is to determine the incipient precipitation or flocculation onset by adding a precipitant [15]. Asphaltene contain condensed aromatic systems carrying alkyl, cycloalkyl and heteroatom constituents [16-17]. The aliphatic portions are soluble in aliphatic solvent such as n-heptane, but polar portions are insoluble in this solvent. However, the titration with this solvent is applied to identify the onset flocculation point of asphaltene.

In this work, the flocculation points of crude oils were evaluated by a titration method with n-heptane. The optical absorption of solutions of crude oil / n-heptane samples in the near-ultraviolet range has been measured in a V-570 model of Jasco spectrophotometer. The flocculation point is defined as the amount of n-heptane needed to obtain the maximum light intensity corresponding to the beginning of aggregation and coagulation of the asphaltenes. A wavelength of 1600 nm was considered to determinate the flocculation point. The sample cuvets had a path length of 5 mm. The studied ranges of the n-heptane volume in the crude oil weight ratios were from 0.01 to 1.5 cm^3/gr

(~20 samples). Temperature and stirring speed during sample preparation were the same in all titrations. The optical absorption measurements were started 30 min after preparation of all solutions (10 samples) during a day. The 1200 to 1800 nm near infrared (NIR) spectrum was scanned for each solution. The measurements were performed from dilute to concentrate solutions. In the initial stages of titration, the optical density of the mixture decreases as the heptane is added due to the dilution of the mixture. The power of transmitted light goes up until the onset of asphaltene flocculation, at which point the power of transmitted light begins to go down. This technique is used to measure the amount of heptane needed to cause the onset of flocculation. A stable crude oil requires more heptane and vice versa.

Stability indexes

The characteristics of crude and its corresponding asphaltene and resin fraction were used to introduce several different stability indexes such as (aromatic + resins) / asphaltenes and (aromatic + resins)/ (asphaltene + saturates) ratios [5], spot test data, the hydrogen to carbon ratio (*H/C*) value of the asphaltenes, and the asphaltene aromaticity (*fa* parameter) [18]. The ratio of resins plus aromatics to saturates plus asphaltenes and (aromatic+resins)/asphaltene ratio was used as the colloidal stability index for asphalts. It is supposed that the dispersion power of maltenes is reflected by these ratios and, as a consequence, a relationship between the stability of the asphaltenes in the crude oil and these ratios would be expected. The heptane soluble part of crude (i.e., saturates, aromatics, and resins, collectively) is known as maltenes. The aromatic high molecular weight asphaltenes are peptized by maltenes (most likely the resins contained in the maltenes).

The other index is the (Δ (*H/C*))/ (*H/C*) ratio in which Δ (*H/C*) represents the *H/C* ratios difference value between the resin an asphaltene. The aromaticity is the ratio between the numbers of aromatic carbons over the total number of carbons.

Results and discussion

Table 1 shows a summary of the main characteristics of the studied crude oils. The characterization of their resins and n-hexane derived asphaltene are presented in Table 2. Characteristics in these tables include the elemental composition, SARA analysis, API degree of crudes, and the aromaticity of extracted asphaltenes. The aromaticity value is determined by x-ray diffraction, following the Shirokoff et al. analysis procedure [10].

Table 1. Properties of crude oils

Properties	A	B	C
Total Acid Number mgKOH/grSample	0.13	0.10	0.12
Total Base Number mgKOH/grSample	<0.05	<0.05	<0.05
API gravity	23.8	32.3	26.6

Table 2. Properties of crude oils come from SARA test, elemental analysis and X-ray diffraction.

Properties	**A**	**B**	**C**
% wt Asphaltene	17.7	10.4	15.2
% wt Resin	2.4	2.0	3.7
% wt Aromatic	19.7	31.4	7.9
% wt Aliphatic	30.5	33.8	29.6
Asphaltene			
N mass%	0.5	1	1.2
C mass%	82.4	83.6	83.3
H mass%	7.6	7.6	7.8
H/C	1.11	1.09	1.12
Resin			
N mass%	2.6	2.7	2.6
C mass%	82.1	81.7	81.4
H mass%	9.2	9	9.3
H/C	1.34	1.32	1.37
Aromaticity factor (f_a)	0.16	0.2	0.11

The aromaticity values obtained were spanned from 0.11 to 0.2, which indicate relative low aromaticity. The *H/C* values of the asphaltene and resin of all samples are greater than unity. The *H/C* values reveal that the crudes asphaltene and resin fractions are not very aromatic. A high *H/C* ratio indicates the presence of straight-chain compounds, whereas a low H/C ratio is a good indication of the presence of polynuclear aromatic systems. Comparison of the data shows that there is no significant difference between the *H/C* values of each crude asphaltene, and resins as well.

Chemical composition and stability: The stability of the three crude oils was determined by means of the onset flocculation points; the more stable the crude, the larger the volume of n-heptane needed to begin flocculation. According to the flocculation points the stability of the crude tested follows the order: C>A>B.

In Figs. 2 and 3, flocculation onset (cm^3 n-Heptane/gr crude oil) is shown as a function of two stability indexes. As can be seen, the increase in these indexes corresponds to the decrease in the volume of n-heptane added for flocculation onset, and the increase of instability. Therefore in these crude oils, the sample B has a greater stability index deposit in lower volumes of n-heptane. The lower the value of indexes the more stable the crudes are. This is reflected in the higher onset of flocculation (n-heptane volume) and lower stability index. Although crude composition has a considerable effect on asphaltene precipitation, it seems an unexpected relation between the colloidal indexes and the flocculation point. Therefore, the composition of the dispersion medium presented by these ratios does not seem to play a key role in the asphaltene stability for the studied crude oils. This result was also concluded in another investigation [18]. The compositional ratios are not suitable indexes and structural parameters of asphaltenes and resins are a deeper chemical characterization for the good definition of the stability index.

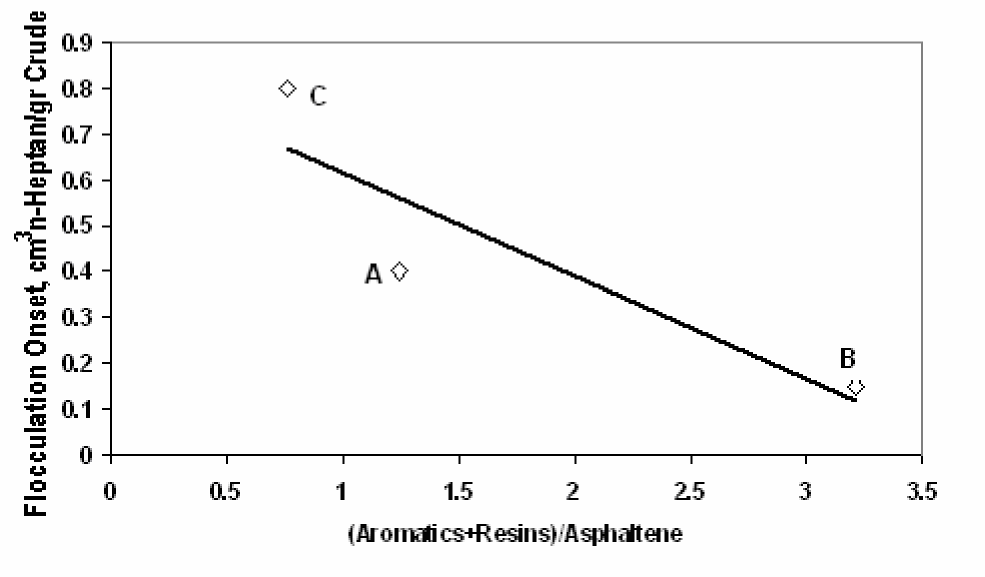

Figure 2. Flocculation onset as a function of stability index (aromatic+resins)/asphaltene.

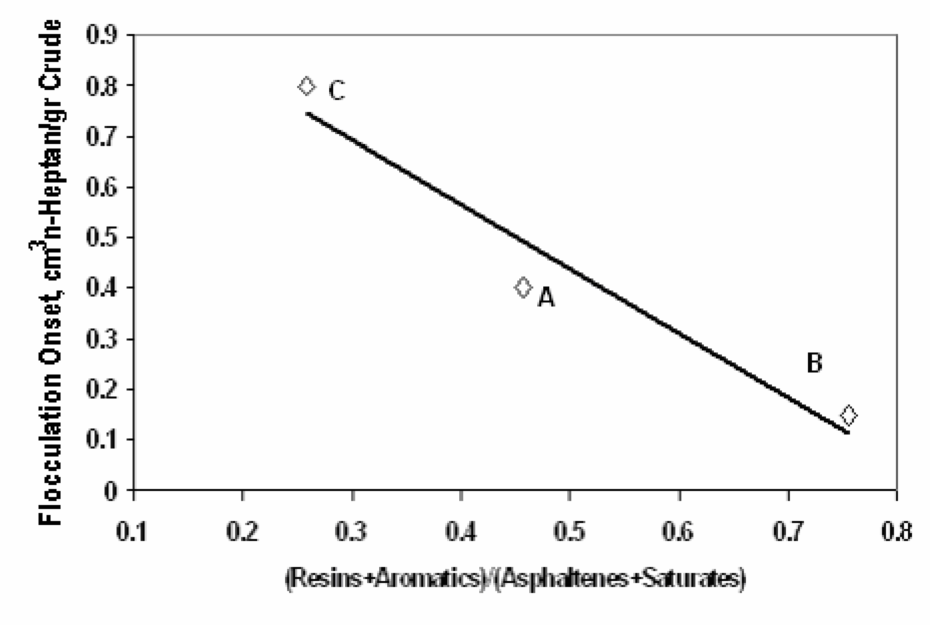

Figure 3. Flocculation onset as a function of stability index (aromatic+resins)/ (asphaltene+saturates).

Figure 4 demonstrates the relation between the onset of flocculation and the instability index. The increase in instability index corresponds to the decrease in the onset of flocculation (n-heptane volume).

In Figure 5 the main structural parameter of the asphaltenes is plotted as a function of instability index. The increase in instability index corresponds to the increase in the aromaticity factor, the decrease in the *H/C* ratio. The f_a parameter is the *CA/C* ratio in which *CA* and *C* are the number of aromatic and total carbon atoms per structural unit of asphaltene [10], and a high *H/C* ratio indicates the presence of long aliphatic straight-chain compounds, whereas a low *H/C* ratio is a good indication of the presence of polynuclear aromatic systems.

Therefore, the oil that has an asphaltene with high f_a or a lower *H/C* ratio is more unstable [11]. Figure 5 depicts how flocculation onset of the crude oils increase with f_a value and decrease with *H/C* ratio. Generally the increase in stability (n-heptane added) corresponds to the increase in *H/C* ratio and decrease in f_a.

Figure 6 relates the (Δ (*H/C*))/ (*H/C*) index to the flocculation onset of crudes. This index defines the difference value between the percentage of straight-aliphatic-chain in resin with regard to asphaltene. The increase of this index causes an increase in flocculation onset. A similar approach has been conducted on four crude oils to estimate those stability indexes [16, 18]. The trends of measurements in this research are confirmed by those results. The crude oils samples that have been used in their research have a relatively different nature in comparison to our samples. As illustrated in Table 2, there is no meaningful relation between the flocculation onset and the API gravity of these oils. That means light oils may have a lower flocculation onset than heavy oils.

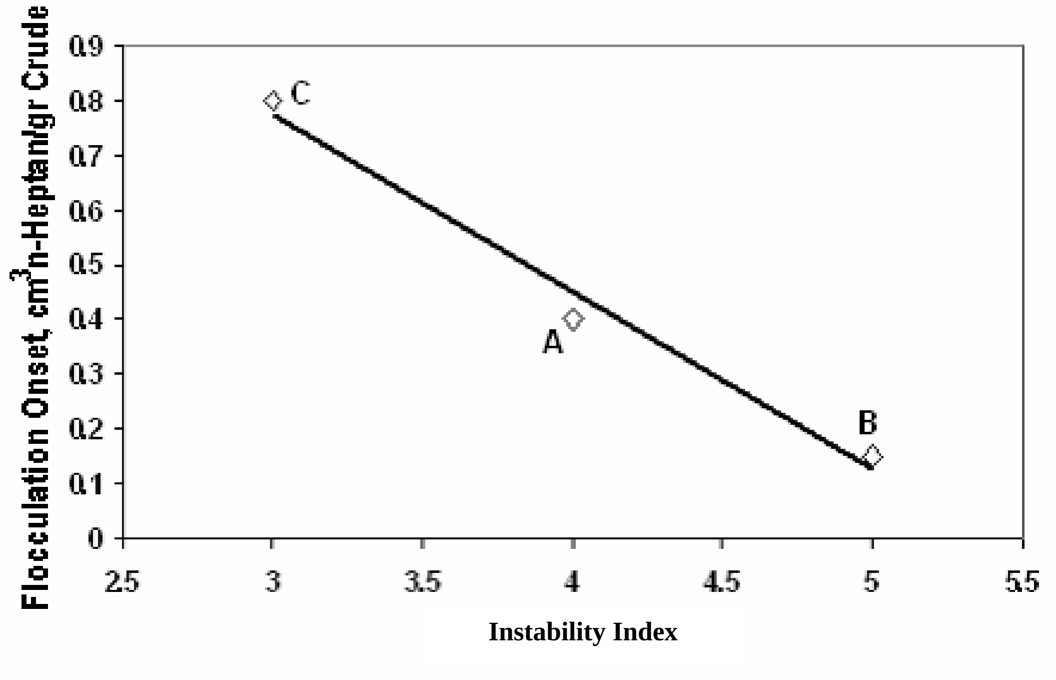

Figure 4. Stability measurements as a function of instability index.

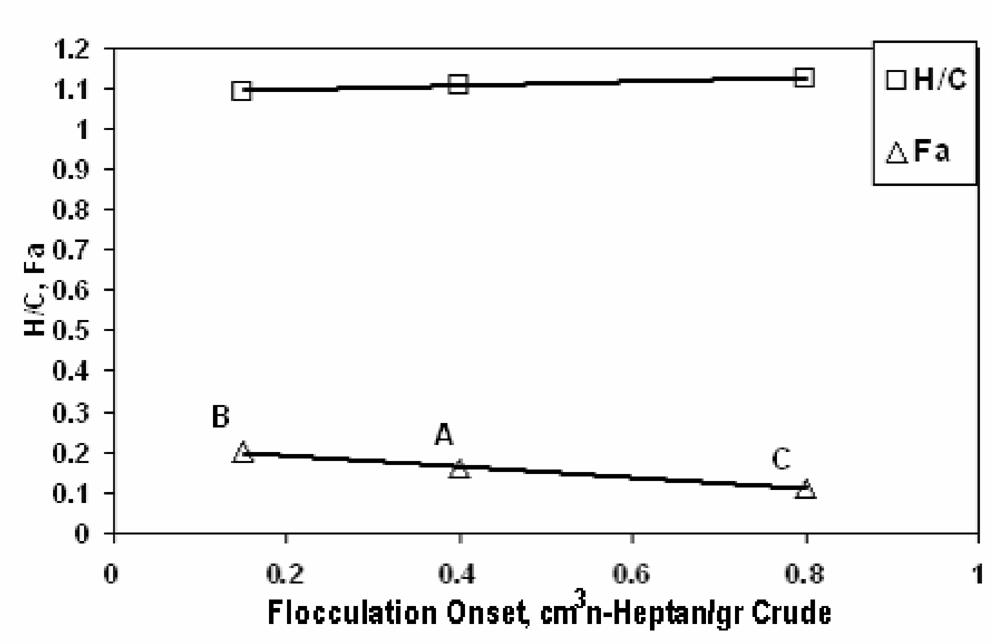

Figure 5. Relation among flocculation onsets of the crude oils and structural parameters of the asphaltenes.

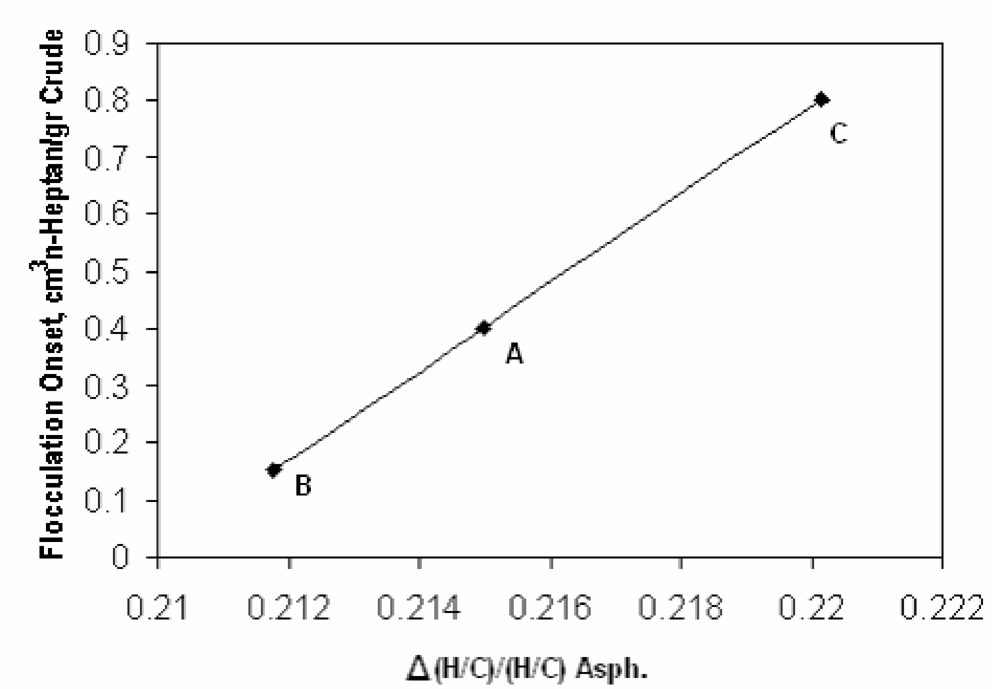

Figure 6. Relation among the flocculation onsets of the crude oils and the (Δ (*H/C*))/ (*H/C*) ratio

Conclusions

The results obtained seem to indicate some degree of compatibility or similarity between resins and asphaltenes from the same crude oil. Crude oil composition is not a key index to estimate the stability of these crude oils. For stable crude oils, asphaltenes and resins have more hydrogen and less aromatic carbons in comparison to asphaltenes and resins from unstable crude oils.

The nature of asphaltenes is one of the most important factors involved in the stability of crude oils. In particular, the structural and compositional characteristics of the asphaltenes strongly influence their deposition problems. Asphaltenes from unstable crude oils are characterized by high aromaticity and low hydrogen content. On the contrary, asphaltenes from stable crude oils show low aromaticity and high hydrogen content. Colloidal stability indexes such ratios of resins plus aromatics to saturates plus asphaltenes, and resins plus aromatics to asphaltenes ratio are not suitable and general stability indexes.

Acknowledgments

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