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Polydispersity of heavy organics in crude oils and their role in oil well fouling

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Abstract

In this report, the polydisperse data of heavy organic fractions of crude oil and solid deposit were produced to investigate the causes of deposition in oil wells. The oilfields of the study have experienced, for several years, shutdowns and decrease in the production ratios due to heavy organics deposition. Several measures such as mechanical cleaning and periodic aromatic washes have been adopted to maintain the production level; nevertheless the costs associated with these procedures are very high.

The SARA method was employed to separate the samples into four distinct fractions, namely Saturates, Aromatics, Resins and Asphaltenes. The total asphaltene content of the crude oil samples was determined using *n*-pentane, *n*-heptane, and *n*-nonane as the precipitating solvents. Polydispersity and molecular weight of each fraction have been further characterized by Gel Permeation Chromatography (GPC). The presence of diamondoids in the solid deposits was also investigated by GC-MS. This technique has been carried out on various crude oil samples collected from an oil field.

The results provided useful information on the interaction between the various heavy organic species responsible for the deposition phenomena. Solid samples from different wells resulted in similar composition concluding that these crude oils undergo similar deposition mechanisms. These studies showed that the crude oils produced from different wells in this oilfield are very similar in nature. The asphaltenes contained in some of the crude oil samples displayed a rather strong tendency to self-associate; they also render the highest amounts of precipitation. While diamondoids and alkyl-substituted diamondoids were confirmed to be present in the crude oils produced no evidence was found of their occurrence in the deposits.

The polydispersity analysis procedure presented here provides a good understanding of the overall behavior of the species that precipitate and also of the interactions among these species. It is concluded that while most of the heavy organics contained in these crude oils may produce precipitates, asphaltene is the major cause of flocculation of the precipitates, which may result in deposition and plugging of oil-producing wells.

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1. Introduction

The recovery of useful products from petroleum has been for several years an increasingly important task that is based on the understanding of the physicochemical properties of the crude oil mixture. During the past several years, extensive research works were devoted to the formulation of models to predict the complex phase

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transitions in petroleum fluids during production and processing (Park and Mansoori, 1988a,b; Pacheco-Sanchez and Mansoori, 1989; Kawawaka et al., 1991; Park et al., 1993; Branco et al., 2001; Hu et al., 2004). Moreover, the potential appearance of solid deposits in wells, pipelines and equipment with unfavorable economic and operational consequences, requires predictive models which could successfully predict the conditions under which solids form. Thus, based on standardized analysis of gas and oil, engineers dealing with these fluids can consider possible actions to prevent or correct solid formation such as altering operating conditions or introducing chemical inhibition.

The need to understand the appearance of solid deposits in crude oils leads us to develop methods of characterization in order to analyze the different types of species, which may form solid particles and their behavior in crude oils.

1.1. Characterization

For petroleum fluids composition and properties vary continuously from the simplest structures to macromolecules. Characterization is a key first step to understand the stability of the crude oil and implement measures to prevent its break up to vapor, liquid and solid (known as deposit). Once the characterization is accomplished and suitable data is generated, by using appropriate molecular, macromolecular and kinetic theories a set of equations that represent the physicochemical properties and behavior of the petroleum fluid to a satisfactory level of accuracy may be developed. The common problem one must face consists then of identification of the discrete components of the crude, the definition of families or fractions of similar components and understanding the nature and role of interactions in between various species.

The complete and detailed characterization of a petroleum fluid is quite difficult, time consuming and expensive. To simplify the procedure, petroleum is considered to be composed of a number of light discrete components and a heavy end. The heavy end is assumed to consist of four major fractions of similar species. At the conditions of the original oil in the reservoir the light and heavy ends are mutually soluble forming one phase so long as certain conditions are maintained in the reservoir. Variations in temperature, pressure or composition may alter this balance and some of the species may segregate and form another liquid or solid phase. Once separated, the complex species may aggregate due to their large size differences, hydrogen bonding or polar groups interactions and form larger particles

named flocs (or supramolecules). Flocs could precipitate out of the mixture as solid deposits which in many cases would plug wells, pipelines and processing equipment. Some of the mechanisms by which these phenomena occur are known (Kawanaka et al., 1989; Mansoori, 1997), but the exact mechanism is still not well understood. It is clear that stability of each species depends upon the nature and amount of the other species in the crude oil. Therefore the characterization of all the constituents of the crude oil may give us an insight into their stabilities and interactions.

The characterization of petroleum into fractions with homogeneous physicochemical properties is primarily made by distillation or simulated distillation through gas chromatography on the basis of volatility (Green et al., 1964). Typically, the PVT laboratory will generate the data for a fluid by depressurization of a bottom-hole or reconstituted oil sample to obtain separate liquid and gas fractions. The gas–oil ratio (GOR) is recorded and the separated fractions are analyzed by gas chromatography (GC) to obtain their compositions. For the separated gas, the components are quite real discrete components of known molecular weights. The GC analysis of the liquid also identifies some discrete components, but most of the heavy-end components cannot be identified by GC analysis alone. Conventionally, the GC analysis is expressed as a series of single carbon number cuts terminating with a C_{n+} fraction that specifies the remainder (Chorn and Mansoori, 1989).

1.2. Heavy fraction analysis

Within the crude oil, the heavy fraction is the most troublesome due to the presence of a large variety of heavy organic compounds. These compounds are generally complex and it is difficult to exactly identify them based on their chemical structures. The characterization of the heavy fraction is then based on the identification of a number of families with certain properties which can be easily distinguishable from each other.

While simulated distillation by gas chromatography is a routine means for characterization of the light end, it is not applicable for heavy-end characterization due to inability of GC for characterization of large molecules. Therefore the methods employed rely on solubility and other chromatographic techniques (Leontaritis and Mansoori, 1989). The SARA procedure (Jewell et al., 1974) modified for characterization of the heavy end as already described by Vazquez and Mansoori (2000) was used to separate a sample into four classes of compounds, namely saturates, aromatic, resins and asphaltenes. The saturate fraction consists of a viscous whitish

translucent liquid mainly composed of paraffins and diamondoids. From the four fractions separated from the heavy-end only the saturates fraction is easily distinguishable and separated from the rest of the oil due to the absence of π -bonds in between saturate hydrocarbon molecules. The aromatic fraction is a viscous reddish liquid composed of aromatic hydrocarbons with various degrees of condensation, alkyl-substitution and heteroatom (i.e. sulfur, oxygen, nitrogen) content forming a continuum with respect to polarity, molecular weight and other properties. The resin fraction is a dark brown colored, thick viscous liquid to semi-solid with a higher degree of condensation and heteroatom content than the aromatics. It plays an important role in asphaltene flocculation (Kawanaka et al., 1989; Mansoori, 1997, 2002; Eliassi et al., 2005). The asphaltene fraction looks like a dark brown to black, amorphous solid. Together with resins, asphaltenes form the most polar and heaviest fraction of the crude oil. Structurally, both, resins and asphaltenes have similar features, but asphaltenes present more complex polymeric structures with a large variety of repeating blocks, which have in common a polycondensed aromatic and naphthenic nucleus with aliphatic, chains attached (Yen, 1974).

As it will be demonstrated in this report all the fractions separated from petroleum generally possess broad distributions of molecular weights which make the heavy organics a highly polydispersed mixture. There is some overlap on the components of these fractions and therefore the distinction among them is rather arbitrarily made on the basis of conditions employed to effect the separation.

2. Sampling and experimental procedure

The heavy fractions characterized in this work were obtained from the following sources:

- i. The crude oil sample from the same well E, referred to as “Crude Oil E”, for which the composition data were available (Table 1). This surface sample was obtained according to the *API-RP 44* procedure for sampling petroleum reservoir fluids. The operating conditions in the separator, where the sampling was performed, were 6.0 bar (gauge pressure) and 335 K. Approximately 2 L of oil at these conditions were stored in stainless steel containers such that the pressure was maintained inside. The containers were flashed at room conditions (1 bar and 300 K) and the remaining oil transferred to non-pressurized metallic containers from which the aliquots for the experiments were withdrawn.

Table 1
Composition of crude oil E

Component	Mol%	Density (g/cm ³)	Molecular weight
Nitrogen	0.386		
Carbon dioxide	1.587		
Hydrogen sulfide	0.602		
Methane	40.448		
Ethane	12.710		
Propane	7.208		
<i>Iso</i> -butane	1.237		
<i>n</i> -Butane	3.323		
<i>Iso</i> -pentane	0.960		
<i>n</i> -Pentane	1.025		
Hexanes	2.653		
Heptanes	3.312	0.7280	97
Octanes	3.010	0.7492	111
Nonanes	2.689	0.7681	124
Decanes	2.427	0.7881	139
Undecanes plus	16.423	0.8918	281
Total	100.000		
C ₇₊ fraction	27.861	0.8516	212

- ii. Two samples of solid material deposited inside two wells identified as *S1* and *S2*, referred to as “Solid S1” and “Solid S2”. The solid samples were black powdery material, brittle to the touch and appeared to be aggregates composed by smaller amorphous particles.

All the samples used in the experiments belonged to the same oilfield of interest.

The modified SARA procedure described by Vazquez and Mansoori (2000) was used for separation of heavy fraction of the samples.

Gel permeation chromatography (GPC) (Leontaritis and Mansoori, 1989) was used to produce molecular weight distribution, the average molecular weight and polydispersity values in every fraction. Each fraction (saturates, aromatics, resins and asphaltenes) was dissolved in THF at a concentration of 0.25% (weight/volume). Care was taken to avoid the contact of the samples with open air during the preparation. All samples were filtered through a 0.45 μ m membrane filter to remove any insoluble material from the solutions. The filtered solutions were injected through the GPC system, consisting of four columns connected in series with a resolution in the range of 100 to 600,000. The mobile phase for the analyses was THF at a flow rate of 1 mL/min. The temperature was set at 30 °C. The eluting fluid was analyzed with an RI and a UV detector at operating wavelength of 254 nm. The data, acquired at a rate of 2.5 points per s, were processed using calibration curves obtained with narrow-dispersity polystyrene standards.

The combined GC-MS technique was used to determine the existence of diamondoids in the solid deposits

Table 2

Composition of the heavy organic fraction of crude oil E obtained by the modified Sara method

Light ends	32.4700
Saturates	44.0217±0.4940
Aromatics	20.5443±0.2214
Resins	1.2817±0.0597
nC ₅ -Asphaltenes	0.5951±0.0030
Toluene-insoluble	0.0208±0.0030
Total recovery	98.9336

analyzed as described by Vazquez and Mansoori (2000). The analysis was carried on the saturates fraction, rather than on the whole sample in order to avoid the interferences posed by aromatic compounds (Wingert, 1992). Solubility data reported for diamondoids suggest that these hydrocarbons will preferentially partition themselves into the low-boiling fraction of any crude oil. The analyses were conducted in a Finnigan GC/MS instrument equipped with a gas chromatograph and capillary injector (Vazquez and Mansoori, 2000). A fused silica capillary column of 100 m length and 0.25 mm ID with a 0.5 μm DB-1 stationary phase (dimethyl-polysiloxane) was used for the analyses. The mass spectrometer generated positive ions by electron impact at 70 eV. The ion source was maintained at 200 °C and EM=1200 was used. Mass spectra were obtained by scanning masses from 50 to 400. The GC oven temperature was programmed as follows: 50 °C for 5 min and then from 50 °C to 250 °C at 2 °C/min, finally the temperature was held at 250 °C for 120 min. For the solids, the analyses were performed in a capillary column with DB-5MS as stationary phase. The temperature was programmed at 50 °C for 5 min and then

Table 3

Sara analysis composition of the heavy organic fraction of a second sample of crude oil E, exposed to air and to natural evaporation

Light ends	26.32±0.52
Saturates	44.2182±2.3812
Aromatics	19.6999±0.5507
Resins	2.1002±0.2767
nC ₅ -Asphaltenes	0.7322±0.0058
Toluene-insoluble	0.0208±0.0030
Total recovery	93.0953

raised to 325 °C at 4 °C/min and maintained for 30 min more. The mass spectrometer injector temperature was maintained at 300 °C and the masses were scanned from 40 to 550. The saturate fraction was dissolved in chloroform at 25,000 ng/μL, then 2 μL of the solution were injected to the system with a split ratio of 10:1. The carrier flow rate was set at 1.2 mL/min.

3. Results and discussion

3.1. Analysis of crude oil samples

The crude oil samples were fractionated by the modified SARA technique as described by Vazquez and Mansoori (2000). The experiment was repeated several times and the average results, reported as wt.%, are presented in Table 2. The results obtained from the fractionation of crude oil E, were compared with those obtained from crude oils of different wells pertaining to the same oilfield as shown in Fig. 1. All crude oils presented slight differences in composition (Fig. 1); this is not surprising considering that petroleum fluids may present variations in their composition according to

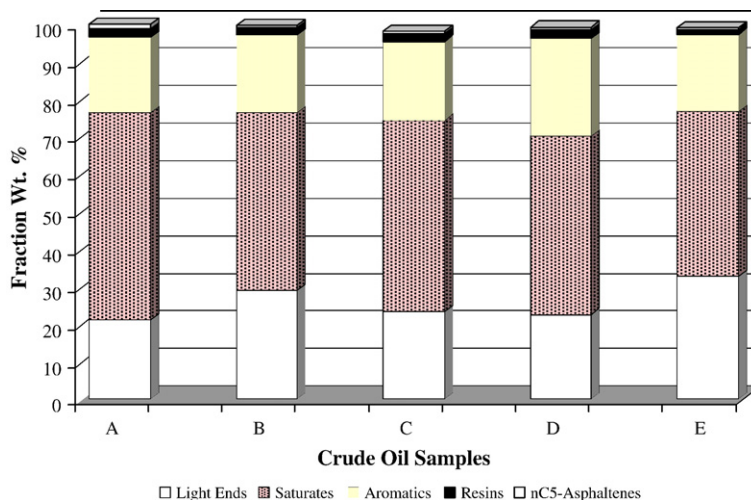


Fig. 1. Schematic composition of crude oils from five different wells fractionated by the modified SARA method.

Table 4
Weight percent of precipitated asphaltenes from five crude oil samples

Crude oil	<i>n</i> -Pentane	<i>n</i> -Heptane	<i>n</i> -Nonane
A	1.0084±0.0062	0.4418±0.0071	0.3233±na
B	0.8041±0.0088	0.3088±0.0079	0.2352±na
C	0.5412±0.0062	0.1119±0.0028	0.0691±na
D	0.7052±0.0127	0.2288±0.0101	0.1423±na
E	0.4584±0.0102	0.1553±0.0011	0.0738±0.0002

The data of this table is the same as Fig. 1 of Vazquez and Mansoori (2000).

location and depth of the well as well as operator errors in sampling. Nevertheless, from an overall comparison the five crude oils seem quite similar in composition. Another important observation is the small amount of resins when compared with the asphaltene content. In general, the mass ratio of asphaltenes to resins in crude oils around the world have been found to be quite small, in the range of 0–0.26. For the crude oil under study here the average ratio was found to be 0.39. Of course heavy oils may have much higher amount of asphaltenes compared with resins. But heavy oil nature and production scheme is quite different from crude oils. Since resins are the main factor by which the asphaltenes could remain dispersed in this crude oil (due to the lack of light aromatics in the crude), the overall compositions appear to be hostile for the stability of asphaltenes in this crude oil.

In order to establish to what extent the differences among the composition of the five crude oils could be attributed to their source or might have been affected by the evaporation of light ends; a second sample of crude oil E, handled in different manner, was characterized.

Whereas the first sample was not allowed to be in contact with air and the container was equipped with a sampling valve so that vapor did not escape when the aliquots were drawn. The second sample was exposed to natural evaporation every time the aliquots were drawn. It was found that the latter procedure yielded significantly different results as is demonstrated in Table 3. Large variations were observed in the resin and asphaltene contents with respect to time. For instance, the *n*C₅-asphaltene content varied from 0.6327% to 0.7587% in a two-month period.

3.1.1. Asphaltene precipitation

The total amount of asphaltenes precipitated from crude oil E with three different paraffinic solvents was also determined (Vazquez and Mansoori, 2000). The values obtained were compared with those of the wellhead samples previously analyzed. The results are reported in Table 4. The data reported in this table is

the same as Fig. 1 of Vazquez and Mansoori (2000). In Table 4 it can be observed that the amounts of asphaltenes precipitated as a function of the solvent used are in agreement with the general trend reported in the literature (Branco et al., 2001; Mousavi-Dehghani et al., 2004). The asphaltene wt.% decreases as the molecular weight of the solvent increases and for solvents with large number of carbon atoms the amount of asphaltenes precipitation does not change significantly. This is due to the fact that the solvent power of a hydrocarbon for asphaltene increases as its molecular weight. However, this is not the complete picture. Another factor that determines the precipitation of asphaltenes from crude oil is the peptizing effect of resin molecules, which prevent asphaltene self-association when present in sufficient concentration.

The solvent power of the medium also affects interactions among asphaltene and resin molecules. When the solvent has a low solvent power, as in the case of light normal paraffins, they dislike both asphaltene and resin. Therefore, for low molecular weight paraffins, the precipitate contains asphaltene and resin; however as the molecular weight of the solvent increases, it becomes a better solvent for resin than for asphaltene. Thus the precipitate is composed mainly of asphaltene. As a result of these two factors one can expect that the amount of precipitate decreases as the molecular weight of the solvent increases. It is also expected that the amount of resin that co-precipitates along with the asphaltene decreases in the same fashion.

3.1.2. Asphaltene molecular weight distributions

It should be pointed out that properties of asphaltenes and resins separated from a crude oil vary according to the solvent used for their deposition (Park and Mansoori, 1988a,b; Branco et al., 2001). This may not be generally the case about the separated aromatics and saturates. There is always some amount of resin which may co-deposit along with asphaltene. It must also be understood that even some higher-MW paraffins (wax) may co-precipitate with asphaltene and resin when lighter *n*-paraffins are used as the depositing agent for asphaltene.

Table 5
Average molecular weights obtained by GPC for the asphaltenes precipitated from crude oil E

Fraction	Average MW	Polydispersity
<i>n</i> C ₅ -Asphaltenes	1277	2.6519
<i>n</i> C ₇ -Asphaltenes	1592	2.7411
<i>n</i> C ₇ -Asphaltenes	1737	2.7116

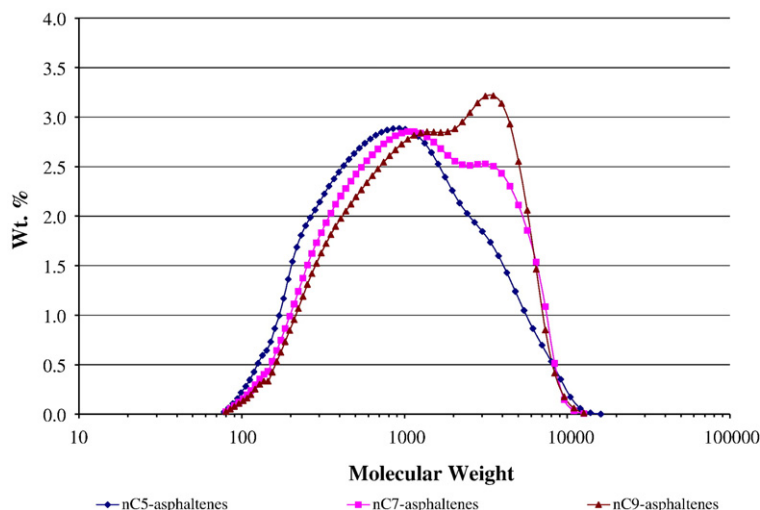


Fig. 2. Molecular weight distributions obtained by GPC for the various asphaltene fractions of crude oil E.

One must bear in mind, that the asphaltene, considered as unit sheets with an aromatic polycyclic center and surrounded by aliphatic radicals, when dissolved in polar or aromatic solvents interact with each other to form micelles consisting of several layers via π - π association or heteroatom coordination (Yen, 1974). These micelles in turn may further associate to form large aggregates (called micelle-coacervates) depending on the solvent polarity, the asphaltene concentration and the temperature (Priyanto et al., 2001a,b). In these interactions the participating monomers are polydisperse in both structure and molecular weight. Hence a uniform micelle is probably non-existent in asphaltene solutions. Therefore, it may be expected that these three

types of asphaltenes will exhibit different MW distributions. As mentioned above, these MW distributions will depend also on the level of inter-molecular interactions among asphaltenes, resins and co-precipitated high MW paraffins.

Table 5 contains the average molecular weights obtained for each of the asphaltene fractions in the crude oil E. According to Table 5 the nC_7 -asphaltenes exhibit higher average MW than the nC_5 -asphaltenes, but smaller than the nC_9 -asphaltenes. The data confirm that the resins, which co-precipitate with asphaltenes when nC_5 is used as the precipitating agent, prevent, to some extent, asphaltene molecules to self-associate into large aggregates. This data is also consistent with the

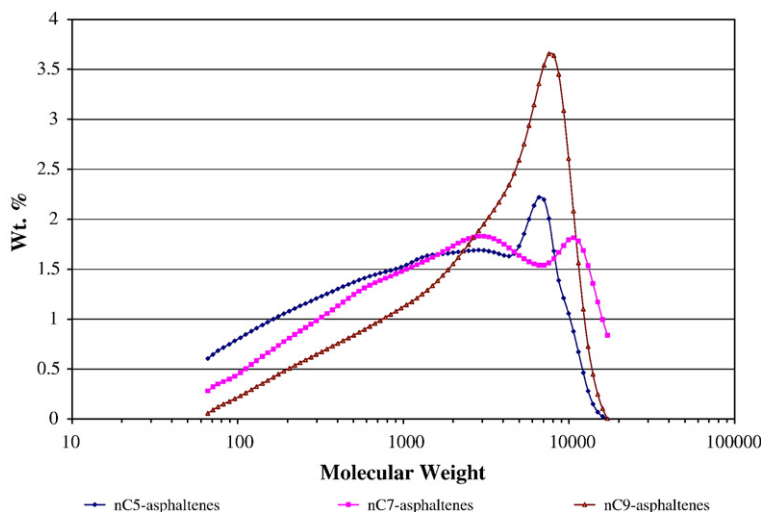


Fig. 3. Molecular weight distributions obtained by GPC for the various asphaltene fractions of crude oil A.

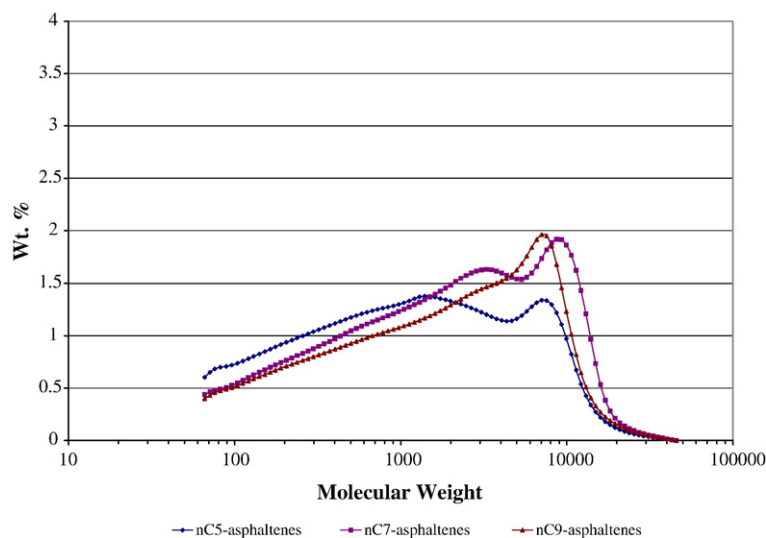


Fig. 4. Molecular weight distributions obtained by GPC for the various asphaltene fractions of crude oil D.

fact that when the resin content is lowered (as in the case of the nC_7 - and nC_9 -asphaltenes), larger aggregates are formed, and therefore, more complex asphaltenes are precipitated.

More important to understand the behavior of asphaltenes is the MW distribution curves obtained for the various asphaltene fractions derived from the crude oils. For instance, in Fig. 2 we have a comparison of these curves for crude oil E. A careful inspection of this figure reveals that all distributions are bimodal, suggesting the existence of at least two different types of species in solution as also discussed by Vazquez and Mansoori (2000). It is also noted that the population of high-molecular-weight species (i.e. the second peak) increases as the number of carbon atoms in the paraffin solvent increases. On the other hand, the population of low-molecular-weight species (i.e. first peak) decreases in the same fashion. This observation suggests that when n -pentane is used, the resins, which co-precipitate, prevent to some extent the self-association of the asphaltenes. On the other hand when the resin content decreases (as in the case of the asphaltenes precipitated with n -nonane) the self-association is promoted to larger extent. The polydispersity of the various asphaltenes reported in Table 5 does not change significantly, but it is observed to increase when the molecular weight of the precipitating solvent increases.

This general trend was observed in the other crude oils characterized and analyzed. It was also observed that the asphaltenes precipitated from the wellhead crude oils are most prone to self-association, as the higher intensity of the second peak and the displacement

of the distributions towards higher values of molecular weight suggest. For instance in Fig. 3 the various asphaltene molecular weight distributions for crude oil A are shown. As it can be seen, the population of the high molecular weight species is markedly large. In fact, this crude oil was found to render the highest amounts of precipitated asphaltenes as it is shown in Table 4. All the asphaltene fractions obtained from the crude oils whose samples were taken at the wellhead, displayed similar behavior (see for example Figs. 3 and 4).

This behavior can be explained, as a result of the equilibrium among the *asphaltenes*, *micelles* and *micelle aggregates* (coacervates) present in the solution (Pacheco-Sanchez and Mansoori, 1998; Vazquez and Mansoori, 2000; Priyanto et al., 2001a,b). The asphaltene molecules constitute the first population depicted in the left side of the distribution with MW of less than 400, the micelles, second population, are clearly distinguished in the first peak between 1000–4000. Finally, the micelle-coacervates, with MW of more than 4000, are depicted in the second peak.

Table 6

Average molecular weights obtained by GPC for the aromatic and resin fractions derived from the crude oils under study

Crude oil	Aromatic fraction	Resin fraction
A	731	1022
B	652	1042
C	669	981
D	799	976
E	288	768

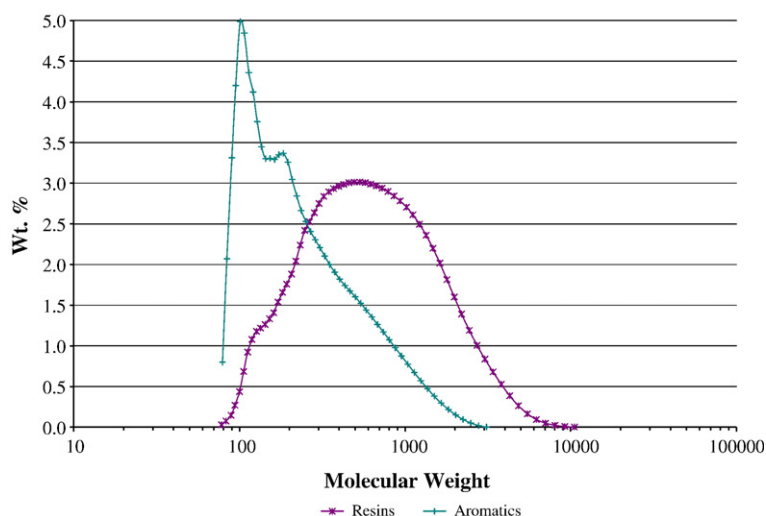


Fig. 5. Molecular weight distributions curves obtained by GPC for the aromatic and resin fractions derived from crude oil E.

In general, determining the molecular weight of asphaltenes is not a straightforward measurement. Several factors such as aggregate formation and the presence of adsorbed resin material on asphaltene leads to discrepancies in the values obtained. For instance a wide range of asphaltene molecular weights (500–50,000) has been reported in the literature (Yen and Chilingarian, 1994).

The tendency of the asphaltenes to self-associate in solution, one of their most characteristic features, makes the determination of molecular weight a difficult task. Several techniques such as vapor pressure osmometry (VPO), mass spectrometry (MS) and gel permeation chromatography (GPC) have been used extensively. Recently, the small-

angle neutron scattering technique (SANS) has been applied to determine the size of asphaltene particles. All methods however, are influenced by the conditions of the analysis (i.e. temperature, asphaltene concentration and solvent polarity) and the overlap of the separated fractions (see for example Roux et al., 2001). In general, no method has proven to give absolute molecular weights. For instance, the VPO technique gives high molecular values, even in good solvents due to molecular association (Yarranton et al., 2000), on the other hand data produced from MS studies are affected by the volatility of the sample and may give low apparent values (see for example Wilhelms et al., 1993).

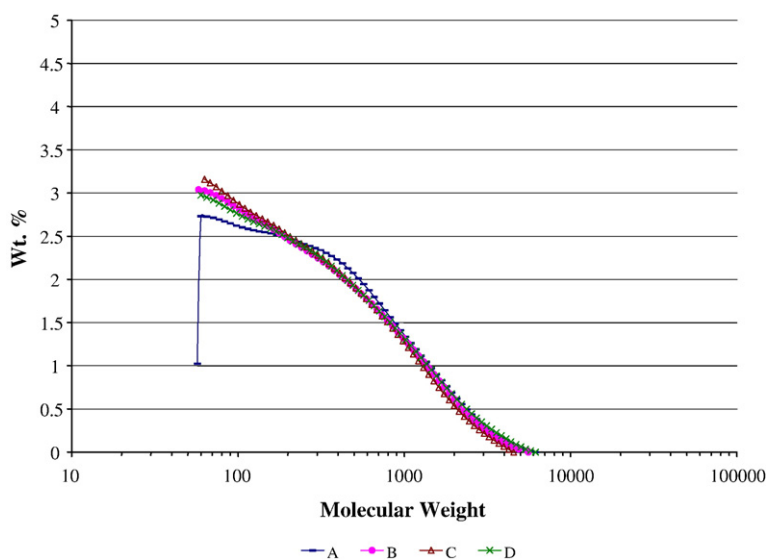


Fig. 6. Molecular weight distributions curves obtained by GPC for the aromatic fractions derived from the wellhead crude oil samples analyzed.

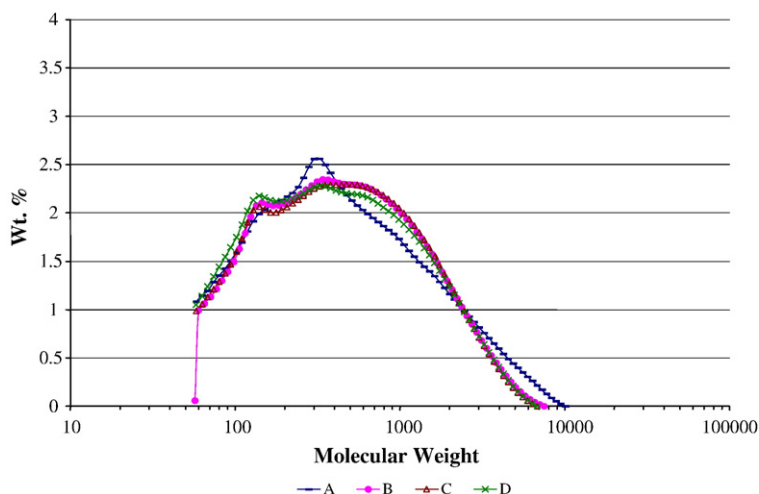


Fig. 7. Molecular weight distributions curves obtained by GPC for the resin fractions derived from the wellhead crude oil samples analyzed.

Gel permeation chromatography (GPC) is the most widely used technique to determine the molecular weight of asphaltenes since in addition to the average parameters, the molecular weight distributions obtained are clear indicatives of the interaction among the several species in solution (Jewell et al., 1974; Leontaritis and Mansoori, 1989; Vazquez and Mansoori, 2000; Ali et al., 2006). It must be understood however that this technique provides molecular weights relative to the standards used for calibration.

3.1.3. Aromatics and resins molecular weight distributions

Table 6 contains a summary of the average molecular weights obtained for the aromatic and resin fractions of all crude oils. As it was expected, the resin fractions exhibit higher molecular weights than the aromatic fractions.

Fig. 5 shows the MW distribution for the aromatic and resins fractions of crude oil E. It can be observed that the resin fraction exhibits not only higher MW values but also a wider distribution. In fact, the shape of the curve is normal indicating that, with respect to size, resins distribute evenly around their mean in the crude oil. It also resembles somehow the nC_5 -asphaltene distribution (reported in Fig. 2), suggesting the structural similarity between these species. In fact several studies have suggested that this similarity is responsible for their affinity to each other in solutions and petroleum (Chang and Fogler, 1994). It should be pointed out that asphaltenes flocculate and grow in size as a result of instabilities in the crude oil but resins do not do so.

Furthermore, the overlapping of all three fractions (asphaltenes, aromatic and resins) denotes that they are

part of a continuous complex mixture in which each fraction is related to general characteristics more than to specific compounds. Similar shapes were found in the MW distributions of the other crude oils analyzed, although the distributions obtained resulted more poly-disperse and were displaced towards higher molecular weights (Figs. 6 and 7). Since these samples correspond to the wellhead crude oils, which experienced free evaporation during sampling and handling, it is believed that not only the asphaltene, but also the resin and aromatic fractions suffer alterations once the stability of the crude oil is disrupted, although they are less pronounced.

3.2. Analysis of solid deposits

The solid deposits S1 and S2 were characterized using the SARA separation technique, the solid S2 was characterized using two different separation schemes (Vazquez and Mansoori, 2000). This set of experiments was performed in order to compare the two solid samples and the differences on the fractions obtained with the two schemes used. The aromatic, resin and asphaltene fractions obtained from both samples were

Table 7
Composition of two solid deposits using the Sara method

	S1	S2
Saturates	43.9049±3.8131	39.3538±1.8739
Aromatics	19.2118±2.6315	27.0760±3.4767
Resins	5.9958±0.1727	4.5769±0.1918
nC_5 -Asphaltenes	53.7467±1.7466	56.3870±0.0229
Toluene-insoluble	7.4433	8.8990
Total recovery	130.30248	136.2926

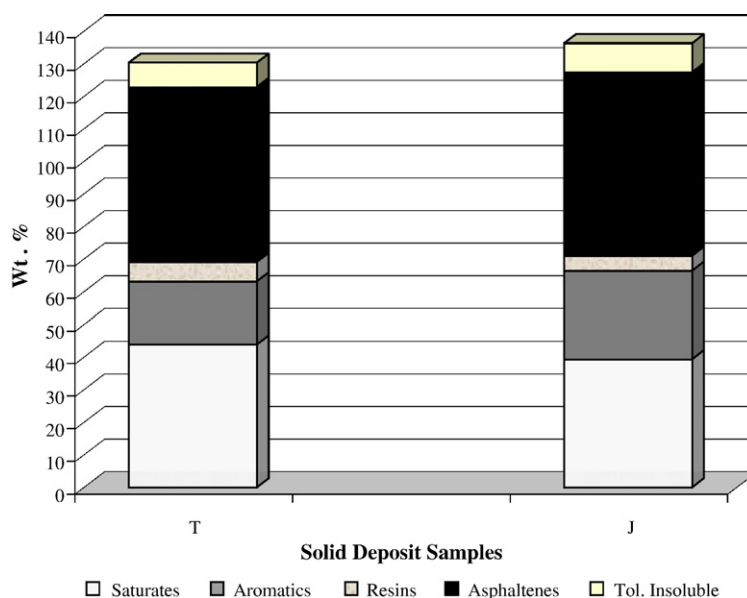


Fig. 8. Schematic composition of the solid deposits collected inside two wells and fractionated by the SARA method.

analyzed by means of GPC. The saturate fractions were analyzed using GC-MS.

The solid deposit samples were pulverized and dissolved in a small quantity of toluene. Upon addition of toluene the solids formed larger aggregates and adhered to the glass surface they came in contact with, only after more toluene was added and under vigorous agitation, the aggregates dissolved in the toluene and formed a homogeneous solution. The adherence to glass surface was also observed when the solid material came in contact with paraffinic solvents.

The SARA separation technique was also used to fractionate the solids dissolved in toluene. After four repetitions of the SARA procedure on each solid sample, an interesting observation was made and that was the weight increase of the original sample of 35% on average. In view of this observation, additional samples were diluted in toluene and then submitted to prolonged evaporation at vacuum conditions (at 25 mm Hg and room temperature) and the samples' weight was monitored. However, the samples' weight did not reduce to their original weight again. It is believed that this weight increase was due to the occlusion of solvent molecules within the asphaltene aggregates. It is known that asphaltene in aromatic and polar solvents form molecular aggregates and above the CMC (critical micelle concentration) the asphaltene molecules will associate to form larger aggregates (micelle coacervates), trapping some of the solvent molecules during evaporation (Pacheco-Sanchez and Mansoori, 1989; Priyanto et al., 2001a,b). Another possibility for the

weight increase could be attributed to the reaction of some species in the solid with the oxygen in the air. However this is rather unlikely since the contact of the samples with air were kept minimum. In any case, it is believed that the combination of several factors (physical and chemical) could be responsible for the weight increase of the samples. The results of the SARA analysis are reported in Table 7 and in Fig. 8. Note from Table 7 that the solid deposits are mainly comprised of asphaltene and saturate (paraffins and diamondoids) compounds. Another important observation to be made is the considerable amount of toluene-insoluble material (assumed to be of inorganic nature) which were not trapped in the filters before SARA analysis of the sample. The appearance of solid deposits during SARA analysis suggests that there is a strong interaction between this toluene-insoluble material and the other heavy organic fractions of the crude.

The hypothesis that some of the constituents of the solid deposit may have undergone physical/chemical transformations during the separation procedure prompted

Table 8
Composition of solid S2 using two separation schemes

	Scheme I	Scheme II
Saturates	28.8745±1.552	13.7752
Aromatics	19.8661±0.5786	17.0128
Resins	3.3581±0.1612	2.7184
<i>n</i> C ₅ -Asphaltenes	41.3720±0.076	56.1899
Toluene-insoluble	6.5293	8.8990
Total recovery	100.0000	98.5950

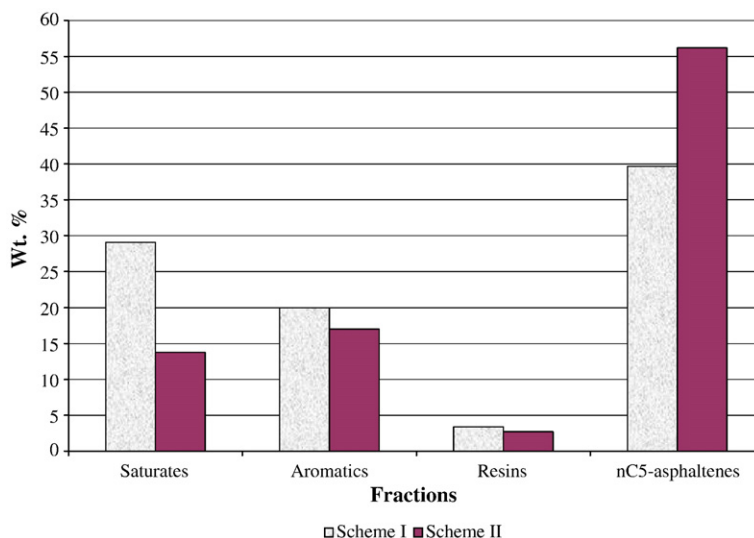


Fig. 9. Schematic composition of solid S2 using two different separation schemes.

a new set of experiments in which the first step of dissolution in toluene was eliminated. Two SARA separations were performed on the solid S2 without prior dissolution in toluene. The average recovery of 98.58% confirmed the assumption that toluene dissolution affects the yields of separation.

The results of SARA separation performed on solid sample S2 are shown in Table 8. For the sake of comparison, the values of the first separation performed on the same solid S2, displayed in the left column, were normalized to 100%. It can be observed that the saturate and asphaltene fractions exhibited dramatic changes in composition according to the scheme of separation employed, the resins were moderately affected and the aromatic fractions experienced minor changes. Furthermore, in Fig. 9 can be seen that the saturate fraction decreases in a similar percentage to the increase in the asphaltene fraction. This suggests that a considerable amount of the paraffinic components (wax) remain trapped within the large solid aggregates of the deposits when the sample is not pre-diluted in toluene, and enforces the idea that these species greatly interact with the asphaltenes during the deposition mechanism.

In addition to the fractionation of the solid deposits with two different procedures, the nC_5 -asphaltene from the second scheme were subsequently precipitated with n -heptane following the same procedure used for the precipitation with n -pentane.

3.2.1. Molecular weights of the fractions

The nC_5 -asphaltene, the aromatic and resin fractions obtained by the SARA method in both schemes, as well

as the nC_7 -asphaltene were analyzed by means of GPC. The fractions dissolved in THF at a concentration of 0.25% (weight/volume) and filtered through a 0.45 μ m membrane were injected to the system. One injection of 75 μ L was made of each solution. The average molecular weights and polydispersity index are summarized in Table 9. The values observed are very similar for the aromatic and resin fractions, thus suggesting that the nature of these fractions is not considerably affected for the scheme of separation used.

Pursuant to the asphaltenes, the higher polydispersity of the nC_5 -asphaltenes from the second separation is supposed to be caused by the presence of major amounts of co-precipitated wax (paraffinic species). However no direct evidence was found of this fact. In the same way, the average molecular weight of the asphaltenes obtained by the second separation resulted slightly higher. It is known that the asphaltenes precipitated with a higher MW n -alkane, will have higher molecular weight values as a result of the decrease in the

Table 9
Average molecular weights for the aromatics, resins and asphaltenes obtained from solid S2

	Scheme I		Scheme II	
	Average MW	Polydispersity	Average MW	Polydispersity
Aromatics	311	1.7464	293	1.4115
Resins	553	1.7112	555	2.0291
nC_5 -Asphaltenes	2299	3.4600	3140	4.5767
nC_7 -Asphaltenes			3425	4.0129

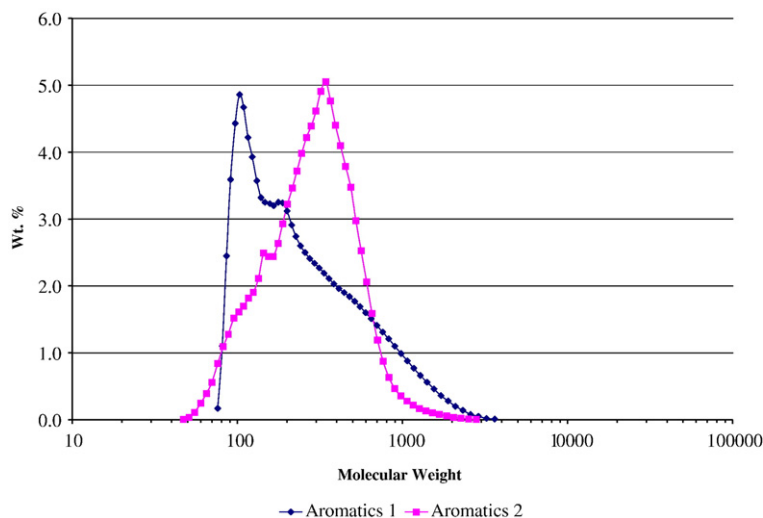


Fig. 10. Molecular weight distributions curves obtained by GPC for the aromatic fractions derived from the solid S2 with two separation procedures.

proportion of resins. Surprisingly, the molecular weight for the nC_7 -asphaltenes did not show big differences when compared with the nC_5 -asphaltenes. This can be explained in terms of the very low concentration of resins present in the solid.

It is also important to analyze the differences in the amount and properties of the asphaltenes precipitated from the solid deposits and the crude oil. Assuming that aggregation effects follow the phenomena of destabilization it would be reasonable to expect in the asphaltenes of the deposits higher amounts of precipitation and higher molecular weights. The results obtained show that this is the case for crude oil E, but not for the

other crude oil samples for which the values resulted on the same order. This observation confirms that these four oil samples were past the onset of deposition as it was suggested by the presence of suspended particles in the crude oil and the broad molecular weight distribution of asphaltenes obtained by GPC.

The molecular weight distributions of the fractions obtained in both separation schemes display some interesting differences. In the case of the aromatics (Fig. 10), the second fraction exhibits a shift in the main peak to large MW values, whereas the shape of the curve is almost symmetric. The polydispersity of this second fraction is also smaller. For the resins (Fig. 11), the

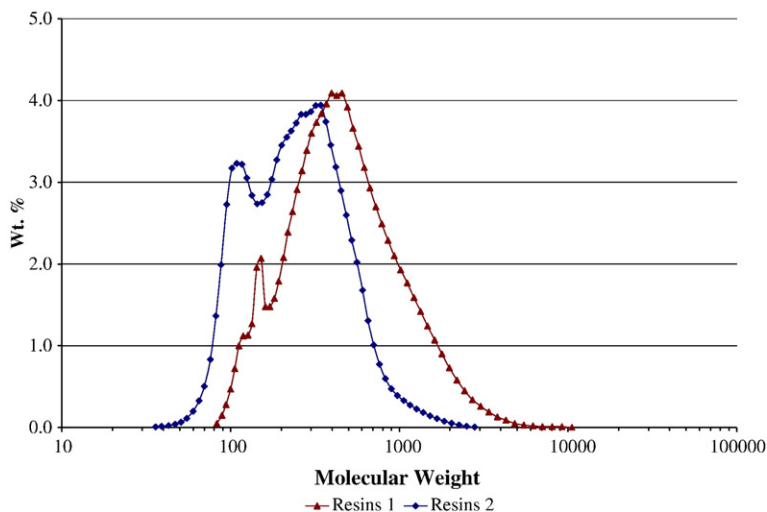


Fig. 11. Molecular weight distributions curves obtained by GPC for the resin fractions derived from the solid S2 with two separation procedures.

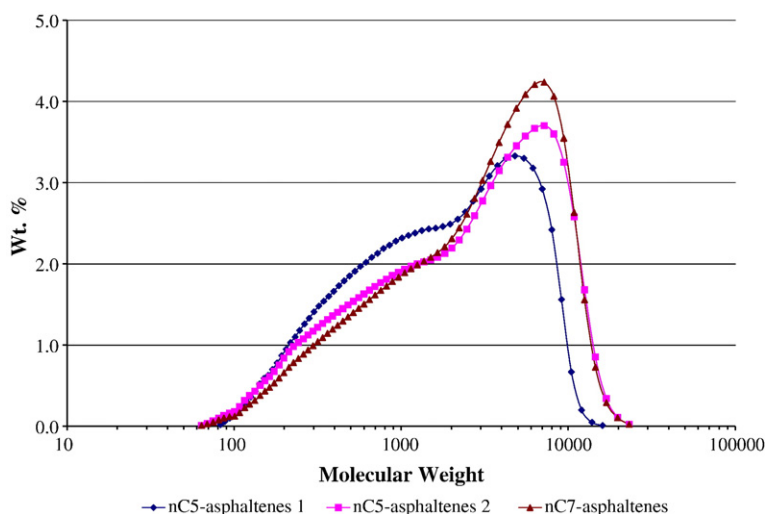


Fig. 12. Molecular weight distributions curves obtained by GPC for the asphaltenes derived from the solid S2 with two separation procedures.

second fraction has a broader distribution with the main peak displaced to higher molecular weights; both curves however, present similar shape.

The asphaltene distributions (Fig. 12), exhibit the same bimodal shape, but displaced to larger molecular weights in the asphaltenes of the second separation. It is interesting to note the similarity in the shape of the nC_5 -asphaltenes and nC_7 -asphaltenes distributions. This, again, seems to be a result of the low amount of resins present in the solid.

The MW distributions of the nC_5 -asphaltenes obtained from the solid samples display a prominent peak displaced to high molecular weights (10,000); this shape resembles the molecular weight distributions obtained for the nC_9 -asphaltenes precipitated from the crude oil samples. This observation seems to indicate that once the equilibrium among the several species in the crude oil is disrupted the asphaltenes may react predominantly among themselves to form larger particles, rather than with the other species present in the crude oil.

The molecular weight distributions for the aromatic and resin fractions of the solid deposit S1 were also obtained by means of GPC. The average molecular weights are summarized in Table 10. The average molecular weights of both fractions resulted much higher

Table 10
Average molecular weights for the aromatic and resin fractions obtained from solid S1

	Average MW	Polydispersity
Aromatics	755	3.7329
Resins	856	3.2893

than those reported for the solid S2, the same can be said about the polydispersity. The molecular weight distributions in Fig. 13 show that the resin distribution is almost symmetric with three distinguishable peaks. In the case of the aromatics, the molecular weight distribution presents a very broad shape tailed to high molecular weights. The shape, similar to the resin distribution and the unusual values measured, as well as the intense overlap of both distributions could be an indicative that the separation was not successful accomplished. It is important to mention that due to the small amounts of this sample (0.75 g) it was not possible to perform more experiments. So far the results obtained could not allow us to conclude whether or not both solids are structurally similar, even though both of them were found similar in composition.

3.2.2. Normal-paraffin distribution

GC-MS analyses were conducted on the saturate fractions of both solid deposits. From these analyses, the overall carbon number distribution of normal paraffins was also determined.

It must be pointed out that the GC-MS data can also help us to determine the existence and amount of diamondoids (adamantane, diamantane, triamantane etc.) in the sample. Although, tria-, tetra-, penta-, and hexamantane could also be present in the solids, it was decided that if adamantane and diamantane were found, then there is a possibility that higher adamantologues are also present in these solids. Adamantane, if present, will elute from the column between nC_{10} and nC_{11} ; diamantane will elute between nC_{15} and nC_{16} ; and triamantane will elute between nC_{19} and nC_{20} .

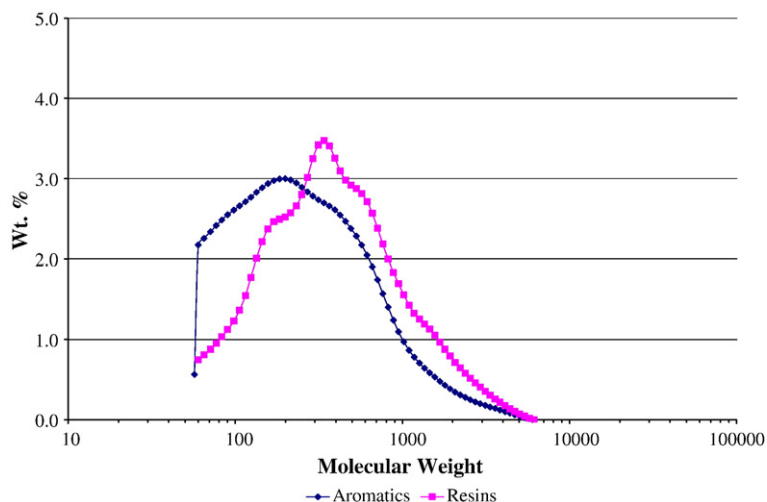


Fig. 13. Molecular weight distributions curves obtained by GPC for the aromatic and resin fractions derived from the solid S1.

In Fig. 14, which corresponds to the solid S1, the first identifiable peak corresponds to nC_{19} , whereas the last identifiable peak resulted to be nC_{29} , that can slightly be distinguished at 63.9 min. behind a large peak of unknown identity. Beyond nC_{29} the intensity becomes very low while the noise increases in such a way that it is not possible to identify those compounds. If higher diamondoids exist in the sample however, they must be in very low quantities. Compared with the chromatogram obtained for the solid S2 it is clear that the solid S1

is comprised by higher molecular weight paraffinic compounds (Fig. 15).

The portion of the total ion chromatogram between nC_{15} and nC_{16} of solid S2 (Fig. 14) was scanned for the existence of diamantane (m/z 188) whose base peak is 188 (M^+). In the same way, the total ion chromatogram in Fig. 15 was scanned for the existence of triamantane. However, the single ion chromatograms obtained did not display significant intensities. No evidence was found of the existence of diamondoids in the solid

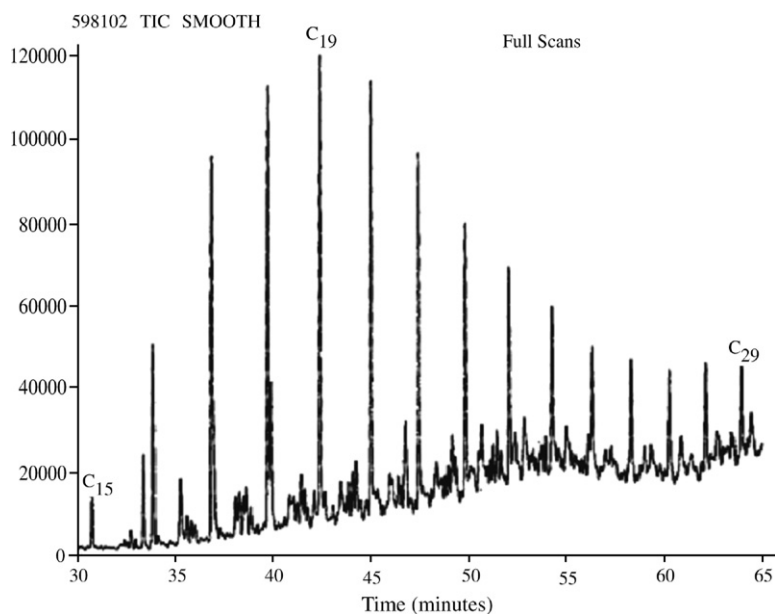


Fig. 14. Total ion chromatogram obtained for the saturate fraction separated from the solid deposit S2.

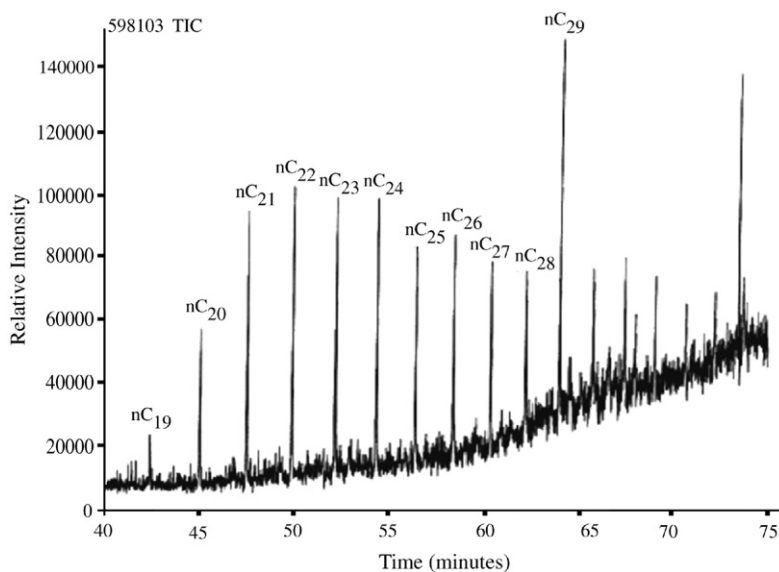


Fig. 15. Total ion chromatogram obtained for the saturate fraction separated from the solid deposit S1.

deposits, therefore suggesting that these species did not exist in the samples.

4. Conclusions

4.1. Crude oils

The analyses conducted on the crude oil samples demonstrated that these oils are very sensitive to the sampling and handling procedures. Given the small ratios of resins to asphaltenes and the large amounts of light material (mostly of paraffinic nature) found in these crude oils, the overall composition appears to be hostile for the stability of asphaltenes in the oil mixture. Therefore upon changes in pressure and temperature the equilibrium between the resins, asphaltenes and the medium is disrupted. The asphaltenes self-associate forming large aggregates which segregate out forming the solid deposits. The presence of suspended solids in all the crude oil samples analyzed, confirmed that they had already initiated the deposition phenomena.

The problem with these kinds of samples is that the characterization may not correspond to the original species as they exist in the crude oil. This is particularly true for the asphaltenes, the GPC analyses shown that whereas the aromatic and resin fractions experienced slight variations in their MW distributions, the asphaltene fractions displayed big differences in all the crude oils analyzed.

It was important to establish whether the differences between the crude oils were originated for the handling procedure or the source itself. The comparison of all the MW distributions denote that the four crude oils handled

in a similar manner, exhibit also very similar shape chromatograms, on the other hand these distributions markedly differ from the crude oil that was handled in a controlled manner (i.e. crude oil E). Since the conditions under which the first crude oil samples were obtained were not controlled, they were considered not reliable nor representative of the true nature of the heavy fractions of the crude oils under study. Nevertheless, from a qualitative point of view the analyses indicate that the crude oils present similar behavior. These studies also revealed that the heavy fractions separated from crude oil E could be considered the most representative of the real nature of these species as they originally exist in the crude oil reservoir.

The results from the GPC studies of the asphaltene fractions demonstrated the tendency of these species to self-associate, as the bimodal shape of the distribution curves indicates. It is also observed that the intensity of these interactions among asphaltenes increases as the amount of resins which co-precipitate decreases.

A relationship among the MW distributions of the asphaltenes and the yields of precipitation was also observed. Those oils whose asphaltene population was displaced towards higher MW values render the highest amounts of precipitated asphaltenes.

4.2. Solid deposits

The composition of the solid deposits suggests a strong interaction between the asphaltenes, paraffins and inorganic material in the deposition process. A possible explanation from these is that mineral particles assist

the precipitation of asphaltenes, once the equilibrium between the asphaltene and the resins is disrupted, the asphaltene tends to adhere to mineral material from the reservoir. These attractive forces would also result in the formation of larger aggregates. During this process paraffins may get trapped within the solid aggregates. The analysis of the SARA separations revealed that both solid deposits are similar in composition and have undergone similar deposition mechanism.

The existence of diamondoids in the crude oils of the oilfields under study was previously confirmed by us when it was thought that these compounds may participate in the deposition mechanism as nucleation sites. However, the GC-MS studies did not confirm the presence of diamondoids in the solid samples of this study. This observation suggests that diamondoids seem not to participate in the heavy organic deposition; however the crude oils from which the solid deposits were analyzed have not been analyzed for the presence of diamondoids.

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