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## Heavy Organics Characterization of Crude Oils from Southeastern Mexican Oilfields (Aromatics, Asphaltenes, Resins, Saturates)

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### Summary

In this paper, the authors present the characterization of crude oils produced in the southern region of Mexico. A modified SARA procedure has been employed to separate the crude into four distinct fractions: Saturates, Aromatics, Resins and Asphaltenes. This modified technique has been performed on five light crude oils (35-37 °API). The fractions obtained from this separation have further been characterized using gel permeation chromatography (GPC) and gas chromatography-mass spectrometry (GC-MS) in order to establish the basic differences and similarities among the crude oils produced from the oilfields of interest.

The total asphaltene content of these crude oil samples has been determined using n-pentane, n-heptane, and n-nonane as the precipitating solvents. The molecular weight of these various asphaltene fractions was investigated by GPC. It is demonstrated that the asphaltenes contained in these crude oils possess a rather strong tendency to self-associate. This is indicated by the bimodal nature of the molecular weight distributions obtained.

Diamondoids and alkyl-substituted diamondoids have been confirmed to be present in the crude oils produced in the oilfields under study.

The results presented in this paper have provided a good understanding of the overall behavior of the species that precipitate. These studies helped to increase our understanding 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 render in deposition and plugging of oil-producing wells.

### 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 thermodynamic and transport properties of the complex crude oil mixture<sup>1</sup>. During the past several years, extensive work has been developed in the formulation of models to predict the phase and transport behavior of petroleum fluids. For complex

mixtures such as petroleum, composed of a great number of similar chemical species, the most common problem one must face consists on the identification of the components of the mixture and the definition of families or fractions of similar components<sup>2</sup>.

Within the complex crude oil mixture, more attention has been given to the *heavy fractions* in order to develop methods to predict heavy organic deposition (HOD) during the production and processing of crude oils<sup>3-6</sup>.

In the simplest case, petroleum is considered to be composed of four major fractions of similar species which are mutually soluble forming one phase as long as certain conditions are maintained in the mixture. Variations in temperature, pressure or composition may alter this equilibrium and some of these species can segregate and form another liquid or solid phase<sup>7-9</sup>. Once separated, the polar molecules may start to aggregate by hydrogen bonding or other polar group interactions and form larger particles that precipitate out of the mixture as solid deposits which in many cases plug wells, pipelines and processing equipment<sup>10</sup>. The mechanism by which this phenomena occurs is still unknown, but it is clear that each species depends upon the others in the system and therefore the characterization of the heavy fractions in the crude oil will give us an insight of their nature and the interactions among them.

SARA is one of the standard methods widely used to achieve the separation of the heaviest fractions of the petroleum (vacuum residuum), which cannot be fractionated by distillation due to the possibility of thermal decomposition of their components at high temperatures<sup>11</sup>. This method provides an excellent tool to compare a variety of different petroleum fluids. In addition, this information provides an insight into the environment surrounding the asphaltene molecules within the crude oil. Consequently, the interactions among asphaltenes, resins, paraffin / wax and other heavy material that play important roles in heavy organic deposition may be better understood.

Another important information, particularly useful for the tuning of the theoretical models used to predict the phase behavior of heavy organic

compounds in crude oils is the Total Asphaltene Content. The yield and nature of the asphaltenes precipitated vary according to the solvent used for the precipitation; low molecular weight paraffins are commonly used to obtain different asphaltene fractions.

The GPC technique is the most widely used method to determine the molecular weight of asphaltenes. This technique provides molecular weights relative to the calibration standards used. Nevertheless, the MW distribution curves obtained by GPC are clear indicatives of the interaction among the species in solution.

The combined GC-MS technique was used to determine the existence of diamondoids in the crude oils analyzed. The analysis were carried on the saturated fractions of the crude oils, rather than in the whole crude oil in order to avoid the interferences posed by aromatic compounds<sup>12</sup>. Solubility data reported for diamondoids suggest that these hydrocarbons will preferentially partition themselves into the low-boiling fraction of any crude oil. Therefore, the low-boiling fraction of the crude oils was also analyzed. This low-boiling fraction was found to be mostly composed of saturate hydrocarbons, however the amount of low-boiling aromatic compounds was not determined.

Even when these diamondoids are common in petroleum fluids, their presence in crude oils is usually ignored due to their low concentration in these fluids<sup>13</sup>. However, the mechanics of petroleum production leads to an environment that favors the precipitation of diamondoids<sup>14</sup>. These compounds are very stable and possess high melting points (i.e. Adamantane m.p. 269°C) due to their unique rigid but strain free ring system then, the cooling of petroleum to low temperatures causes most of the diamondoids to crystallize<sup>13</sup>. For instance, it has been observed that phase segregation of diamondoids from dry petroleum streams takes place upon reduction of pressure and/or temperature of the system.

Considering the high amounts of gas associated with the crude oils produced in the oilfields of interest it is believed that diamondoids, may nucleate out of solution due to drastic changes in pressure and temperature during the production cycle and act as aggregation sites for other heavy organic species. If so, this species must be taken into consideration in any theoretical formulations for the modeling of heavy organic deposition phenomena.

Note that even though diamondoid crystals will re-dissolve in the liquid phase their appearance will cause a momentary imbalance at the vapor-liquid interface where asphaltenes tend to adsorb. This could potentially lead to further interactions with asphaltene and other surface-active species present at the interface. This momentary imbalance and further interaction could, in principle, lead to subsequent

phase segregation of heavy organics concentrated at the interface.

## Experimental

**Modified SARA Procedure.** The modified SARA procedure<sup>15</sup>, adopted at the TRL for the characterization of the light crude oils under study, can be outlined as follows (Fig. 1):

- i. The removal of the light ends from the crude oil sample by vacuum evaporation at 25 mm Hg and room temperature, until the weight of the sample reaches a constant value.
- ii. The separation of the vacuum residuum into asphaltenes and maltenes by precipitation with n-pentane followed by vacuum filtration of the mixture.
- iii. The fractionation of the maltenes from the previous step, into Saturates, Aromatics and Resins by means of open-column chromatography using silica gel.

A refined separation technique is required to obtain consistent results. For instance, a careful procedure must be developed to withdraw the aliquots of the main sample. Several factors such as natural occurring evaporation or a deficient homogenizing of the main sample have been demonstrated to render significant differences in the results obtained. Therefore when handling light crude oils, the error involved in losses of sample due to evaporation must be minimized by using gas-tight vials and drawing the aliquots as quickly as possible. The main container must be also equipped with a sampling valve in such a way that vapor is not allowed to escape the container, in this way the liquid analyzed is always in equilibrium with its vapor. In the same fashion, the main sample must be properly homogenized every time an aliquot is withdrawn.

**Total Asphaltene Content.** The procedure, implemented at the TRL as a modified version of the IP 143/90<sup>16</sup>, was performed on all the crude oil samples using three different solvents (n-pentane, n-heptane and n-nonane) for the precipitation. Some other solvents such as n-hexane, n-octane and n-decane were also used to get more detailed information regarding the effect of different solvents on the amount and characteristics of the asphaltenes precipitated for one crude oil sample.

The technique was developed according to the characteristics of the crude oils under study, for which, several sets of experiments were performed previously and it was determined that the following variables were the most significant in order to get reliable and reproducible results<sup>17</sup>.

- *Ratio of Solvent to Sample.* 30 ml / g of sample
- *Heating Step.* 15 minutes at Total Reflux Conditions
- *Mixing Time.* 225 minutes

The experimental procedure is outlined in Fig. 2. It is noteworthy that the yield and quality of the asphaltenes precipitated from petroleum depend not only on the solvent used, but also on the technique employed<sup>18</sup>. Therefore, the rinsing of the filter cake is essential to remove any remainder such as paraffin / wax and resin material trapped within the cake. The cake should be washed and the vacuum filtration should proceed until the cake breaks into small parts and the solid becomes a fine black powder. Once the filtration step is finished, the complete drying of the cake is very important to remove all the solvent from the solid particles

**GPC Analysis.** The MW of the different asphaltenes precipitated from the crude oil samples as well as the aromatic and resin fractions were obtained by GPC analysis.

In general, determining the MW of asphaltenes is not a straightforward measurement. Several factors such as the solvent used and the presence of adsorbed resin material on the asphaltenes lead to discrepancies in the values obtained. In fact, experimental work indicates that no method will give absolute results<sup>19</sup>.

Each fraction 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 45  $\mu\text{m}$  membrane filter to remove any insoluble material from the solutions. The filtered solutions were injected through the GPC system; the data were acquired with an RI and a UV detectors. The calibration curves were obtained using narrow-dispersity polystyrene standards.

**GC-MS Studies.** The analyses were conducted in a Finnigan GC/MS instrument equipped with a gas chromatograph and capillary injector operated in the split mode. A fused silica capillary column, 100 m  $\times$  0.25 mm ID with a 0.5  $\mu\text{m}$  DB-1 stationary phase (dimethyl-polysiloxane). The Mass spectrometer generated positive ions by electron impact at 70 eV. The ion source was maintained at 200  $^{\circ}\text{C}$  and EM=1200 was used. Mass spectra were obtained by scanning masses from 50 to 400.

The oven temperature was programmed as follows: 50  $^{\circ}\text{C}$  for 5 minutes and then from 50  $^{\circ}\text{C}$  to 250  $^{\circ}\text{C}$  at 2  $^{\circ}\text{C}/\text{min}$ , finally the temperature was held at 250  $^{\circ}\text{C}$  for 120 minutes.

## Results and Discussion

Once the modified SARA technique was proven to give reproducible results, two separations were performed on five crude oils from the fields of interest. The results obtained, reported as wt. %, are shown in Fig. 3.

Note that all crude oils exhibit differences in composition, this is not surprising considering that petroleum will present wide variations in the

proportion of their constituents according to the source material and variations in maturation conditions. However, from an overall perspective the five crude oils were found to show similar trends in composition.

From Fig. 3 it is clear that some of the differences between the crude oils are related to the light-end fractions, nevertheless the combined light end-saturate fractions are almost the same for all the whole crude oils under study. It is also noteworthy the large proportion of these two combined fractions within the crude oils with an average value of approx. 70 %.

Another important observation is the small amount of resins when compared with the asphaltene content. Being the resins the main factor by which the asphaltenes remain dispersed in the oil medium, the overall compositions appear to be hostile for the stability of asphaltenes.

On a second set of experiments the solid deposits from two wells of the same oilfield were also fractionated by the SARA method<sup>20,21</sup>. The results are shown in Fig. 4. Note from the figure that the solid material is mainly comprised of asphaltenes and wax/paraffinic compounds, another important observation is the considerable amount of toluene-insoluble material. This insoluble material is believed to be inorganic matter such as sand or clays. The overall composition of the solid deposits suggests that there is a strong interaction between these insoluble material and the other heavy organic fractions of the crude.

It can be seen from the same figure that the compositions of both solid samples are very similar, for the asphaltene, saturate and insoluble fractions. This observation suggests that the deposition phenomena in both wells follow similar mechanisms.

The Total amount of asphaltenes is reported in Table 1. In Fig. 5 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<sup>22</sup>. The asphaltene wt % decreases as the molecular weight of the solvent increases and for large solvent carbon numbers the amount of asphaltenes exhibit an asymptotic behavior.

Before any analysis of GPC data is performed, one must remember that the properties of asphaltenes varies according to the solvent used for their precipitation and that there is an inherent amount of resins which co-precipitate along with the asphaltenes<sup>23</sup>. It must also be understood that the resin content in the precipitate increases as the number of carbon in the precipitating solvent decreases. This means, that the  $n\text{C}_5$ -asphaltenes will contain more resins than the  $n\text{C}_9$ -asphaltenes. It should also be understood that when n-pentane is used high-MW paraffins co-precipitate with the asphaltene and resins.

One must bear in mind, also, that the asphaltenes, considered as unit sheets with an aromatic condensed cyclic system in the center and surrounded by aliphatic-naphthene radicals, when dissolved in polar or aromatic solvents interact with each other to form *particles*, consisting of several of these sheets grouped in layers via  $\pi$ - $\pi$  association or heteroatom coordination<sup>24</sup>. These particles in turn, can further associate to form large aggregates called *micelles*. 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. This association is influenced by the solvent polarity, the asphaltene concentration and the temperature of determination<sup>25</sup>.

Therefore, it may be expected that these three types of asphaltenes will exhibit different MW distributions. As mentioned above, these MW distributions will depend on the level of intermolecular interactions among asphaltenes, resins and co-precipitated high MW paraffins.

**Table 2** contains all the average molecular weights obtained for each of the asphaltene fractions in the crude oils. As we can see, as a general trend,  $nC_7$ -asphaltenes exhibit higher average MW than the  $nC_5$ -asphaltenes, but smaller than the  $nC_9$ -asphaltenes. These data suggest 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. These data also suggest that when the resin content is lowered (as in the case of the  $nC_7$ -asphaltenes), larger aggregates are formed, and therefore, more complex asphaltenes are precipitated. More important to understand the behavior of asphaltenes are the MW distribution curves obtained for the various asphaltene fractions derived from the crude oils. For instance, in **Fig. 6** 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. It is also noted that the population of low-molecular-weight species (i.e. 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. Nevertheless, the polydispersity of the various asphaltenes does not change significantly, but was observed to increase as the molecular weight of the precipitating solvent increased. It is important to mention that this general trend was observed in all the other crude oils analyzed<sup>26</sup>.

This behavior can be explained on the basis of the current research of the nature of petroleum asphaltenes, as a result of the equilibrium among the

*asphaltenes*, *micelles* and *micelle aggregates* present in the solution<sup>27,28</sup>.

**Table 3** contains a summary of the average molecular weights obtained for the aromatic and resin fractions of all crude oils. As expected, the resin fractions exhibit higher molecular weights than the aromatic fractions. It is interesting to observe that the first four measurements were made in a train of two columns, whereas the last measurement was performed in a train of four columns, this may account for the big differences in the last crude oil values.

**Fig. 7** 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 almost Gaussian and resembles somehow that one of the  $nC_5$ -asphaltenes, suggesting this the structural similarity between these species, which is responsible for their affinity to each other in solution and petroleum<sup>23</sup>. 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 trends were found in all the other crude oils analyzed<sup>29</sup>.

The GC-MS analyses conducted on the saturate fraction of crude oil A are depicted in **Figures 8a-c**. The overall carbon number distribution of normal paraffins was also determined in the fractions.

**Figure 8a** shows a portion of the total ion chromatogram obtained for the saturated fraction of crude oil A. Note that paraffins up to  $nC_{21}$  are shown in this figure. The overall distribution of normal paraffins shows that crude oil A contains little amounts of normal paraffins heavier than  $nC_{25}$ .

It must be pointed out that the main focus in the GC-MS studies was to determine the existence of adamantane and diamantane. Although, tri-, tetra-, penta-, and hexamantane could also be present in this crude oil, it was decided that if adamantane and diamantane are found in this crude oil then there is a possibility that higher adamantologues are also present in this crude oil. Adamantane is expected to elute from the column between  $nC_{10}$  and  $nC_{11}$ ; diamantane is expected to elute between  $nC_{15}$  and  $nC_{16}$ ; and triamantane is expected to elute between  $nC_{19}$  and  $nC_{20}$ . Thus, it was reasonable to truncate the total ion chromatogram as shown in **Figure 8a**.

An adamantane standard (99+% purity), purchased from Aldrich, was dissolved in n-hexane and run through the GC-MS using the temperature program used for the saturated fraction. In this way, the retention time for adamantane was determined as well as its mass spectrum. A retention time of 53.29 minutes was found for the adamantane standard. Note that the retention time for the adamantane standard falls exactly between  $nC_{10}$  (45.49 min) and

$nC_{11}$  (54.17min) of the total ion chromatogram (Fig. 8a), which is in agreement with previous observations. Consequently, if adamantane is present in this fraction of crude oil A it should be found around the same retention time as that of the standard. Figure 8b shows the single ion chromatogram for  $m/z$  136 (adamantane molecular weight). Note that the most prominent peak is found at 53.29 minutes, which is the retention time for adamantane. Furthermore, the mass spectrum under this peak (Fig. 8c) is very similar to that obtained for the standard. This confirms the existence of adamantane in the saturated fraction of the vacuum residuum of crude oil A.

The portion of the total ion chromatogram in Figure 8a between  $nC_{15}$  (83.73min) and  $nC_{16}$  (95.97 min) was also scanned for the existence of adamantane ( $m/z$  188) whose base peak is 188 ( $M^+$ ). However, the single ion chromatogram obtained did not show significant intensities. Therefore, it was concluded that if adamantane and triamantane are present in crude oil A, their concentrations are much smaller than that of adamantane. However, alkyl-substituted adamantanes were also found in crude oil A as reported in Table 4. Note that all these compounds were found to elute between  $nC_{10}$  and  $nC_{13}$ . It is believed that many other alkyl-substituted adamantanes exist in crude oil A.

Fig. 9a shows the total ion chromatogram obtained for the low-boiling fraction of crude oil A. Note that this fraction contains considerable amounts of *n*-octane (28.28min), *n*-nonane (37.25min), *n*-decane (46.18 min) and *n*-undecane (54.71 min). It contains smaller amounts of *n*-dodecane (62.78min), *n*-tridecane (70.36 min) and *n*-tetradecane (77.48min). Normal pentadecane was found to be present in trace quantities. The vast number of compounds eluting in between normal paraffins before  $nC_{11}$  were found to be mostly branched alkanes. It must be pointed out that the main focus in these studies was to determine the existence of adamantane and diamantane in the crude oil samples. And to determine how adamantane partitions itself between the low boiling fraction and the vacuum residuum (i.e. saturated fraction).

Figure 9b shows the single ion chromatogram for  $m/z$  136. Note that there is a peak of considerable intensity at a retention time of 53.88 minutes which is very close to that of the adamantane standard. The discrepancy in retention times may be explained by the fact that the data acquisition is not automatic and there is a delay between injection and the data acquisition onset. Figure 9c also shows the mass spectrum under this peak. This spectrum is similar to that obtained for the standard. Therefore, this confirms the existence of adamantane in the low-boiling fraction of crude oil A. By comparing the signal intensities of the  $m/z$  136 peaks in Figures 8b and 9b it is clear that the concentration of adamantane in the low-boiling fraction is about four times higher

than that in the saturate fraction of the vacuum residuum. Thus, adamantane preferentially partitions itself into the low-boiling fraction of crude oil A.

The same alkyl substituted adamantanes found in the saturate fraction were also detected in the low-boiling fraction at similar retention times and in higher concentrations. The single ion chromatogram obtained for  $m/z$  188 did not show significant intensities.

## Conclusions

The results of the SARA (saturates, aromatic, resins, asphaltenes) separation have revealed that these crude oils contain large percentages of saturated compounds. The ratio resins to asphaltenes content was found to be very low. Therefore, the overall composition of the crude oils, produced in these oilfields, suggests a hostile environment against the stability of asphaltenes. The composition of the solid deposits suggests a strong interaction between the asphaltenes, paraffins/wax and inorganic material in the deposition process.

The results from the GPC studies on the asphaltene fractions demonstrated the tendency of these crude oils to self-associate in solution. It is also seen that the intensity of these interactions among asphaltenes increases as the amount of resins which co-precipitate decreases. The MW distributions suggest the existence of species with low molecular weights in the asphaltenes precipitated. All the fractions analyzed exhibit similar shape chromatograms for the different crude oils under study, this suggests that these crude oils present similar behavior.

The experimental results have confirmed the presence of adamantane and alkyl-substituted adamantanes in the crude oils produced in the oilfields of study. Diamantane and higher adamantologues were not detected in these studies performed. This was because the single ion chromatogram for diamantane and triamantane did not show intensities very distinguishable from the noise background. However, it is believed that higher adamantologues do exist in the crude oils under study although in much less quantities than adamantane and its alkyl derivatives.

These studies have also shown that adamantanes preferentially partition themselves into a low-boiling fraction separated from the crude oils at 27 °C and 10 mm-Hg. It was found that the concentration of adamantane was four times higher in the low-boiling fraction than in the vacuum residue.

These studies have also revealed that the crude oils produced in the fields under study contain relatively small quantities of *n*-paraffins heavier than  $nC_{28}$ . The GC-MS analyses of the light-ends show that these fractions are primarily comprised of saturate compounds.

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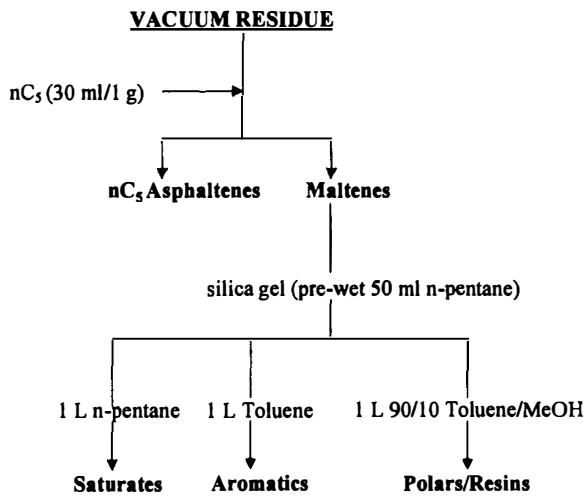


Fig. 1 Schematic representation of the Modified SARA procedure for the separation of vacuum residue derived from light crude oils.

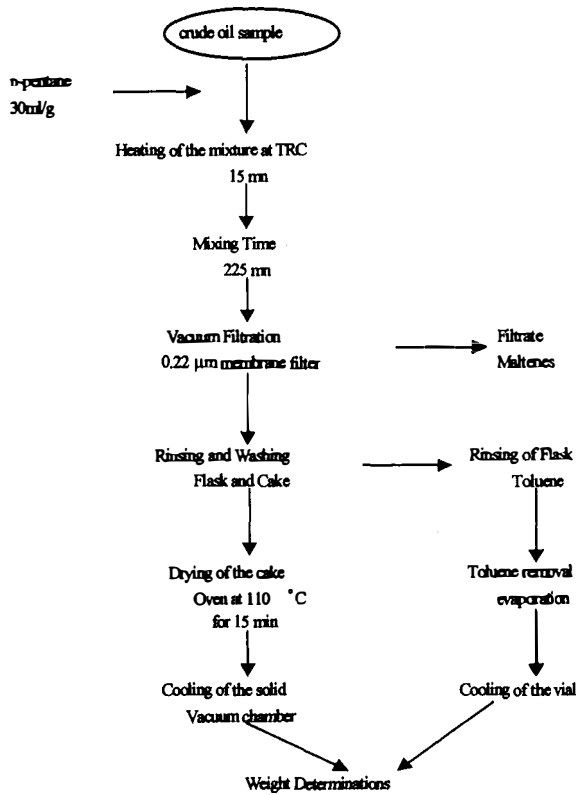


Fig. 2 Schematic representation of the Total Asphaltene Content procedure performed on the crude oils under study.

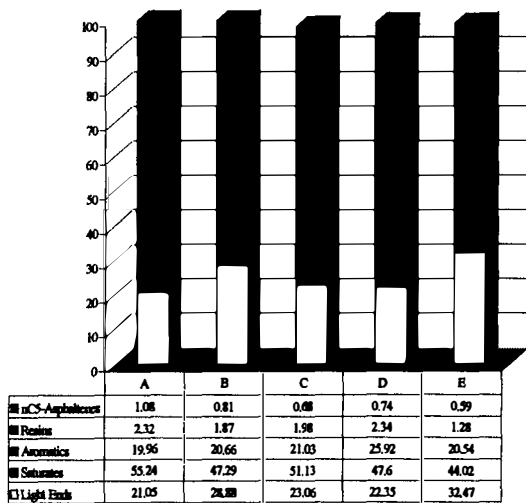


Fig. 3 Schematic composition of the crude oils fractionated by the SARA method.

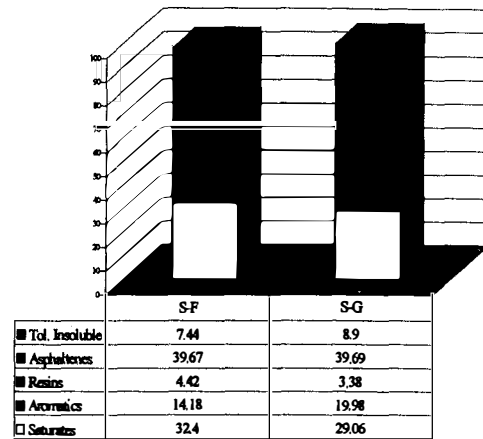


Fig. 4 Schematic composition of the solid deposit fractionated by the SARA method.

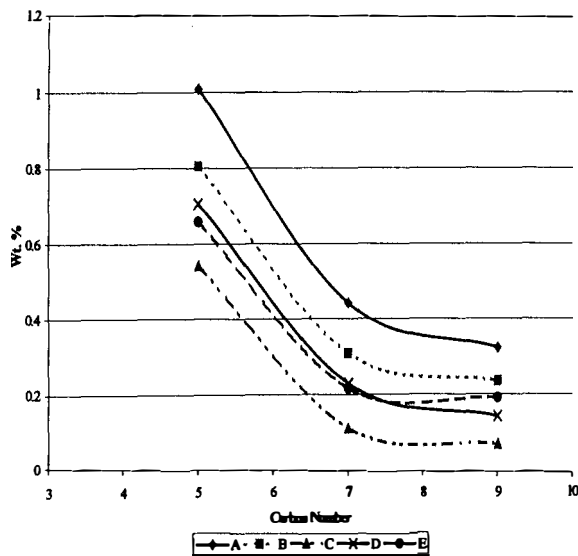


Fig. 5 Total amount of asphaltenes precipitated with Different n-paraffin solvents.

Table 1. Total Asphaltene Content of the crude oil samples obtained with different n-paraffin solvents.

Crude oil	n-pentane	n-heptane	n-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±.0002

Table 2. Average molecular weights obtained for the asphaltenes precipitated from the crude oils.

Crude oil	nC <sub>5</sub> asphaltenes	nC <sub>7</sub> asphaltenes	nC <sub>9</sub> asphaltene
A	2,725	6,198	5,067
B	3,121	4,242	4,261
C	2,535	3,311	3,531
D	3,050	3,787	3,900
E	2,475	3,059	3,651



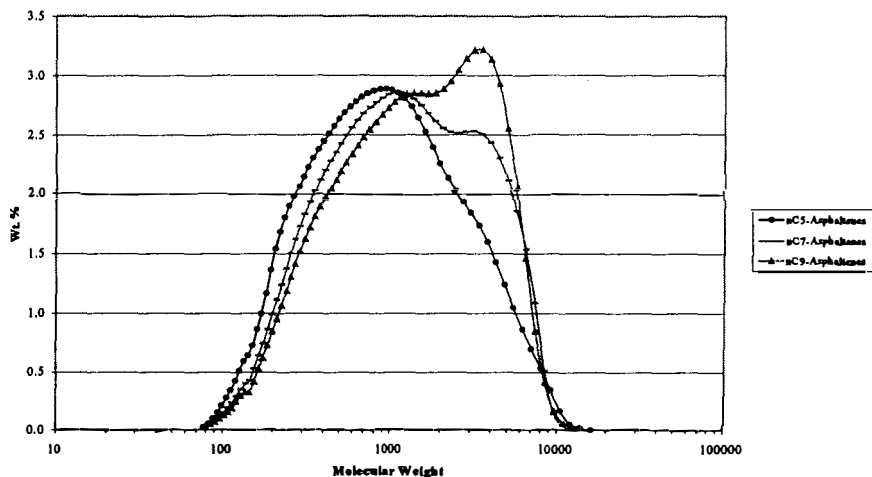


Fig. 6 Molecular weight distribution curves obtained for the different asphaltenes Precipitated from crude oil E.

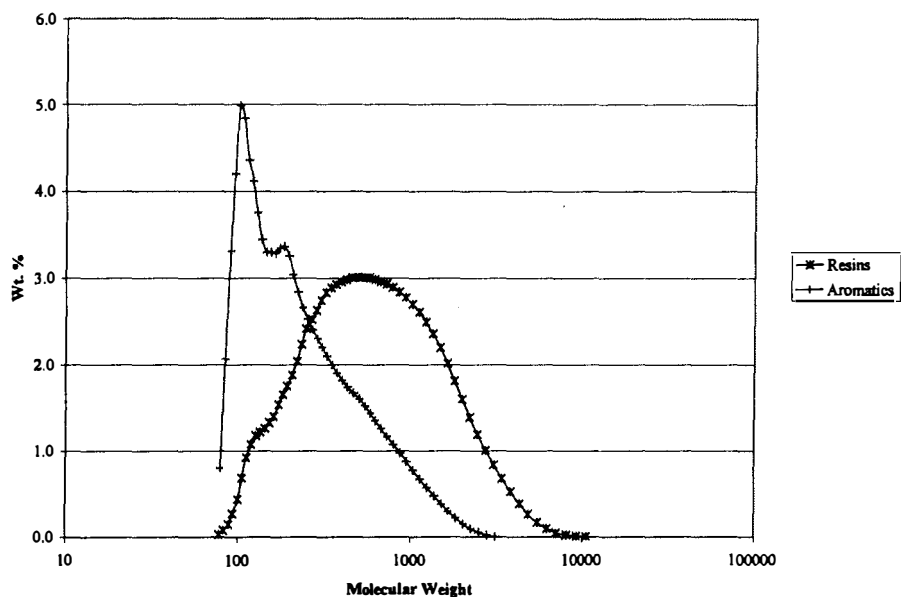


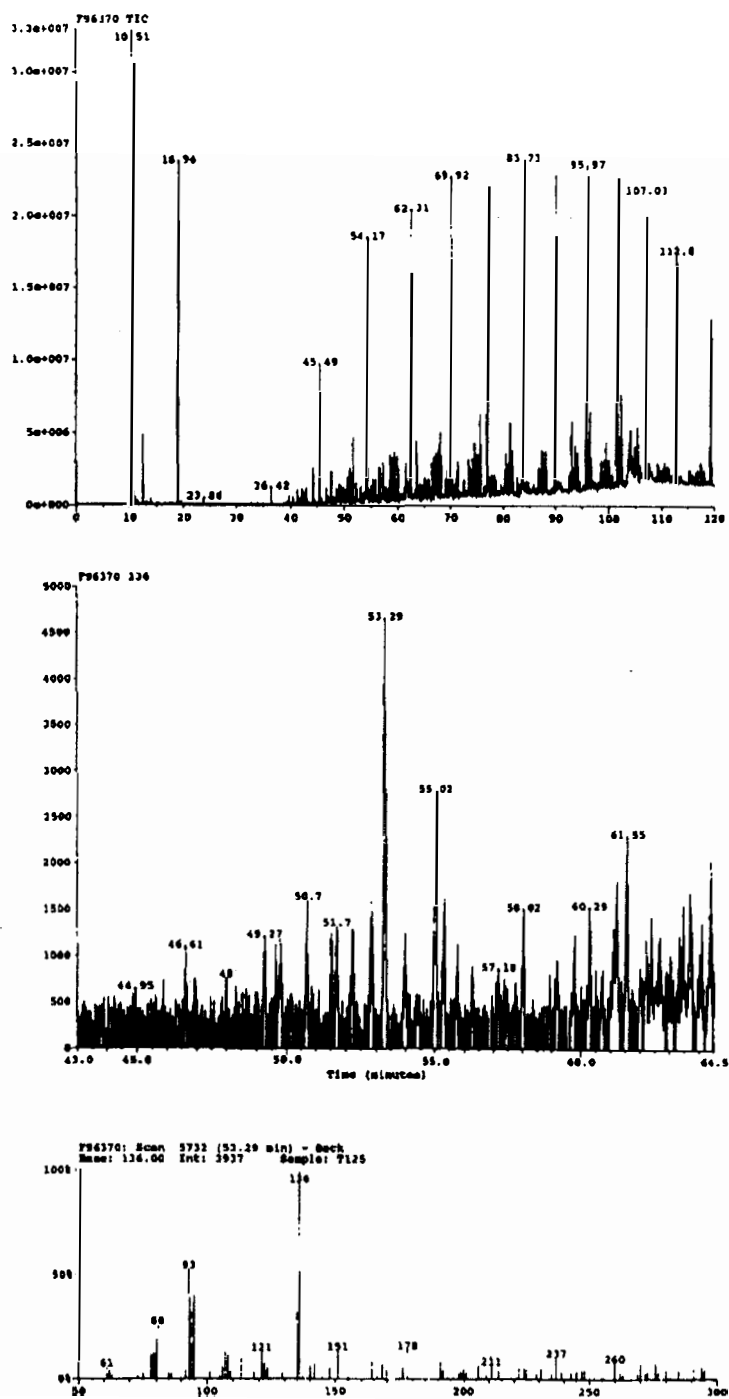
Fig. 7 Molecular weight distribution curves obtained for the aromatic and resin fractions derived from crude oil E.

Table 3. Average molecular weights obtained for the aromatic and resin fractions derived from the crude oils under study.

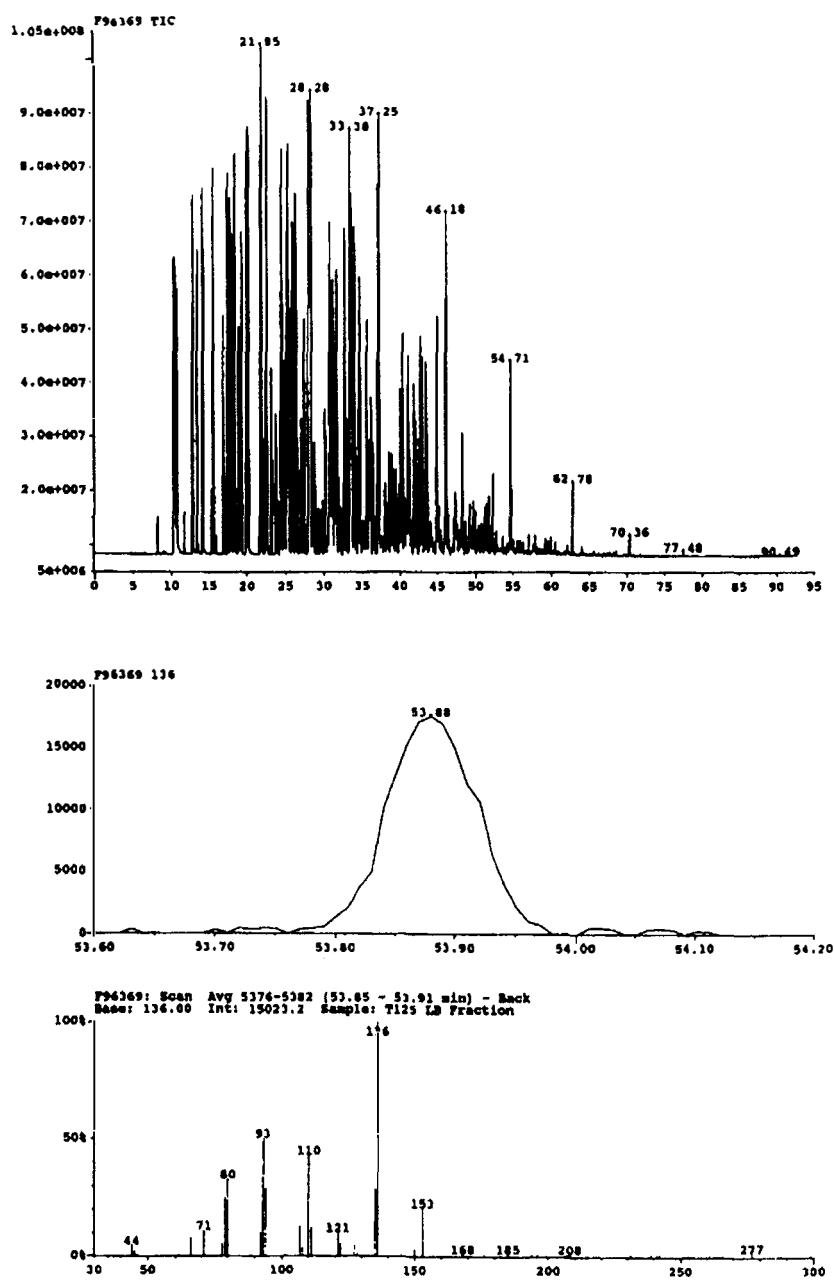
Crude Oil	Aromatic Fraction	Resin Fraction
A	731	1,022
B	652	1,042
C	669	981
D	799	976
E	288	768

Table 4. Alkyl-adamantanes found in crude oil A

Compound	Base Peak	Ret. Time (min.)
1-methyl adamantane	135 (M-CH <sub>3</sub> )	55.59
2-methyl adamantane	135 (M-CH <sub>3</sub> )	60.88
1,4-dimethyl adamantane	149 (M-CH <sub>3</sub> )	61.88
1,2-dimethyl adamantane	149 (M-CH <sub>3</sub> )	64.51
1-ethyl adamantane	135 (M-C <sub>2</sub> H <sub>5</sub> )	66.89



**Fig. 8** a) Total ion chromatogram of the saturated fraction from crude oil A.  
b) Single ion chromatogram for m/z 136 (adamantane molecular weight).  
c) Mass spectrum underneath the most prominent peak (53.29 min.)



**Fig. 9 a)** Total ion chromatogram of the saturated fraction from crude oil A.  
**b)** Single ion chromatogram for  $m/z$  136 (adamantane molecular weight).  
**c)** Mass spectrum underneath the most prominent peak (53.88 min.)