FAST CRUDE-OIL HEAVY-COMPONENT CHARACTERIZATION USING COMBINATION OF ASTM, HPLC, AND GPC METHODS

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Abstract

Resins and asphaltenes are considered important culprits of the asphaltene deposition problem and understanding their phase behavior is crucial to its solution. Predictive models of asphaltene deposition would normally require as input a minimum number of physical, chemical, and thermodynamic properties of the resins and asphaltenes.

The main objective of the paper is to propose an improved technique for quick determination of the resin (i.e., asphaltene peptizing agent) content of a hydrocarbon mixture that simultaneously separates the resins for further analysis. The technique is a combination of ASTM standard and HPLC methods. The results of this technique were checked satisfactorily against those of another equivalent conventional method, which is more time consuming and less reproducible. Furthermore, molecular size distributions of asphaltenes and resins were determined for two crude oils of widely different asphaltene and resin content and place of origin using GPC. A relationship between the asphaltene-number average molecular weight (relative to polystyrene) and the flocculant paraffin carbon number is suggested.

Introduction

Asphaltene deposition is the cause of major economic and safety problems during production and processing of both natural and synthetic hydrocarbons as reported by various researchers and engineers working on the subject (Katz and Beu, 1945; Haskett and Tartera, 1965; Lichaa, 1977; Adialalis, 1982; Tuttle, 1983). A detailed discussion of the field experiences and laboratory research related to the asphaltene deposition problem was presented by the authors earlier (Leontaritis and Mansoori, 1988). Also earlier a thermodynamic–colloidal model was proposed (Leontaritis and Mansoori, 1987) for predicting asphaltene flocculation during petroleum production and processing.

Experimental data suggest that asphaltenes and resins are very important components of the crude oil because they play a crucial role in the asphaltene deposition problem. Yet, not enough is known about their physical and chemical properties, and especially thermodynamic properties required by mathematical models predicting the phenomenon of asphaltene flocculation. In the model mentioned above (Leontaritis and Mansoori, 1987) resins are a component of the asphaltene-free crude oil responsible for peptizing the asphaltenes (see Fig.
9, to be discussed later). As a result they are included in the phase calculations of the oil at different state conditions. For these calculations various properties of each oil constituent, such as critical point data and molecular weight, are necessary.

The experimental work presented here is geared towards determining the above properties of the asphaltenes and resins. It should be kept in mind that the fraction resins in this paper refers to those compounds of the crude oil that are responsible for keeping the asphaltenes in colloidal suspension. Henceforth, the terms resin and asphaltene peptizing agent are used interchangeably in this paper. The results of the work presented here by no means are all inclusive and/or conclusive. However, they suggest how an improved fast technique using a combination of ASTM standard, HPLC, and GPC methods may be used for determination of oil resin content, molecular weight distributions, and other properties of resins and asphaltenes. The main objective of the paper is to show how a relatively simple ASTM/HPLC hydrocarbon group separation technique can be used to determine the resin or asphaltene peptizer content of a crude. Also, since the proposed method separates the resin fraction from the rest of the crude it can be used as a separation step for methods seeking to determine the properties of resins. Furthermore, experimental work is presented correlating the number average molecular weight of asphaltenes of a certain crude oil with the paraffin flocculant carbon number.

### Experimental procedures

Conventional methods for characterizing asphaltenes and resins (i.e., finding their physical, chemical, and thermodynamic properties) consist primarily of physically separating these compounds from the original oil and then subjecting them to different analyses using a host of available analytical techniques. The separation step is apparently the most difficult and error-prone in these methods. In the technique presented here the separation of resins is accomplished by HPLC and the results are satisfactorily reproducible, as many researchers using the HPLC have shown (Jewell et al., 1972; Sautoni and Swab, 1975; Drushel, 1978; Dark, 1982). Two asphaltenic crude oils were used in these studies, the heavier 27.13 API gravity Brookhaven oil and the lighter 30.21 API gravity DK-107 oil. Crude oil physical properties are shown on Table 1. The experimental methods for asphaltenes and resins are discussed below.

### Asphaltenes

The asphaltenes were separated from the crude oil using the method ASTM D-3279. This method does not prescribe the micron rating of the filtration apparatus needed. A 0.1 μm cellulosic membrane filter was used in these experiments. The dried asphaltenes were dissolved in tetrahydrofuran (THF) to make a 0.1% by weight solution. 100 μl injections were made into the GPC to obtain the asphaltene distribution. Three equal size (3.9 mm × 30 cm) ultrastyragel columns in series of

<table>
<thead>
<tr>
<th>Property</th>
<th>Brookhaven Oil</th>
<th>DK-107 Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>dark black</td>
<td>brown</td>
</tr>
<tr>
<td>Density</td>
<td></td>
<td></td>
</tr>
<tr>
<td>at 25°C</td>
<td>0.883</td>
<td>0.863</td>
</tr>
<tr>
<td>at 15.56°C</td>
<td>0.892</td>
<td>0.875</td>
</tr>
<tr>
<td>API gravity</td>
<td>27.13</td>
<td>30.21</td>
</tr>
<tr>
<td>Surface tension</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(dynes/cm) 25°C</td>
<td>24.89</td>
<td>23.29</td>
</tr>
<tr>
<td>Viscosity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(centipoise) 25°C</td>
<td>41.24</td>
<td>9.53</td>
</tr>
</tbody>
</table>

*From Vuong (1985).*

**TABLE 1**

Crude oil properties

K.J. Leontaritis and G.A. Mansoori

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500 Å, $10^3$ Å and $10^3$ Å rating were used to obtain the distributions.

Resins

The resins were separated from the crude using two different methods, one using “adsorption” and another using HPLC fractionation. The term “adsorption” is used here to designate the entire resin separation method as discussed below.

Resin separation by “adsorption”

This procedure is similar to the one discussed by Sachanen (1945) and Koots and Speight (1975). It mainly consists of passing asphaltene-free oil through a bed of a common adsorbent, e.g., fuller’s earth, to separate the resins from the oil. A light paraffin, e.g., n-pentane, is then passed through the bed to preferentially desorb any non-resins that were adsorbed in the bed. In turn, a strong desorbent, e.g., chloroform, is used to desorb the resins from the bed. The resins are recovered after evaporation of the desorbent. The separated resins were dissolved in tetrahydrofuran (THF) to make a 0.1% by weight solution. 100 µl injections were made into the GPC to obtain the resin molecular size distributions. The column set-up described above for the asphaltenes was also used for the resins.

Resin separation by HPLC fractionation

The procedure described above is laborious, time consuming, and has high risk of inaccuracy. However, there exist other methods (Jewell et al., 1972; Sautoni and Swab, 1975; Drushel, 1978; Dark, 1982) for splitting the crude oil into four fractions, namely, the asphaltenes, paraffins, aromatics, and polars. The method by Dark (1982) or the “literature” method (as it will be called from now on), as well as some other methods, is similar to the recommended ASTM clay-gel chromatographic method for crude oil hydrocarbon group separation, the ASTM D-2007. An important difference between the two methods is that the literature method takes, at the most, one hour and the results are easily reproducible, whereas the ASTM method may take anywhere between 2 to 4 days.

The key oil fraction here that is of major interest is the “polar” fraction. Another name given to this fraction in the literature is “heteroatoms” (Sachanen (1945) and Hirschberg et al. (1984)). By the description of each method it is evident that the words “resins”, “polars”, and “heteroatoms” refer to very similar but not necessarily identical compounds. In our terminology, as mentioned earlier, resins represent those compounds of the crude oil that are responsible for peptizing the asphaltenes and keep them in suspension. The purpose of the proposed method is to effect separation of these peptizing agents from the crude oil and make them available for further analysis, i.e., for determination of critical properties, molecular weight, gravity, etc. However, further improvements of the technique are possible and these are discussed later.

The HPLC method consists of basically three steps: (1) a 0.5 g sample of crude oil is dissolved
in 20 ml of n-C₆; (2) the mixture is then filtered to remove the precipitated asphaltenes; and (3) the hexane solubles are run through the HPLC. The paraffins elute first and are detected by a refractive index detector. The aromatics elute next and the polars elute after the column is backflushed and they are both detected by a UV absorbance detector.

This method gives the composition of the crude in terms of the above-mentioned four fractions and also separates each group for further analysis. Figure 2 shows a flow chart for the high performance liquid chromatography system used, most of which is manufactured by Waters. The column used was an energy analysis (NH₂) column (3.9 mm × 30 cm). Sample concentration was 0.5 g per 20 ml n-hexane and dosage at 10 ml. The carrier solvent was hexane at a flow rate of 2 ml/min.

**Results and discussion**

The results of the analysis are separated into two categories; asphaltenes and resins.

**Asphaltene results**

The asphaltenes were flocculated from Brookhaven oil and DK-107 oil using the following six paraffin flocculants: n-pentane; n-hexane; n-heptane; n-decane; n-dodecane; and n-hexadecane. Figures 3 and 4 show the relationship of the amount of asphaltenes flocculated versus the flocculant carbon number for each crude oil. The typical drop of the flocculated amount of asphaltenes as the carbon number increases is clearly evident from these plots. In fact if butane or lighter paraffins had been used the flocculated amounts would be even higher. This has been discussed by a number of researchers on the subject (Yen, 1972; McKay et al., 1978; Boduszynski et al., 1980; Speight, 1981; Mansoori, 1988). The explanation given for this phenomenon is that more and more resins are flocculating together with the asphaltenes, as the paraffin flocculant becomes lighter. Consequently, a pertinent question is which paraffin separates only and all the asphaltenes? The answer is probably none, even though from our preliminary data indications are that n-pentane comes close. That is why an efficient and accurate separation method for both asphaltenes and peptizing agents is required.

Samples of n-pentane, n-hexane, and n-heptane asphaltenes flocculated from both crude oils were prepared, as described previously, and run through a Waters GPC. The particle size distributions of all the samples were determined and are shown in Figs. 5 and 6. Samples of the n-decane, n-dodecane, and n-hexadecane asphaltenes were not run through the GPC because of experimental difficulties in the oven drying purification step. The asphaltene particle size distributions if compared to each other show a trend that is a function of the flocculant carbon number. The n-C₅ asphaltenes have more of the larger particles than the n-C₆ asphaltene which in turn have more than the n-C₇ asphaltenes for both crude oils. It should be
Fig. 3. Brookhaven oil asphaltene contents.

Fig. 4. DK-107 oil asphaltene contents.
Fig. 5. Molecular weight distributions of Brookhaven oil asphaltenes.

Fig. 6. Molecular weight distributions of DK-107 oil asphaltenes.
noted that in GPC the heavier compounds elute first.

Figure 7 shows a plot of the average molecular weight of the asphaltenes, as determined by GPC, versus the carbon number of the paraffin flocculant. These molecular weights were determined relative to narrow dispersity polystyrene standards and no claim can be made as to whether they are "absolutely" true or not. However, Fig 7 demonstrates a functional relationship which appears to be true for both crudes, namely, the logarithmic average molecular weight of the asphaltenes is linearly related to the carbon number of the paraffin flocculant. These experimental points were fitted to a polynomial of first degree and the following equations were developed:

**Brookhaven asphaltenes:**

\[
\log_{10}(MW_{\text{asph.}}) = 3.561 - 0.0640 \times (\text{Carbon No.}) \quad (1)
\]

**DK-107 asphaltenes:**

\[
\log_{10}(MW_{\text{asph.}}) = 3.465 - 0.065 \times (\text{Carbon No.}) \quad (2)
\]

These two linear equations have nearly identical slopes. The usefulness of these equations is still to be shown, as research on the subject continues. The main thrust of the research will be to collect more data with higher carbon number paraffins to verify the validity of the above equations.

**Resin results**

The Brookhaven oil resins were run through the GPC and their molecular weight size distribution was generated as shown in Fig. 8. This is a standard normal distribution and, as a result, it indicates that, with respect to size, resins distribute evenly around their mean in the crude oil. Their number average molecular weight (relative to polystyrene) is \(\sim 430 \pm 30\).

Table 2 presents a summary of the hydrocarbon group separation analysis data for both
Fig. 8. Molecular weight size distribution of Brookhaven oil resins.

TABLE 2

Hydrocarbon group separation by HPLC method

<table>
<thead>
<tr>
<th>Component</th>
<th>Brookhaven Oil</th>
<th>DK-107 Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Asphaltenes (wt%)</td>
<td>1.25 ± 0.03&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.53 ± 0.03</td>
</tr>
<tr>
<td>Saturates (wt%)</td>
<td>70.57 ± 0.42</td>
<td>47.00 ± 0.28</td>
</tr>
<tr>
<td>Aromatics (wt%)</td>
<td>22.94 ± 0.33</td>
<td>43.22 ± 0.17</td>
</tr>
<tr>
<td>Polars (wt%)</td>
<td>5.24 ± 0.06</td>
<td>9.25 ± 0.08</td>
</tr>
</tbody>
</table>

<sup>a</sup>A minimum of three measurements for each data point was made to determine the precision, which was taken as the average distance from the mean.

<sup>b</sup>These are n-C<sub>6</sub> asphaltenes.

Brookhaven oil and DK-107 oil using the HPLC method. The precision of the data was computed by using at least three experimental measurements for finding the arithmetic mean and then calculating the average distance from the arithmetic mean. The results of the modified HPLC method for determining resin content are compared with those of the adsorption method on Table 3. The same comments for computing precision mentioned above apply here as well.

TABLE 3

Comparison of crude oil resin (or asphaltene peptizer) content by “adsorption” method and HPLC method

<table>
<thead>
<tr>
<th>Crude oil</th>
<th>Resin content by adsorption (wt%)</th>
<th>Polars content by HPLC (wt%)</th>
<th>Resin content* by HPLC (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brookhaven</td>
<td>4.59 ± 0.12&lt;sup&gt;b&lt;/sup&gt;</td>
<td>5.24 ± 0.06</td>
<td>4.84 ± 0.23</td>
</tr>
<tr>
<td>DK-107</td>
<td>8.30 ± 0.27</td>
<td>9.25 ± 0.08</td>
<td>8.73 ± 0.14</td>
</tr>
</tbody>
</table>

<sup>"The resin content by HPLC is obtained by deducting the difference of the n-C<sub>α</sub> and n-C<sub>β</sub> asphaltenes from the polars content by HPLC. The n-C<sub>α</sub> asphaltenes are 1.65 ± 0.05 and 1.05 ± 0.03 wt% respectively for Brookhaven and DK-107 oils. The n-C<sub>α</sub> asphaltenes are given on Table 2.

<sup>b</sup>A minimum of three measurements for each data point was made to determine the precision, which was taken as the average distance from the mean.

Discussion of results

As mentioned earlier the ultimate objective of this experimental work is to generate data and/or suggest methods for obtaining the physico-chemical, and especially thermodynamic, properties of asphaltenes and resins.
Effective and consistent separation of asphaltenes and especially peptizing agents from the crude oil for further analysis is a major stumbling block in the characterization process.

Figure 9 depicts how the peptization of asphaltenes, which are considered particles colloidally suspended in crude oil, is effected by the "adsorbed" resins. This process is the basis of the thermodynamic-colloidal model proposed earlier by Leontaritis and Mansoori, 1987. A number of experimenters (Swanson, 1942; Katz and Beu, 1945; Yen, 1972; Lichaa, 1977; Speight, 1981) demonstrated that once the adsorption equilibrium of the resins between the solid and liquid phases is disturbed, i.e., by adding a paraffin solvent, the asphaltene particles flocculate irreversibly. This means that, in order for the asphaltenes to flocculate, they grow in size and as a result their apparent molecular weight changes. If the flocculated asphaltenes are redissolved in a good solvent, i.e., benzene or toluene, after some time passes they begin to grow in size again. However, if the asphaltenes are redissolved in benzene (or another appropriate solvent) that contains enough resins for complete peptization then the particles remain permanently peptized and do not grow in size (Swanson, 1942). This suggests that any experimental work that is destined for characterizing asphaltenes as they exist in the original oil is better to be performed while the asphaltene particles are still peptized as Fig. 9 depicts, if the data are to correspond to the original asphaltene particles.

All the experimental work presented in this paper regarding the asphaltenes has been performed after the asphaltenes were separated from the original crude oil and, as a result, the data may not necessarily apply to the original asphaltenes. The determination of the original asphaltene particle properties has been extremely difficult. Yen (1972) and Boduszynski et al. (1980) interpreted some of their data to apply to asphaltenes in their original non-aggregated state. The model proposed earlier by Leontaritis and Mansoori (1987) does not require any asphaltene properties and thus the problem of acquiring true asphaltene properties is bypassed. In the literature there have been proposed models (e.g., Hirschberg et al., 1984) that require input of asphaltene properties.

In hydrocarbon mixtures (as in most mixtures), size difference between the components is a major factor affecting their solubility. In this case, resins are expected to be more soluble in heavier than lighter paraffins. As a result, it is expected to require smaller amounts of the heavier flocculants for dissolving the same amount of resins. Consequently, the required amount of flocculant for arriving at the onset will be inversely proportional to the flocculant molecular weight, provided that the amount of resins that needs to be desorbed from the asphaltenes in order to arrive at the onset is constant regardless of the flocculant used (refer to Fig. 9). This trend has been observed experimentally (e.g., Hirschberg et al., 1984).

Furthermore, the amount of asphaltenes...
flocculated with a given flocculant is affected by the amount of resins left in the asphaltene phase, i.e., left adsorbed on the asphaltenes after flocculation (Speight, 1981). Figures 3 and 4 show the typical drop reported for the amount of flocculated asphaltenes versus the carbon number (or molecular weight) of the paraffin flocculant for each of the two crudes. This drop corroborates the statement made in the above paragraph of the increase in solubility between resins and heavier paraffins, i.e., for the same amount of paraffin flocculant added more resins will be removed from the asphaltenes by the heavier paraffins. Hence, the amount of asphaltene precipitate will decrease as the paraffin molecular weight increases.

The asphaltene size distributions determined by GPC, shown on Figs. 5 and 6, are the ones the asphaltenes have in tetrahydrofuran (THF) solvent, and as a result they do not contradict the discussion made in the previous two paragraphs. These distributions or apparent molecular weights are a function of the GPC carrier solvent used (in this case THF), among other things. The fact that the distributions are different for each flocculant solvent indicates that the asphaltene flocculation process is affected by the flocculant. In other words, the strength of the bonds formed during flocculation relative to the THF solvent is a function of the flocculant solvent (i.e., n-C₅, n-C₆, n-C₇). It is even more remarkable that the logarithmic number average molecular weight (relative to polystyrene) of these distributions is linearly related to the carbon number of the flocculant.

At this time no definite conclusions may be drawn about the experimental trend described above mainly because the number of experimental points is small (only three paraffin flocculants); more experimental points with heavier paraffins are needed. However, during the above experiments it was observed that, in the filtering step of the flocculated asphaltenes, plugging of the membrane filter becomes more severe (i.e., the required filtration time of the paraffin-crude mixture becomes larger for the same amount of sample) as the carbon number of the paraffin flocculant increases. This indicates that the original asphaltenes aggregate in smaller size particles as the paraffin molecule size increases. It seems that because the larger paraffin solvent molecules tend to hinder tight packing of the original asphaltene particles, the asphaltene aggregates due to these larger solvent molecules contain a larger amount of the original, smaller particles. As a result, the apparent molecular weights of asphaltenes flocculated by larger paraffins are expected to be smaller than those flocculated by smaller paraffins. This is supported by the trend in the distribution curves of Figs. 5 and 6 and the measured average molecular weights.

The resin situation is different because the resin molecules are in true solution in the original oil and so the problem of aggregation does not exist. Thus the resins can be separated from the original oil and subjected to reasonably severe experimental analysis without any alteration to their molecular size and structure. This is a bonus from nature for, in certain situations, accurate resin thermodynamic properties are needed for predicting asphaltene flocculation (Leontaritis and Mansoori, 1987).

Table 3 indicates that, taking into account the experimental error involved in determining the resin content of a crude by the conventional adsorption method and the error involved in determining the polars content of a crude by the HPLC method, the fraction called “resins” becomes nearly equal to the fraction called “polars” if the difference between the amount of n-C₅ and n-C₆ asphaltenes is deducted from the amount of polars. This is not entirely unexpected because any asphaltenes that are left behind in the oil by the HPLC hydrocarbon group separation method (during the asphaltene flocculation step using hexane) will be retained in the column and afterwards elute with the resins in the backflush mode to be counted as polars.

Based on the results of Table 3, it may be concluded that it is possible to determine the
resin content of a crude, as defined by the traditional adsorption method, through use of HPLC. One such method suggested by the results of Table 3 would involve the following steps: (a) determine the n-C₅ and n-C₆ asphaltene contents of the crude using the ASTM D-3279 standard method; (b) use the HPLC method to find the polar content of the crude; and (c) deduct the difference of the n-C₅ and n-C₆ asphaltenes from the polar content to determine the resin content of the crude. It should be noted that the method proposed above for determining the resin content of a crude is based on the results of only two crudes. The credibility of the method will be enhanced after more crudes are analyzed with the same satisfactory results. A possible improvement to the above method would be to develop an asphaltene separation method that determines accurately the “total” asphaltene fraction of the crude instead of assuming that n-pentane asphaltenes are the total fraction. For instance, that might be accomplished by successive fractionation/separation of asphaltenes using a combination of lighter and heavier paraffins or even other asphaltene flocculants. The n-C₆ asphaltene content would be deducted from the true total asphaltene content, and the result would subsequently be deducted from the polars content, as determined by the HPLC method, to yield the resin or asphaltene peptizer content.

The HPLC method is more precise and faster than the adsorption method. Also the possibility of losses using the HPLC method is nil. To the contrary, the losses of the adsorption method can be substantial during the adsorption–desorption steps. The fact that the resin content of each crude, as determined by adsorption, is consistently lower than that determined by HPLC, see Table 3, indicates that some losses may be incurred when using the adsorption method.

Conclusions

A simple, rapid, and precise technique for determining the resin or asphaltene peptizer content of a crude was proposed. This technique involves high performance liquid chromatography and ASTM standard methods and was satisfactorily tested against a conventional laborious “adsorption” method. The proposed method may be used as a resin separation step for methods seeking to do further analysis of the resin fraction. Further possible improvements of the proposed method were also suggested.

A functional relationship was demonstrated between the asphaltene-number average molecular weight (relative to polystyrene) and the carbon number of the paraffin flocculant used to separate the asphaltenes from the crude. This indicates that the paraffin solvent takes part in or influences the asphaltene aggregation process.

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References


Hirschberg, A., De Jong, L.N.J., Schipper, B.A. and Mei-


