

AN EVALUATION OF THE DELAYED-COKING PRODUCT YIELD OF HEAVY FEEDSTOCKS USING ASPHALTENE CONTENT AND CARBON RESIDUE

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ÉVALUATION DU RENDEMENT EN PRODUIT DE COKÉFACTION DIFFÉRÉE DE PÉTROLE LOURD À L'AIDE DE LA TENEUR EN ASPHALTÈNES ET DU RÉSIDU DE COKE

La composition et le résidu de coke de six résidus de raffinage de différents pétroles lourds ont été évalués afin de déterminer des tendances. La composition élémentaire, la teneur en métaux-traces, le résidu de coke et la densité spécifique ont été déterminés sur le résidu complet. Chaque résidu a été désasphalténé dans l'heptane et les produits solubles dans l'heptane ont été séparés en fractions saturée, aromatique et polaire sur du gel de silice activée. La composition élémentaire, la teneur en métaux-traces, la masse moléculaire et le résidu de coke ont été déterminés sur les asphaltènes. La relation entre les résidus de coke et les caractéristiques des asphaltènes a été étudiée, ce qui a permis d'établir une corrélation entre les différentes caractéristiques. Le produit de la masse moléculaire apparente de la globalité des asphaltènes, du pourcentage d'asphaltènes dans le résidu complet et de la teneur en hétéroatomes dans les asphaltènes présente une bonne corrélation avec les valeurs de résidus de coke et peut donc être utilisé pour prévoir les rendements en produit de cokéfaction différée. Les asphaltènes ont été séparés en quatre fractions en fonction de leur taille moléculaire apparente par chromatographie d'exclusion préparative (CE). La teneur en soufre, la masse moléculaire et la teneur en métaux-traces ont été déterminées sur les fractions de chromatographie d'exclusion préparative. Les bilans matières montrent que les résultats obtenus sur les fractions sont en accord avec les résultats obtenus sur le produit initial. Ceci indique que les contributions des propriétés des fractions peuvent être étudiées et mises en relation avec les propriétés du produit global.

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Six residua from different crude oils were evaluated for composition and carbon residue forming tendencies. The whole residua were evaluated for elemental composition, trace metals content, carbon

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residue, and specific gravity. Each residuum was deasphalted in heptane, and the heptane-soluble materials were separated into saturate, aromatic, and polar fractions on activated silica gel. The asphaltenes were evaluated for elemental composition, trace metals content, molecular weight, and carbon residue. The relationship between carbon residues and features of the asphaltenes was studied, and a correlation of contributing features was developed. The asphaltenes were further separated into four fractions according to apparent molecular size by preparative size exclusion chromatography (SEC). The preparative size exclusion chromatographic fractions from the asphaltenes were evaluated for sulfur content, molecular weight, and trace metals content. Material balances showed that the data obtained on the fractions account for the data obtained on the original material. This indicates that the contributions of the properties of the fractions can be studied and related to properties of the whole material.

EVALUACIÓN DEL RENDIMIENTO EN PRODUCTO DE COQUIZACIÓN DIFERIDA DE PETRÓLEO PESADO MEDIANTE LA CONCENTRACIÓN DE ASFALTENOS Y DEL RESIDUO DE COQUE

Se ha procedido a la evaluación de la composición y del residuo de coque de seis residuos de refino de diversos petróleos pesados con objeto de determinar sus tendencias respectivas. La composición elemental, la concentración de trazas de metales, el residuo de coque y la densidad específica se han determinado mediante el residuo completo. Cada residuo se ha desasfaltado en el heptano y los productos solubles en el heptano se han separado en forma de fracciones saturada, aromática y polar sobre gel de sílice activado. La composición elemental, la concentración de trazas de metales, la masa molecular y el residuo de coque se han determinado sobre los asfaltenos. Se ha procedido al estudio de la relación entre los residuos de coque y las características de los asfaltenos, lo cual ha permitido establecer una correlación entre las distintas características. El producto de la masa molecular aparente de la globalidad de los asfaltenos, del porcentaje de asfaltenos en el residuo completo y de la concentración en heteroátomos presenta una correcta correlación con los valores de residuos de coque y, por ende, se puede utilizar para prever los rendimientos en cuanto a producto de coquización diferida. Los asfaltenos se han separado en cuatro fracciones según su dimensión molecular aparente por cromatografía de exclusión preparativa (CE). La concentración de azufre, la masa molecular y la concentración de trazas de metales se han determinado por medio de las fracciones de cromatografía de exclusión preparativa. Los balances de materias vienen a demostrar que los resultados conseguidos por medio de las fracciones están en concordancia con los resultados obtenidos mediante el producto inicial. De este modo se indica que las contribuciones de las propiedades de las fracciones se pueden estudiar y poner en relación con las propiedades del producto global.

INTRODUCTION

Petroleum is an extremely complex mixture and consists predominantly of hydrocarbons as well as compounds containing nitrogen, oxygen, and sulfur. Most petroleum also contain minor amounts of nickel, vanadium, and iron.

Petroleum may be qualitatively described as brownish green to black liquids of specific gravity in a range from about 0.810 to 0.985 and having a boiling range from about 20°C (68°F) to above 350°C (660°F), above which active decomposition ensues when distillation is attempted. The oils contain from 0 to 35% or more of components boiling in the gasoline range, as well as varying proportions of kerosene hydrocarbons and higher boiling constituents up to the viscous and nonvolatile compounds present in lubricants and the asphalts. The composition of the petroleum obtained from the well is variable and depends not only on the original composition of the petroleum in situ but also on the manner of production and the stage reached in the life of the well or reservoir.

A residuum (also shortened to "resid") is the residue obtained from petroleum after nondestructive distillation has removed all the volatile materials (Speight, 1991). The temperature of the distillation is usually maintained below 350°C (660°F) since the rate of thermal decomposition of petroleum constituents is substantial above this temperature. Residua are black, viscous materials and are obtained by distillation of a crude oil under atmospheric pressure (atmospheric residuum) or under reduced pressure (vacuum residuum). They may be liquid at room temperature (generally atmospheric residua) or almost solid (generally vacuum residua) depending upon the nature of the crude oil.

The use of heavy oils as refinery feedstocks is increasing. Heavy oils are distinguished from conventional petroleum by API gravity, with heavy oils being less than 20° API (Meyer and DeWitt, 1990). The combination of high viscosity at operational temperatures and high concentrations of elements other than carbon and hydrogen causes unique difficulties in the processing of these materials (Speight, 1991). Low atomic hydrogen-to-carbon ratios mean that hydrogenation or coking steps will be necessary.

The chemical composition of heavy oils and residua is complex and the precise chemical and physical constitution of residua is not well understood because

of the overall lack of well-documented and acceptable analytical procedures. Physical methods of fractionation usually indicate high proportions of asphaltenes and resins, even in combined amounts up to 50% (or higher) of the residuum. High concentrations of sulfur, nitrogen, oxygen, and metals indigenous to crudes (Ni, V, Fe) also result in considerable hydrogen demand. The constituents of heavy feedstocks may also be corrosive to refinery equipment.

Catalyst deterioration during use, because of coke lay-down and metals deposition, is a continuing issue in catalyst-based processes. Frequent replacement of an expensive catalyst causes a major imbalance to process economics. Thus, a detailed knowledge of the nature of the feedstock constituents, through analytical and characterization procedures, is a necessary part of pre-refining inspections.

In the early days of petroleum refining, it was considered sufficient to define feedstocks in terms of simple physical properties (Speight, 1981; Speight, 1991). The data obtained by these methods were considered adequate for the prediction of feedstock behavior in refining operations.

However, with the influx of different types of petroleum into refineries, and the subsequent wide variations in behavior, there has been the need to define feedstocks in more detail. This is especially true for those feedstocks that are the starting materials for a whole host of catalytic processes.

Strategies for upgrading residua emphasize the differences among their compositions, which will influence the selection of methods for their conversion to products (Schuetze and Hofmann, 1984). Hydrodesulfurization (HDS) and hydrodemetallization (HDM) efficiencies can not be predicted by such conventional measurements as total sulfur, metals, or asphaltene contents, or Conradson carbon residue (CCR) values (Dolbear *et al.*, 1987). Properties of residua determined by conventional methods are not good predictors of their behavior in upgrading processes (Dawson *et al.*, 1989). More knowledge is needed about the components of residua that cause specific problems in processing (Gray, 1990).

Many techniques are applicable to the characterization of heavy oils and residua but few have been developed to a satisfactory stage of systematic methodology (Boduszynski, 1988; Speight, 1991). Information is needed to enhance understanding of the nature and interrelationships of residua constituents

which can be employed to develop models that explain and predict refining characteristics.

An exhaustive analysis of Cerro Negro crude oil in an eight year study resulted in a separation of the oil into scores of chemical fractions (Green *et al.*, 1989). A conclusion of this study was that the compositional complexity of Cerro Negro crude virtually defies comprehension. Such an approach is very time consuming and expensive. Compositional parameters useful for predicting processing behavior must be obtainable with straightforward methodology, at reasonable cost, and in relatively short times.

In many studies of fossil fuel materials, SAPA (saturate, aromatic, polar, asphaltene) separations with studies of the fractions generated often are performed. The procedure is relatively inexpensive, rapid, and straightforward, and provides a characteristic fraction distribution for each residuum. Asphaltene contents of heavy oil residua provide a better measure of coking propensities than carbon residue values (Kircher, 1991). The metals contents of SAPA polar fractions may be predictive of HDM activity (Reynolds, 1991). A SAPA separation (Corbett and Petrossi, 1978) with elemental and structural information can be used to develop a petroleum map to add an extra dimension to compositional studies (Long and Speight, 1989)

Size exclusion chromatography (SEC) profiles can be indicators of residua processabilities (Sanchez *et al.*, 1984). These provide apparent molecular weight distributions which can be indicative of states of dispersions of polar molecules in less polar material (Sheu *et al.*, 1991). The effectiveness by which the less polar solvent phase disperses the polar associated phase determines many important properties of residua. Associated polar species can demonstrate an apparent high molecular weight due to their size. These can play a major role in processes such as hydrocracking, where catalyst involvement is high (Speight, 1984). Associated species persist even at processing temperatures (Rao and Serrano, 1986) and affect reactivity (Dawson *et al.*, 1989).

The data derived from the analytical procedures can be employed to give the refiner an indication of the behavior of the feedstock during refining (Gary and Handwerk, 1984) and, also, the prediction of process options that may lead to improvements in product character and/or yield. With the complexity of modern refinery feedstocks, there are disadvantages on relying upon the use of bulk properties as the sole means of

predicting current-day feedstock behavior (Dolbear *et al.*, 1987). Other means of evaluation are necessary and this is where the fractionation data can be a very valuable aid to understanding feedstock behavior and process options.

For example, by careful selection of an appropriate technique it is possible to obtain a detailed overview of feedstock/product composition which can be used for process predictions. Using the adsorbent separation as an example (Corbett and Petrossi, 1978), it becomes possible to develop a petroleum map (Long and Speight, 1989).

However, it must be recognized that such a "map" does not give any indication of the complex interactions that occur between, for example, fractions such as the asphaltenes and resins (Koots and Speight, 1975) but it does allow predictions of feedstocks behavior. It must also be recognized that such a representation will vary for different feedstocks.

To proceed from bulk property data to full scale production is not the preferred step. Further evaluation of the processability of the feedstock is usually necessary through the use of feedstock/product composition data which will, in conjunction with bulk property data, be of substantial aid in moving to pilot scale operations. It may then be possible to develop correlations between the data obtained from the actual plant operations (as well as the pilot plant data) with one or more of the physical properties determined as part of the initial evaluation.

Some researchers, in addition to deriving broad generalities from the use of various analytical techniques, are attempting to assign specific models to the predictability of crude oil processing. The overall goal of the modeling studies is to predict the behavior of the feedstock during processing. If this be the case, the model then fills a very useful function, that of being able to predict conversion chemistry and physics, which is, perhaps, the sole reason for the existence of the model.

In summary, the use of analytical data has been, and remains, an integral part of refinery operations. There is the need to understand nature of the constituents of the heavier feedstocks in more detail in order to be able to predict product yield and product distribution. The analytical methods currently at hand are an aid to accomplishing this goal. But it is only when a full understanding of the character of the heavier feedstocks is available that a confident predictability will emerge.

Since the major complex constituents of crude oils are concentrated in the residua, the current work demonstrated the application of a characterization scheme using six residua from different heavy crude oils.

Separation

To study the residua in detail, it is necessary to subdivide them into several well-defined fractions. This can best be achieved by removing the asphaltenes prior to fractionation using solid adsorbents. Trace metals which are concentrated in the asphaltenes can sustain significant losses if carried through subsequent chromatographic separations. Asphaltenes should be isolated using a standard procedure in which one volume of each residuum is mixed with at least 40 volumes of a hydrocarbon solvent such as *n*-heptane (Speight *et al.*, 1984).

Initial fractionation of the deasphaltened oil (maltenes) can be accomplished with a SAPA separation based on either a silica gel or aluminum oxide chromatographic procedure, or a more complex ion-exchange separation (Snyder and Saunders, 1979; Jewel, 1979). A SAPA separation using activated silica gel was selected for the current work.

Size Exclusion Chromatography

A preparative separation of asphaltenes can provide fractions for subsequent analysis. With such a separation, information can be obtained such as apparent molecular weights, which are related to the levels of association of polar species in the fractions, and the distribution of sulfur and metals. In the current study, preparative size exclusion chromatography was performed on the asphaltenes from each residuum. Four fractions of approximately equal weight were obtained, ranging from relatively high to low apparent molecular size distributions. The separation was performed on Bio-Rad S-X1 styrene-divinylbenzene polymer beads with a toluene mobile phase.

Elemental and Metals Analysis

Each original residuum, the asphaltenes, and the saturate, aromatic, and polar fractions were analyzed for weight percent carbon, hydrogen, nitrogen, oxygen, and sulfur. The whole residua, the asphaltenes, the

aromatic and polar fractions, and the four fractions obtained from the asphaltenes by size exclusion chromatography were analyzed for nickel, vanadium, copper, and iron. These are the metals commonly associated with problems in the upgrading process.

Carbon Residue

Conradson carbon residue (CCR) and microcarbon residue (MCR) tests were performed on the whole samples. MCR were determined for the asphaltenes and aromatic, and polar fractions from each sample. The microcarbon residue test, which uses less than 1 g of sample, correlates with the Conradson carbon residue test, which consumes 5-10 g sample (Long and Speight, 1989). These values are believed to relate to coking behavior in a refinery (Gary and Handwerk, 1984; Speight, 1991). The contributions of skeletal structure and functional groups in petroleum residua constituents to coking behavior is a possible area for future work.

Molecular Weight

Molecular weight and molecular size are the most misunderstood parameters of petroleum constituents. There are many reports of molecular weights in the 100.000-300.000 range (Speight *et al.*, 1987). However, molecular weights in this range are not realistic and true values for even the most high molecular weight constituents, the asphaltenes, very rarely exceed 3.000. The molecular weights of the constituents are extremely important because molecular weight plays a role in determining physical properties and behavior. In the same manner, molecular size can effectively determine the potential for any polar constituent to participate in any inter- and intramolecular interactions. Vapor pressure osmometry (VPO) measurements were performed on the residua, the asphaltenes, the saturate, aromatic, and polar fractions, and the four preparative size exclusion fractions from the asphaltenes. Although pyridine would be considered more desirable for breaking up molecular associations between more polar petroleum materials, toluene was used in the present study at 60°C (140°F) according to ASTM D250 since complete solubility could not be achieved in pyridine for residua asphaltenes.

1 EXPERIMENTAL

1.1 Samples

The samples were nominal 950+°F (510+°C) residua provided by and Mobil. The residua were labeled A through F for proprietary reasons. Portions of the residua were poured into glass jars with Teflon-lined lids after heating in an oven at about 190-230°F (88-110°C) under an inert gas flow. They were stored under nitrogen at 44°F (7°C).

1.2 Separation and Analyses

Details of the separations and the analytical procedures used are provided elsewhere (Schabron *et al.*, 1993).

2 RESULTS AND DISCUSSION

2.1 Separation and Characterization

The data presented in Table 1 demonstrate the overall approach used for residua characterization and to compare the various key features of the residua. A major emphasis is the properties of the asphaltenes as they relate to carbon residue results. All but two of the residua, C and E, which are waxy materials, have specific gravities greater than 1. The presence of wax was apparent in the results of many of the characterization analyses. The pour points of the six residua ranged from 90-205°F (32-96°C). The results of simulated distillation showed that the amount of material distilled by 950°F (510°C) ranged from 0.79-11.33 wt.% for the six residua. At 1.000°F (538°C), the range was from 4.17-14.68 wt.%. Total recoveries for the SAPA separations for the six residua were good, ranging from 99.5-102.8 wt.%. A blank run without sample was performed with the silica gel column. The blank values were calculated based on a typical maltene loading of 16 g. The results showed a blank contribution of 0.18 wt.% each for the saturate and polar fractions, and 0.22 wt.% for the aromatic fraction.

The molecular weight data (Table 2) show that there is little difference in molecular weights for the saturate fractions for the six residua. These range from 668-720 g/mole. A similar observation can be made for the aromatic fractions (718-860 g/mole) and polar fractions

TABLE 1
Analytical data for six residua

	Residuum					
	A	B	C	D	E	F
Specific Gravity, 140°F(60°)	1.034	1.050	0.977	1.011	0.972	1.025
Elemental, wt. %						
C	84.1	84.2	86.7	84.2	86.9	85.6
H	9.9	9.7	12.5	10.5	11.6	10.3
N	0.7	0.6	0.4	0.4	0.4	0.4
O	0.7	0.7	0.7	0.4	0.5	1.0
S	5.6	5.6	0.4	5.8	1.3	2.0
H/C Ratio	1.4	1.4	1.7	1.5	1.6	1.4
Carbon Residue, wt. %						
CCR	25.6	29.2	7.5	15.9	9.7	16.7
MCR	25.8	28.2	8.8	17.4	11.0	20.4
Metals, mg/kg						
Ni	116	108	23.7	29.0	11.0	176
V	612	526	5.2	92.3	34.8	174
Fe	13.2	39.5	38.4	9.1	16.8	72.4
Cu	<2	<2	<2	<2	2.1	<2
Separation, wt. %						
Saturate	10.8	11.8	45.7	18.9	27.5	6.3
Aromatic	48.4	45.0	25.8	61.2	54.7	47.1
Polar	11.1	11.4	12.0	12.2	14.9	37.4
Asphaltenes	29.2	32.4	16.4	8.6	4.4	12.0

TABLE 2
VPO number average molecular weights of residua fractions (toluene, g/mole)

	Residuum					
	A	B	C	D	E	F
Saturate	700	720	690	668	693	692
Aromatic	860	850	820	796	718	773
Polar ^a	1.300	1.220	1.250	1.500	1.000	1.200
Asphaltenes ^a	4.150	3.590	1.210	5.850	2.500	4.400

^a Measured at three concentrations, extrapolated to zero concentration.

(1.000-1.500 g/mole), respectively. The largest difference for the residua occurs in the asphaltenes, with apparent molecular weights ranging from 1.210-5.850 g/mole. The lowest asphaltene molecular weights occur for the two waxy residua, C (1.200 g/mole) and E (2.500 g/mole).

2.2 Process Modeling

The development of models to predict the refinability of refinery feedstocks is not new. However, what is needed is the ability to apply the model to various feedstocks with some degree of confidence.

An early model worthy of note was developed (Speight, 1981 and references therein) as a series of formulae for estimating product yields from delayed coking operations for two different feedstocks:

– Wilmington crude oil residuum

$$\text{Coke, wt.}\% = 39.68 - 1.60 \times \text{°API}$$

$$\text{Gas (< C}_4\text{), wt.}\% = 11.27 - 0.14 \times \text{°API}$$

$$\text{Gasoline, wt.}\% = 20.5 - 0.36 \times \text{°API}$$

– East Texas crude oil residuum

$$\text{Coke, wt.}\% = 45.76 - 1.78 \times \text{°API}$$

$$\text{Gas (< C}_4\text{), wt.}\% = 11.92 - 0.16 \times \text{°API}$$

$$\text{Gasoline, wt.}\% = 20.5 - 0.36 \times \text{°API}$$

More recently, models for the prediction of asphaltene behavior during refining, more particularly the onset of phase separation that leads to coke deposition have also been developed (Wiehe, 1993). Application of this model to the behavior of asphaltenes during processing offers new insights into the predictability of feedstock behavior.

Therefore, other avenues were also sought that might aid in predictability of feedstocks in general rather than use of one particular fraction, recognizing that interaction of the fractions might exert some influence during processing. In this work, the simplest tests were used to provide data for the models, on the basis that the simpler the means by which the data are derived, the more valuable the model.

2.3 Correlation of Asphaltene Content with Carbon Residue

Asphaltene content provides a rough correlation with carbon residue values (Speight, 1994). For the six residua evaluated in the present study, the correlation between percent asphaltenes and CCR yields a correlation coefficient (*r*) value of only 0.8272. It is not only the amount of asphaltenes present, but their composition which affects residue formation.

The presence of waxy materials from the waxy crudes, which will not form much association and residue, and the presence of heteroatoms, which can enhance residue formation needs to be accounted for. A fine tuning of this correlation can be achieved by including considerations for the association effects due

to the polarity or wax content, and heteroatom content of the asphaltenes. The elemental analysis results for the asphaltenes and 3-point molecular weights in toluene extrapolated to zero concentration and the apparent molecular weight values are a function of association in the toluene solvent under measurement conditions (Table 3). These can, however, be used to adjust the asphaltene content for the presence of relatively non-associative species due to the presence of waxes, or highly associative species.

TABLE 3
Analytical data for asphaltenes

Elemental Composition, wt. %						
Asphaltene	VPO MW	C	H	N	O	S
A	4.150	83.4	7.7	1.5	1.0	7.2
B	3.590	83.5	7.5	1.4	1.1	7.3
C	1.210	86.8	11.8	0.5	1.1	0.3
D	5.850	82.4	7.6	1.0	0.8	8.4
E	2.500	86.4	8.8	1.0	1.4	2.2
F	4.400	84.7	8.4	2.5	1.7	2.2

The heteroatom content also plays a role in association and residue-forming tendency. A correlation factor which relates well to Conradson carbon residue values is obtained by multiplying the weight percent of asphaltenes in the residuum times the molecular weight in toluene times the fractional heteroatom content of the asphaltenes (1.00 – fractional C + H content) (Table 4 and Fig. 1).

The correlation coefficient for the six residua in this study is 0.9780 and the correlation with the microcarbon residues values is similar. The heteroatom content also could be expressed as fractional content of (N+O+S) in the asphaltenes with essentially identical results and the correlation worsens somewhat if not all three heteroatoms are included. For example, if sulfur content is ignored, and only (N+O) content is used, the correlation coefficient drops to 0.7733. The effect is less dramatic if N or O are selectively ignored, with resulting correlation coefficients of 0.9650 and 0.9655, respectively.

If the heteroatom content is not considered, a reasonably good relationship with carbon residue can still be obtained by multiplying the fractional asphaltene content by the molecular weight, resulting

TABLE 4
CCR correlation factor for asphaltenes

Asphaltene	VPO MW	Fraction in Residuum	$\times 1 - \text{Fraction (H+C)}$	Correlation Factor (unitless)	CCR, wt. %
A	4.150	0.292	0.089	108	25.6
B	3.590	0.324	0.090	105	29.2
C	1.210	0.164	0.014	2.78	7.5
D	5.850	0.086	0.100	50.3	15.9
E	2.500	0.044	0.048	5.28	9.7
F	4.400	0.120	0.069	36.4	16.7

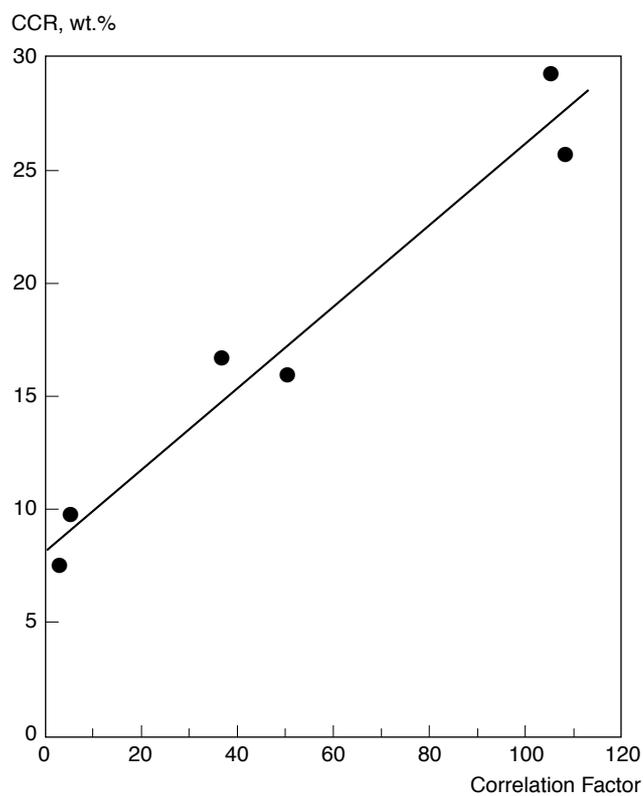


Figure 1
Asphaltene carbon residue correlation factor six residua.

in a correlation coefficient of 0.9740. Only by adding to the data set with the characterization of additional residua will the relative importance of total heteroatom content to the correlation be discerned.

These results suggest that the makeup of the asphaltenes is key to residue forming tendencies in residua, and that the factors which affect this makeup are represented by the amount of asphaltenes in the residuum, the apparent molecular weight of the asphaltenes, or measure of association tendency, and total heteroatom (N+O+S) content. The correlation holds when asphaltenes, which are the major contributors to residue are present, but constituents in the non-asphaltene fractions also contribute to carbon residue formation (Speight, 1994).

The correlation was developed with six specific residua. The asphaltenes were isolated from the residua with *n*-heptane without prior dissolution in a solvent such as toluene which can drastically affect results, and the molecular weight measurements were made in toluene. Data not obtained in an identical manner should not be used to add to the data set. The expression for the correlation can be substituted into the previously published equations (Gary and Handwerk, 1984) relating carbon residue to delayed coking product yield for a variety of petroleum residua:

$$\text{CCR} = 0.180 \times \text{Correlation Factor} + 8.19 \quad (\text{Fig. 1})$$

$$\text{Coke, wt.\%} = 1.6 \times \text{CCR} \quad (\text{Gary and Handwerk, 1984})$$

$$\text{Coke, wt.\%} = 0.288 \times \text{Correlation Factor} + 13.1$$

$$\text{Gas (<C}_4\text{), wt.\%} = 7.8 + 0.144 \times \text{CCR} \quad (\text{Gary and Handwerk, 1984})$$

$$\text{Gas (<C}_4\text{), wt.\%} = 0.0259 \times \text{Correlation Factor} + 8.98$$

$$\text{Gasoline, wt.\%} = 11.29 + 0.343 \times \text{CCR} \quad (\text{Gary and Handwerk, 1984})$$

$$\text{Gasoline, wt.\%} = 0.0617 \times \text{Correlation Factor} + 14.10$$

Substituting the new correlation into these equations allows us to predict yields of coke, gas, and gasoline for six residua from knowledge of the asphaltenes alone. This includes residua heptane asphaltene content, the VPO molecular weight of the asphaltenes in toluene, and the asphaltene heteroatom content.

2.4 Preparative Size Exclusion Chromatography of Asphaltene

To further define the composition of the six asphaltenes, the asphaltenes were separated by preparative size exclusion chromatography into four fractions of approximate equal weight (4 g) which were characterized (Tables 5-10).

For the size exclusion fractions from the asphaltenes, there appears to be almost uniform distribution with a very slight decrease in sulfur for any particular residuum from Fractions I-IV. The only exception is the low molecular weight SEC IV fraction from Residuum E, which is probably waxes. The molecular weights decreased dramatically in the order: SEC I > SEC II > SEC III > SEC IV. The apparent molecular weight for the SEC I fraction for Residuum F, for example is 22.130 g/mole while the SEC IV fraction molecular weight is 1.650 g/mole. The material balance calculated for the whole asphaltene from the molecular weights of the size exclusion fractions is 4.670 g/mole, which compares well with the measured value of 4.440 g/mole. This and similar data for the other five residua asphaltenes suggests that the very large apparent molecular weights observed for the isolated SEC I fractions exist in the total asphaltene material as well. Thus, the SEC I fractions isolated from residua asphaltenes could provide a useful material for studying coking mechanisms.

The waxy residua, C and E show a significant drop in metals content in the low molecular weight SEC IV asphaltene fraction as compared to the other residua, where the decrease is less dramatic. This is probably due to the concentration of significant amounts of paraffinic waxy material in the SEC IV fractions from the waxy residua. By definition of heptane asphaltenes as a solubility class, these will contain high molecular weight waxes which are not soluble in heptane.

The material balances for the various characterization parameters were consistent with proportional contributions from the size exclusion asphaltene fractions for all six residua. This indicates that the contributions from the parts add up to the whole. Therefore, by studying the highest molecular weight asphaltene material (SEC I) in more detail, valuable insight into the residue forming/coking mechanism could be gained. These materials, which exhibit very high apparent molecular weights, are the "bad" part of the "bad" actors in the upgrading process.

TABLE 5
Size exclusion chromatography fraction analysis (Asphaltene A)

	SEC Fraction					Mass Balance to Whole
	Asphaltene	I High MW	II Med/High MW	III Med/Low MW	IV Low MW	
S, wt. %	7.2	7.5	7.5	7.4	6.5	7.2
Metals, mg/kg						
Ni	324	367	347	325	218	314
V	1.680	1.740	1.700	1.640	1.620	1.680
Fe	25.6	38.6	30.4	23.2	18.6	27.8
Cu	<2	<2	<2	<2	<2	<2
VPO MW g/mole	4.150	41.000	21.900	13.800	1.590	5.180

TABLE 6
Size exclusion chromatography fraction analysis (Asphaltene B)

	SEC Fraction					Mass Balance to Whole
	Asphaltene	I High MW	II Med/High MW	III Med/Low MW	IV Low MW	
S, wt. %	7.3	7.4	7.4	7.4	6.9	7.3
Metals, mg/kg						
Ni	276	310	296	286	183	265
V	1.320	1.380	1.340	1.320	1.080	1.270
Fe	102	69.2	56.4	53.0	22.6	49.2
Cu	<2	<2	<2	<2	<2	<2
VPO MW g/mole	3.590	42.500	22.500	15.300	1.670	4.920

TABLE 7
Size exclusion chromatography fraction analysis (Asphaltene C)

	SEC Fraction					Mass Balance to Whole
	Asphaltene	I High MW	II Med/High MW	III Med/Low MW	IV Low MW	
S, wt. %	0.3	0.5	0.4	0.3	0.3	0.4
Metals, mg/kg						
Ni	90.0	164	119	74.2	29.6	93.0
V	19.4	35.1	25.5	18.2	9.6	21.4
Fe	192	289	177	180	39.0	166
Cu	7.8	6.7	4.3	3.2	<2	3.4
VPO MW g/mole	1.210	2.570	1.920	1.190	700	1.210

TABLE 8
Size exclusion chromatography fraction analysis (Asphaltene D)

	SEC Fraction					Mass Balance to Whole
	Asphaltene	I High MW	II Med/High MW	III Med/Low MW	IV Low MW	
S, wt. %	8.4	8.5	8.6	8.6	7.8	8.4
Metals, mg/kg						
Ni	158	196	174	163	85.7	158
V	534	580	545	537	424	527
Fe	75.4	84.8	59.8	64.5	27.2	61.0
Cu	2.5	<2	<2	2.8	<2	<2
VPO MW g/mole	5.850	17.700	13.200	10.300	1.640	5.320

TABLE 9
Size exclusion chromatography fraction analysis (Asphaltene E)

	SEC Fraction					Mass Balance to Whole
	Asphaltene	I High MW	II Med/High MW	III Med/Low MW	IV Low MW	
S, wt. %	2.2	2.8	2.7	2.2	0.8	2.2
Metals, mg/kg						
Ni	89.9	139	126	69.5	13.2	92.2
V	337	482	409	272	75.9	326
Fe	132	162	102	77.7	40.1	99.1
Cu	4.0	5.9	2.3	<2	4.5	3.1
VPO MW g/mole	2.500	24.900	7.870	2.220	762	2.350

TABLE 10
Size exclusion chromatography fraction analysis (Asphaltene F)

	SEC Fraction					Mass Balance to Whole
	Asphaltene	I High MW	II Med/High MW	III Med/Low MW	IV Low MW	
S, wt. %	2.2	2.4	2.3	2.4	2.1	2.3
Metals, mg/kg						
Ni	476	445	429	418	571	467
V	655	604	586	609	745	638
Fe	343	372	322	313	105	274
Cu	2.2	<2	<2	<2	<2	<2
VPO MW g/mole	4.400	22.130	13.720	9.940	1.650	4.670

CONCLUSION

Petroleum residua can be effectively characterized using a fairly simple analytical scheme. The analytical scheme distinguishes different residua from one another and each has a characteristic composition (SAPA) pattern. For the most part, the material balances show that the data obtained on the fractions and asphaltenes account for the data obtained on the original material. Thus, the contribution of the fractions and asphaltenes to properties observed in the whole residuum can be estimated. The product of the apparent molecular weight of the whole asphaltenes, the percent of asphaltenes in the whole residuum, and the heteroatom content of the asphaltenes correlates well with carbon residue data, and thus can be used to predict delayed-coking product yields.

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DISCLAIMER

Mention of specific brand names or models of equipment is for information only and does not imply endorsement of any particular brand.

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