

THE CHARACTERIZATION OF RESIDUAL HYDROCARBON FRACTIONS WITH MODEL COMPOUNDS RETAINING THE ESSENTIAL INFORMATION

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ABSTRACT

A characterization method for heavy residues is proposed. It has been specifically studied for the characterization of high molecular weight mixtures, with the aim of modeling thermal conversion processes such as thermal cracking, Eureka, visbreaking and delayed coking. Only essential commonly available information is necessary. Extensive data based on the use of the Boduszynski-Altgelt methodology based on short-path molecular distillation (DISTACT), sequential elution fractionation technique (SEF) and vapor phase osmometry analyses (VPO), are surprisingly well reproduced. The results also match ^1H and ^{13}C NMR analyses. The proposed model is a valuable tool when complex and lengthy analyses are unavailable as is usually the case.

INTRODUCTION

The use of model compounds and mechanistic kinetic schemes has significantly improved the quality of product characterization when modeling the pyrolysis of high molecular weight mixtures.

Good characterization of the feed is crucial if reliable predictions of yield and quality of products based on mechanistic models are required. The availability of suitable data for heavy fractions is often a problem. In general, only a single density and average molecular weight (or kinematic viscosity) together with the initial boiling point range are available, while the whole distribution of these properties is actually required.

The higher the boiling point of a hydrocarbon fraction, the more difficult its characterization becomes. While the composition of naphthas can be determined, middle distillates can only be described in terms of their constituent groups and for heavy fractions the situation is far more complicated.

Since petroleum products are usually specified by their distillation properties, the boiling range often becomes more important than the actual molecular composition. Thermal cracking limits the cut points in commercial atmospheric and vacuum distillations to 350 and 540 C, respectively. In the laboratory, the use of high-vacuum short-path 'molecular' distillation (DISTACT) allows atmospheric equivalent boiling points (AEBP) of 700 C to be obtained.

Researchers often rely on solubility relations to characterize streams. These are arbitrary in the sense that the results depend on the solvents chosen, the temperatures, contact time, the relative quantities used in the treatment and on the agitation conditions, which results in obvious difficulties when comparing results of different scientists.

Distillation followed by a sequential elution fractionation (SEF) has been proposed by Boduszynski (1). This constitutes a better alternative because it avoids the problems derived from the strictly operational and therefore vague definition of asphaltenes, maltenes and resins (2).

Dente and Bozzano recently developed a global kinetic mechanism for visbreaking and delayed coking. A basic point of their activity has been the definition of model compounds in order to reduce the extremely large number of reactions and involved components in a sufficiently representative kinetic scheme. Using a combination of statistical methods, model compounds have been defined which give a good representation of the dominant phenomena involved.

Starting from the resulting distribution curves of the boiling point, kinematic viscosity or molecular weight, specific gravity and sulfur content, reactants and products can be lumped into a discrete number of pseudocomponents having fixed or varying properties. Alternatively, they can be represented as a mixture of model compounds (3).

METHOD

The feed (atmospheric and vacuum distillation residues) has been characterized by Dente and Bozzano (4) as a mixture of paraffinic, naphthenic and aromatic model compound. The relative amounts can be derived from the above mentioned macroscopic properties.

Once the total amounts of the three different classes of components have been estimated, it is possible to deduce the relative amounts of the pseudocomponents in the class. In fact, a careful elaboration of the data published in the literature (see, for instance, ref. 5), has shown that the statistical distribution of the single pseudocomponents with n_c carbon atoms (in every class) takes the form:

$$\frac{df}{dn_c} = k \exp[-k(n_c - n_{c,\min})] \quad \text{Equation 1}$$

where k is obtained from the average number of carbon atoms of the distribution

$$k = \frac{1}{n_{c,\text{med}} - n_{c,\min}} \quad \text{Equation 2}$$

where:

- f = fraction of the single component on the total of the class
- $n_{c,\text{med}}$ = average number of carbon atoms of the class
- $n_{c,\min}$ = minimum number of carbon atoms of the class
- the index k depends on the class (paraffins, "aromatics", etc.) of components involved

The lumping rule typically groups 5 by 5 carbon atoms, from the minimum number to 58 carbon atoms; above this the splitting rule is 10 by 10 carbon atoms. For more than 98 carbon atoms an equivalent pseudocomponent is assumed to be representative of all the rest. A similar grouping rule can also be applied to the pyrolysis products. Of course, more complicated intrinsic rules are implied for multiple ring components (such as condensed rings polyaromatics and so on). The model compound characteristics can be summarized as follows:

- PAREQ - paraffin with 20% of methylation (i.e. 20% of carbon atoms is in a methyl group). The methylation degree has been deduced by assuming a prevalent polyisoprenoid structure for i-paraffins and a relative amount of n-paraffins into equivalent paraffinic pseudocomponent of about 20%.
- ARO0 - polyaromatic sheet with 50% of methylation at the boundaries and a single alkyl side chain with 20% of methylation. A distribution of all such possibilities includes a proportionality assumption between the molar fractions and the number of aromatic atoms in the molecules. The side chain size of this distribution is averaged and a single average aromatic molecule results which is defined solely by the number of carbon atoms. NMR data of some residues satisfactorily confirm the assumed methylation degree on the aromatic sheet boundary (typically in the range of 0.4-0.5). A direct proportionality between carbon atoms number and aromatic rings in the molecule is present.
- NAFTO0 - a polynaphthenic sheet with 50% of methylation at the boundaries and a single alkyl side chain with 20% of methylation. As in the case of aromatics, an internal distribution into the molecules is assumed. Contrary to the case of aromatic components, the major probabilities are in favor of structures with few rings and long side chains (as is possible to deduce from the API Research Project 60 where naphthenes contained in vacuum gasoil fractions extracted by chromatography are reported). There is, in consequence, an inverse proportionality between number of C atoms and number of rings in the molecule.

The relative amounts of paraffins, aromatics and naphthenes can be estimated from other feed properties and if the carbon distribution for each of the ARO0, NAFTO0 and PAREQ classes is known, the feed is completely characterized. The average number of carbon atoms of each compound class can be calculated to satisfy the global molecular weight and H/C relation. The minimum number of carbon atoms is calculated from the initial boiling point of the feed (Equation 3). For a given number of carbon atoms, the aromatic molecules will boil at higher temperatures than the paraffins, since their specific gravity is higher.

$$MW_{AEBP>500F} = 140 + 3.40 \times 10^{-7} \frac{AEBP^3}{SPGR^{2.5}} \quad \text{Equation 3}$$

$$MW_{AEBP<500F} = MW_{AEBP>500F} \left[1 - 1.4 \times 10^{-4} (600 - AEBP) \right]$$

Partial volumes at 20 C can be calculated using the group contribution method of Hirsch (6). These have been adjusted to 15.5 C with the Rackett equation modified by Yamada and Gunn (7). The additive methods of Schroeder (8) and Le Bas (9), which give surprisingly good values for the molal volume of small hydrocarbon molecules at saturation temperature, show strong discrepancies when compared with the method of Hirsch, which has been developed for heavy fractions.

Dente and Bozzano (4) have pointed out the importance of performing corrections for sulfur before appropriate estimates of the content of paraffins, naphthenes and aromatics (and the H/C ratio) are possible. An equivalent hydrocarbon density is defined as

$$\rho_{eq} = \rho - 0.0066(S\%) \quad \text{Equation 4}$$

RESULTS AND DISCUSSION

The predictions of the procedure are compared with experimental data (available only up to C₁₇) and (calculated) results from the API Research Project 44 (1972) (Figure 1). The agreement is good with the PAREQ curve fitting the data for paraffins fairly well and the ARO0 curve located somewhere between the paraffins and the pure aromatics compounds (the ARO0 compounds are alkyl substituted aromatics). The aromatic curve in Figure 1 results from applying the methodology described above for purely aromatic structures. In this case, the agreement can be seen to be also good.

In Figure 2, a comparison is made with experimental data for Kern River petroleum (2), which is a highly biodegraded crude. As can be seen, its constituents can be considered to be a mixture of paraffinic, naphthenic and aromatic model compounds up to 700 C, which is the current experimental limit. This figure also implies that fractions up to 400 C are mainly paraffinic.

The corresponding molecular weight distribution matches the experimental data of Boduszynski (10) remarkably well, as can be seen in figure 3. The actual matching can be even better than that presented here, since the molecular weight for the last fraction has been measured with vapor pressure osmometry (VPO) using two different solvents. While the results differ, the true MW for this fraction is probably lower than the value measured with the most efficient solvent shown in Figure 3.

Figure 4 presents the molecular weight distribution obtained for an atmospheric residue of an Arabian Heavy crude. The agreement between calculated and experimental results is also good.

Since equation 3 has been developed using a series of petroleum distillations, including Kern River and Arabian Heavy crudes (11,12), the agreement in AEBPs is implicitly good.

Table 1 provides a comparison in terms of some functional groups determined from ¹H and ¹³C NMR analyses applied to a vacuum residue of Baiano petroleum (a light paraffinic crude).

CONCLUSIONS

The methodology described here gives a fairly good characterization of boiling points and molecular weights for residual fractions based on initial boiling point, sulfur content, average specific gravity and molecular weight (or kinematic viscosity).

The feed characterization predicted reproduces the results of NMR and VPO-DISTACT analyses and seems to constitute a viable route for investigating the composition of residual fractions. An important application would be in the modeling of typical resid upgrade processes such as visbreaking and delayed coking (13). In this case, a good definition of residence times for the liquid phase, where the most reactive components are concentrated is necessary.

Since the maximum temperature in these processes is around 500 C, fractions boiling above this will remain mainly in the liquid phase and precise definition of the true boiling point is not required.

Nevertheless, the molecular weight distribution (number of carbon atoms) is of great importance because it affects flash calculations, solubility relations (for precipitation of precursors in coking) and defines the system reaction state and residence time.

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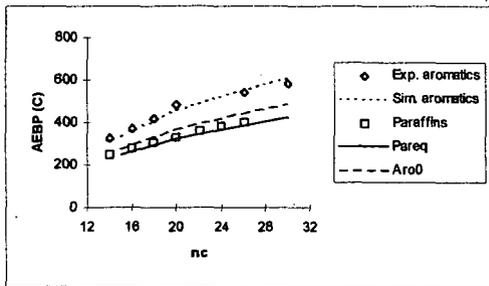


Figure 1 Atmospheric equivalent boiling points as a function of the number of carbon atoms for the model compounds of Dente and Bozzano (1994).

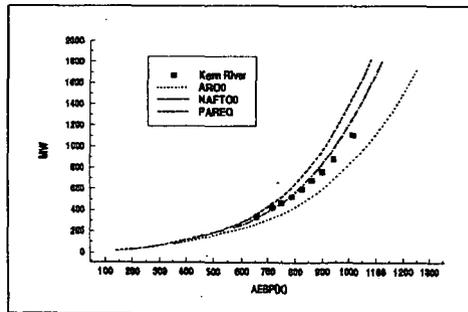


Figure 2 MW vs. AEBP representation of PAREQ/ARO0/NAFT00 model compounds.

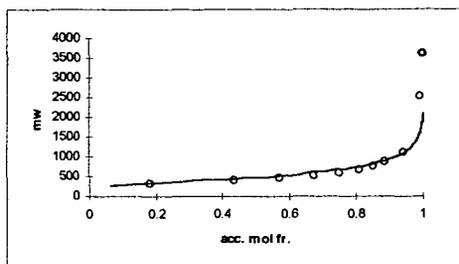


Figure 3 Molecular weight distribution for Kern River residue.

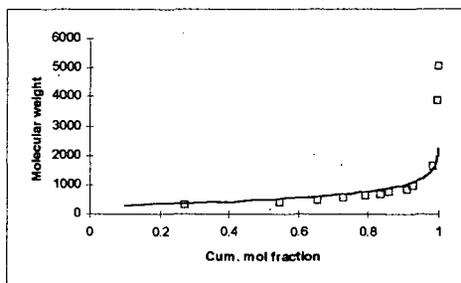


Figure 4 Molecular weight distribution for atmospheric residue of Arabian Heavy crude.

Table 1 Results for VR Baiano.

	Model	NMR data
H/C	1.89	1.80
C _{ar}	11.1	15.4
C _{Ar,H}	4.0	4.3
C _{Ar,CH3}	3.1	4.0
avg. size of side chains	22.2	26.5
C _{sat}	88.9	84.6
(H/C) _{sat}	2.05	2.02