

RELATIONSHIPS BETWEEN THE CHARACTERISTICS OF  
PETROLEUM FEEDSTOCKS AND THE GRAPHITIZABILITY OF THEIR PETROLEUM COKES

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INTRODUCTION

Many investigators have found that the physical properties of petroleum coke are very much dependent upon the composition and characteristics of the feed stocks used to make the coke.

In order to determine the relationships between the characteristics of the raw materials and the physical properties of petroleum cokes derived therefrom, investigations were undertaken to study the carbonization and graphitization processes for various petroleum fractions.

EXPERIMENTAL

Sumatran Light vacuum residue (S/L VR), Sumatran Light vacuum distillate (S/L VD) and Decant Oil from a catalytic cracking process were used as samples. S/L VR was fractionated into saturates, aromatics, resins and asphaltenes by the alumina adsorption method. S/L VD and Decant Oil were separated into saturates and aromatics by the solvent extraction method. Each fraction was subjected to determine the data of density, Conradson carbon, elementary analysis, molecular weight and Nuclear Magnetic Resonance (NMR) measurement. And then, the chemical structural parameters were computed.

Each fraction was carbonized in an autoclave under a pressure of 20 kg/cm<sup>2</sup> (gauge) at increasing temperatures. The fluidity of each fraction during the mesophase transformation was monitored by a Gieseler-type plastometer. The coke products were examined by a scanning electron microscope and a polarized light microscope.

The coke product from each sample was graphitized by heat-treating at 2,600°C for 30 minutes under a nitrogen atmosphere. The graphitized coke was characterized by X-ray diffractometry. The peak intensity I(002) was determined from (002) diffraction peak, which was normalized by the internal standard method.

RESULTS AND DISCUSSION

The composition and properties of petroleum vacuum residue, vacuum distillate, decant oil and their fractions are shown in Table 1. The hydrogen distributions determined from NMR data and structural parameters are summarized in Table 2 (procedure based upon Yamada et al (1)). As can be seen from Table 2, there were considerable differences in chemical structural parameters for the various fractions.

From microscopic observations, the coke derived from saturate fraction showed a generally fibrous texture. On the other hand, coke derived from resin and asphaltene fractions primarily exhibited a mosaic texture, sometimes with pores.

The fluidity curves for S/L VR fractions during carbonization are shown in Fig. 1. The saturate fraction solidified at about 538°C, the

aromatic fraction at 535°C, the resin fraction at 514°C, and the asphaltene fraction at 507°C. For saturates, the liquid state was maintained sufficiently long during the stage of mesophase transformation such that a needle-like coke was formed, as observed microscopically.

With regard to asphaltenes and resins, on the other hand, owing to the relatively low solidification temperature, the growth of mesophase would be suppressed and consequently a mosaic-like texture would be observed. White and Price (2) proposed that it would be convenient to interpret the mesophase transformation reaction by dividing it into fast-reacting and slow-reacting components. That is to say, the former may correspond to asphaltenes and resins, while the latter would be attributed to saturates.

The saturate fraction from S/L VR was heat-treated in an autoclave under a pressure of 20 kg/cm<sup>2</sup> (gauge) at 450°C, at various residence times from 15 to 75 minutes. The saturates heat-treated for 15 minutes were in an isotropic liquid phase until the appearance of spherical bodies. From the component analysis the fa value increased from 0.12 to 0.54 and the molecular weight decreased from 880 to 490. The nucleation and growth of spherical bodies occurred progressively with increasing residence time from 45 minutes to 75 minutes. On the basis of these observations it would be postulated that the mesophase system was converted into a needle-like coke by further heat-treating.

Figure 2 shows the relationships between the X-ray peak intensity I(002) for each graphitized coke and the C/H atomic ratio of the feed materials. This figure shows that the degree of graphitizability of the fractions correlates with the C/H ratios; that is, in decreasing order of graphitizability, saturates > parent residue > aromatics > resins > asphaltenes. This tendency is similar to that of the fluidity behavior previously shown in Fig. 1.

To further clarify the relationships between raw material characteristics and coke quality, trials were conducted to relate the chemical structural parameters shown in Table 2 and X-ray peak intensity I(002). It was generally found that the smaller the value of R (the number of aromatic rings) or the smaller the value of CAL (the number of alkyl side chains), the higher the value of I(002). From these results, it is hypothesized that, if an aromatic ring has too many alkyl side chains, during condensation polymerization the product becomes crosslinked rather than stacked, thereby causing the degree of orientation of the crystallite to be poor.

Reference

- 1) Yamada Y., Furuta T., Sanada Y., Anal. Chem., **48** (11), 1637 (1976).
- 2) White J. L., Price R. J., Carbon **12**, 321 (1974).

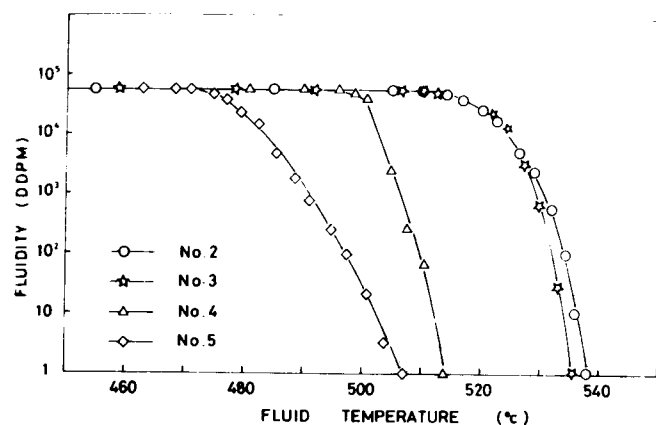
Table 1 Properties of sample used

Petroleum Feedstocks	Sample		Yields (wt%)	sp.gr. (15/4°C)	C.R. (wt%)	Mol. Wt. (VFO)	Elementary Analysis (wt%)		C/H Atomic Ratio	fa (M.R)
	Type	No.					C	H		
S/L VR	Original Oils	1	100.0	0.933	10.5	950	86.3	12.4	0.59	0.19
	Saturates	2	57.5	0.861	0.35	880	85.8	13.2	0.55	0.12
	Aromatics	3	28.8	1.013	23.3	1000	86.5	10.6	0.68	0.38
	Resins	4	11.0	1.018	38.1	1510	85.9	9.6	0.75	0.46
	Asphaltenes	5	1.4	1.059	58.0	2200	88.9	8.2	0.91	0.57
S/L VD	Original Oils	6	100	0.855	0.0	370	86.0	13.8	0.52	0.1
	Saturates	7	88	0.839	0.0	375	85.6	14.2	0.51	0.0
	Aromatics	8	12	1.002	1.4	270	86.8	9.5	0.77	0.53
Decant Oil	Original Oils	9	100	0.931	2.9	295	87.8	11.1	0.66	0.37
	Saturates	10	55	0.827	0.0	330	85.3	14.1	0.50	0.0
	Aromatics	11	45	1.109	7.9	250	91.3	7.4	1.04	0.78

Table 2 Results of hydrogen distribution and structural parameters of the fractions from petroleum feedstocks

Sample No.	Hydrogen Distribution (%)				Structural Parameter							
	H <sub>a</sub>	H <sub>α</sub>	H <sub>β</sub>	H <sub>γ</sub>	R	CPT	CIT	CA	CAL	CBL	CL	
1	1.7	14.0	68.6	15.7	8	20	14	6	3	47	5	
3	7.7	21.0	61.5	9.8	9	26	14	23	10	37	3	
4	10.5	22.2	58.7	8.6	14	32	26	47	18	40	4	
5	15.3	20.0	48.0	16.7	30	62	58	91	32	33	10	
8	16.0	30.9	38.4	13.8	3	10	4	10	4	5	1	
9	11.0	15.0	62.0	12.0	2	8	2	9	4	8	1	
11	41.0	41.0	14.0	4.0	4	12	6	14	3	2	1	

- R : Average number of total rings per molecule.  
 CPT : Number of peripheral carbon in a condensed aromatic sheet.  
 CIT : Number of internal carbon in a condensed aromatic sheet.  
 CA : Total aromatic carbon atoms per molecule.  
 CAL : Number of aliphatic carbon atoms alpha to a condensed aromatic sheet.  
 CBL : Number of carbon atoms other than CAL, CL to a condensed aromatic sheet.  
 CL : Number of aliphatic carbon atoms gamma or further to a condensed aromatic sheet.



- No. 2 Saturates  
 No. 3 Aromatics  
 No. 4 Resins  
 No. 5 Asphaltenes

Fig. 1 Fluidity curve for mesophase formed in sample No. 2, 3, 4, 5 (from S/L VR)

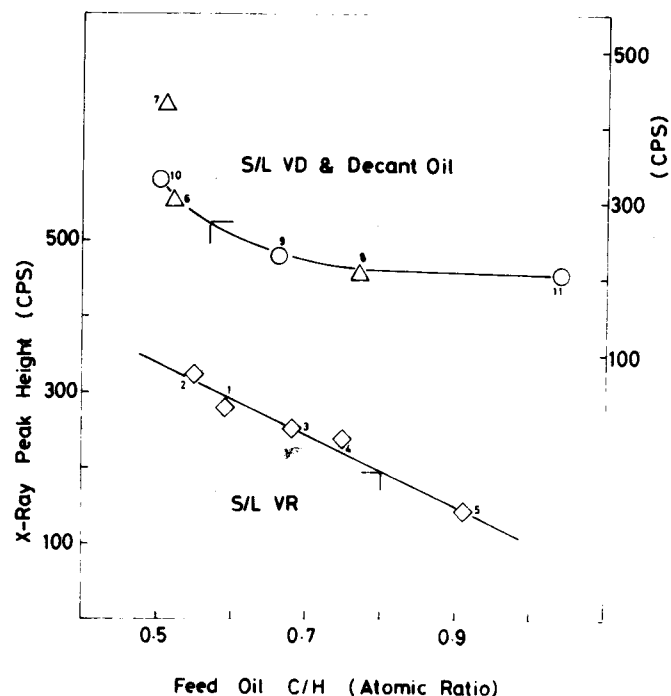


Fig. 2 X-ray peak height of cokes after 2600°C treatment