Relationships between the characteristics of petroleum feedstocks and the graphitizability of the petroleum cokes

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To clarify relationships between characteristics of raw materials and physical properties of derived petroleum cokes, studies are made of the carbonization of petroleum fractions and the graphitization of cokes made by pyrolysis in an autoclave under constant pressures. The coke derived from the saturate fraction which has a low aromaticity had a needle coke structure. The fluidity of carbonization processes is important in controlling the microscopic texture of coke. A relationship was obtained between the chemical structural parameters of the fractions and X-ray peak intensity of the graphitized cokes derived therefrom. It was shown that coke quality had a bearing on the number of condensed aromatic rings and the substituted side chain groups of the raw materials.

1. Introduction

The physical properties of petroleum coke depend upon the composition and characteristics of the feedstocks [1–7]. Scott [1] determined that the thermal expansion coefficient, density and crystallite structure of the petroleum coke are influenced by the aromaticity of feedstocks and by contents of sulphur, metals and asphaltic compounds. Conditions of carbonization of the feedstocks such as heating rate and pyrolyzing temperature also influence the structure and properties of coke [6]. Scott and Folkins [8] commented on the effects that major processing variables during carbonization have on relations with properties of the petroleum cokes of metallurgical grade.

Petroleum feedstocks are composed of a saturate fraction, aromatic fraction, resin fraction and asphaltene fraction. In order to clarify the mechanism of carbonization, attention should be paid to the characteristics of carbonization and graphitization for each component of the feedstocks.

2. Experimental details
2.1. Materials
As starting materials, three petroleum feedstocks were selected; vacuum distillate and residue of Sumatran light crude oil and decant oil from a fluid catalytic cracking process. The vacuum residue was fractionated into saturate fraction (extracted by *n*-heptane), aromatic fraction (extracted by benzene), resin fraction (extracted by benzene and methanol mixture) and asphaltene fraction (insoluble in *n*-heptane) by means of the alumina adsorption method [9]. The vacuum distillate and decant oil were also separated into two fractions, saturate and aromatic, by a solvent extraction method.

Each fraction was subjected to elementary analysis, nuclear magnetic resonance (NMR) measurement and also determinations of density, Conradson carbon and molecular weight. A vapour pressure osmometer was used to determine molecular weights with benzil as a standard. NMR spectra were obtained with a high-resolution NMR spectrometer and by using tetramethylsilane (TMS) as internal standard. The aromaticity f_a of each fraction was calculated according to methods of Williams [10], and Bartle and Smith [11]. Chemical structural parameters were computed for each fraction from density, elementary analysis,

molecular weight and NMR spectra using a computer program [12].

2.2. Experimental techniques
Each fraction was carbonized in an autoclave under a constant pressure of 20 kg cm^{-2} (gauge) at a temperature in the range 450 to 500° C. Partially carbonized samples were obtained by interrupting the heating process at the desired stage. The fluidity of each fraction during carbonization was monitored by a modified Gieseler-type plastometer (ASTM Method D1812). The test was performed by applying a torque equivalent to 50 g weight to the stirrer and with a heating rate of 3° C min^{-1}. The observation of coke texture was made with scanning electron and polarized light microscopes. Sample preparation for microscopic observations was followed by techniques reported elsewhere [13]. The cokes obtained were heat-treated at 2600° C for 30 min in a flow of nitrogen. The graphitized coke was characterized by the peak intensity of the (0 0 2) diffraction line I(0 0 2). Ni-filtered CuK$_\alpha$ radiation produced at 30 kV and 10 mA. A small amount of corn starch was added to the powdered coke sample in order to pack the sample uniformly in an aluminium holder and to obtain better reproducibility of intensity measurements.

3. Results and discussion
3.1. Characteristics of petroleum feedstocks
In Tables I and II, the characteristics of each fraction of the petroleum feedstocks used are summarized. The values of density, Conradson carbon, C/H ratio, and aromaticity f_a, for the aromatic fractions are higher than those for the saturate fractions. The high f_a value of the aromatic fraction from decant oil is due to the low number of and/or the short length of alkyl side chains attached to the aromatic rings. The asphaltene fraction of the vacuum residue has the highest molecular weight. There are considerable differences in chemical structure among the different fractions. The value of R (the number of aromatic rings) and C_{al} (the number of alkyl side chains) for the aromatic fraction of the vacuum residue are larger than those for the decant oil and the vacuum distillate. From this result it is assumed that the aromatic fraction from the vacuum residue is composed of large molecules having rather complex structures.

The structural parameters of the saturate frac-

tions of petroleum feedstocks could not be computed. On the other hand, from NMR spectra showing weak hydrogen signals of aromatics (H_a) and naphthenes (H_β), we can say that there are small amounts of aromatic and naphthenic compounds within the saturate fractions.

3.2. Carbonization
3.2.1. Structures of cokes
The coke derived from original petroleum feedstocks themselves showed a complicated texture distribution along the vertical direction of an autoclave; for example, a fine mosaic texture in the lower portion and a fibrous texture in the upper portion in the case of Sumatran light vacuum residue. However, the coke obtained by carbonization of each fraction showed a uniform texture under the microscope. Polarized light micrographs of the cokes obtained from each fraction of petroleum feedstocks are shown in Fig. 1. Under pressure, the coke from the saturate fractions which had poor aromaticity generally showed a coarse fibrous texture (Fig. 1a,b,g,i). On the other hand, the coke from the resin and the asphaltene fractions of the vacuum residue primarily exhibited a mosaic texture, frequently with a number of small pores (Fig. 1d,e,f). These characteristics are summarized in Table III.

3.2.2. Fluidity behaviours
The fluidity curves for the fractions of the vacuum residue during carbonization are shown in Fig. 2. The ordinate shows the stirrer movement in dial divisions per minute (D.D.P.M.). 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. There is a certain correlation between fluidity change during carbonization and the microscopic texture of the coke obtained. For the saturate fraction, the liquid state was maintained sufficiently long during carbonization for the needle-like coke to be formed, as observed microscopically. For the asphaltene and resin fractions, on the other hand, owing to the relatively low solidification temperature and short duration in the liquid state, the growth of mesophase spheres would be suppressed and consequently a mosaic texture would be observed.

White and Price [3] proposed to divide the precursor components into two groups, fast- and slow-reacting components. According to the present study, the fast-reacting components may cor-

TABLE I Characteristics of the fractions of petroleum feedstocks used

Sample		Yield of fractionation (wt %)	Specific gravity (15/4° C)	Carbon residue (Conradson) (wt %)	Mol wt (vpo)	Elementary Analysis (wt %)				C/H atomic ratio	Aromaticity f_a
Petroleum feedstocks	Type					C	H	N	S		
Vacuum residue	Original oil	100.0	0.933	10.5	950	86.3	12.4	0.3	0.24	0.59	0.19
	Saturates	57.5	0.861	0.35	880	85.8	13.2	0.2	0.0	0.55	0.12
	Aromatics	28.8	1.013	23.3	1000	86.5	10.6	0.8	0.52	0.68	0.38
	Resins	11.0	1.018	38.1	1510	85.9	9.6	1.0	0.53	0.75	0.46
	Asphaltenes	1.4	1.059	58.0	2200	88.9	8.2	1.4	0.89	0.91	0.57
Vacuum distillate	Original oil	100	0.855	0.0	370	86.0	13.8		0.10	0.52	0.1
	Saturates	88	0.839	0.0	375	85.6	14.2		0.04	0.51	0.0
	Aromatics	12	1.002	1.4	270	86.8	9.5		0.55	0.77	0.53
Decant oil	Original oil	100	0.931	2.9	295	87.8	11.1		0.85	0.66	0.37
	Saturates	55	0.827	0.0	330	85.3	14.1		0.12	0.50	0.0
	Aromatics	45	1.109	7.9	250	91.3	7.4		1.78	1.04	0.78

TABLE II Hydrogen distribution and structural parameters of the fractions of petroleum feedstocks used

Sample			Hydrogen distribution (%)					Structural parameters						
Petroleum feedstocks	Type	No.	H_a	H_α	H_β	H_γ	f_a	R	C_{PT}	C_{IT}	C_A	C_{AL}	C_{BL}	C_L
	Original oil	1	1.7	14.0	68.6	15.7	0.10	8	20	14	6	3	47	5
Vacuum residue	Saturates	2	3.4	14.7	73.7	8.2	–	–	–	–	–	–	–	–
	Aromatics	3	7.7	21.0	61.5	9.8	0.32	9	26	14	23	10	37	3
	Resins	4	10.5	22.2	58.7	8.6	0.43	14	32	26	47	18	40	4
	Asphaltenes	5	15.3	20.0	48.0	16.7	0.55	30	62	58	91	32	33	10
	Original oil	6	2.4	8.4	69.3	19.9	–	–	–	–	–	–	–	–
Vacuum distillate	Saturates	7	1.4	11.2	75.4	12.0	–	–	–	–	–	–	–	1
	Aromatics	8	16.9	30.9	38.4	13.8	0.50	3	10	4	10	4	5	1
	Original oil	9	11.0	15.0	62.0	12.0	0.41	2	8	2	9	4	8	1
Decant oil	Saturates	10	0.0	0.0	85.0	15.0	–	–	–	–	–	–	–	–
	Aromatics	11	41.0	41.0	14.0	4.0	0.74	4	12	6	14	3	2	1

H_a : hydrogen on aromatic rings.
H_α : hydrogen on carbon atoms alpha to aromatic rings.
H_β : hydrogen on paraffinic methylene, methine groups and naphthenes. Methylene groups beta or further from aromatic rings. Methyl groups beta to rings.
H_γ : hydrogen of paraffinic methyl and methyl gamma or further from aromatic rings.
f_a : ratio of aromatic carbon to total carbon.
R : average number of total rings per molecule.
C_{pt} : number of peripheral carbon in a condensed aromatic sheet.
C_{it} : number of internal carbon in a condensed aromatic sheet.
C_a : total aromatic carbon atoms per molecule.
C_{al} : number of aliphatic carbon atoms alpha to a condensed aromatic sheet.
C_{bl} : number of carbon atoms other than C_{AL}, C_L to a condensed aromatic sheet.
C_l : number of aliphatic carbon atoms gamma or further to a condensed aromatic sheet.
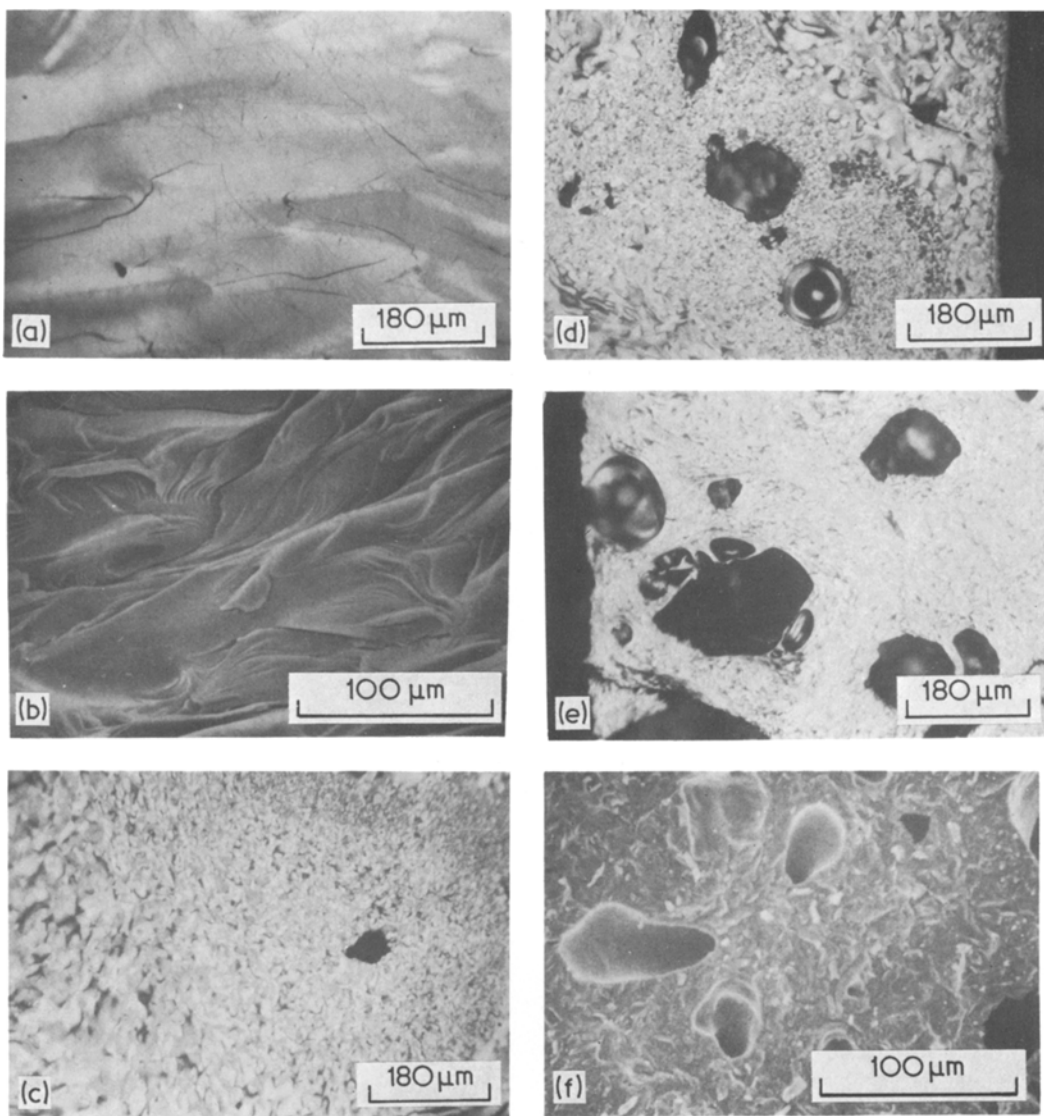
Figure 1 Polarized light micrographs (PLM) under crossed nicols and scanning electron micrographs (SEM) of the cokes obtained from various fractions. Raw cokes from saturate fraction of a vacuum residue (No. 2): (a) PLM; (b) SEM. Raw cokes from aromatic fraction of a vacuum residue (No. 3): (c) PLM. Raw cokes from resin fraction of a vacuum residue (No. 4): (d) PLM. Raw cokes from asphaltene fraction of a vacuum residue (No. 5): (e) PLM; (f) SEM. Raw cokes from saturate fraction of a vacuum distillate (No. 7): (g) PLM. Raw cokes from aromatic fraction of a vacuum distillate (No. 8): (h) PLM. Raw cokes from saturate fraction of a decant oil (No. 10): (i) PLM. Raw cokes from aromatic fraction of a decant oil (No. 11): (j) PLM.

respond to the asphaltene and resin fractions, while the slow-reacting components may be the saturate fraction.

By using the decant oil, the results from our previous studies on component analysis of the fractions and coking test [14] clearly show that the coefficient of thermal expansion (CTE) of cokes is related to the fluidity behaviour during carbonization. Therefore, we can say that to ob-

tain high-quality cokes having low CTE and a fibrous texture, the feedstocks should be kept in a liquid state for a long duration.

3.2.3. Mesophase formation in the saturate fraction of a vacuum residue

It was found that coke derived from the saturate fraction with poor aromaticity, shows fibrous texture under pressure as the liquid state of the
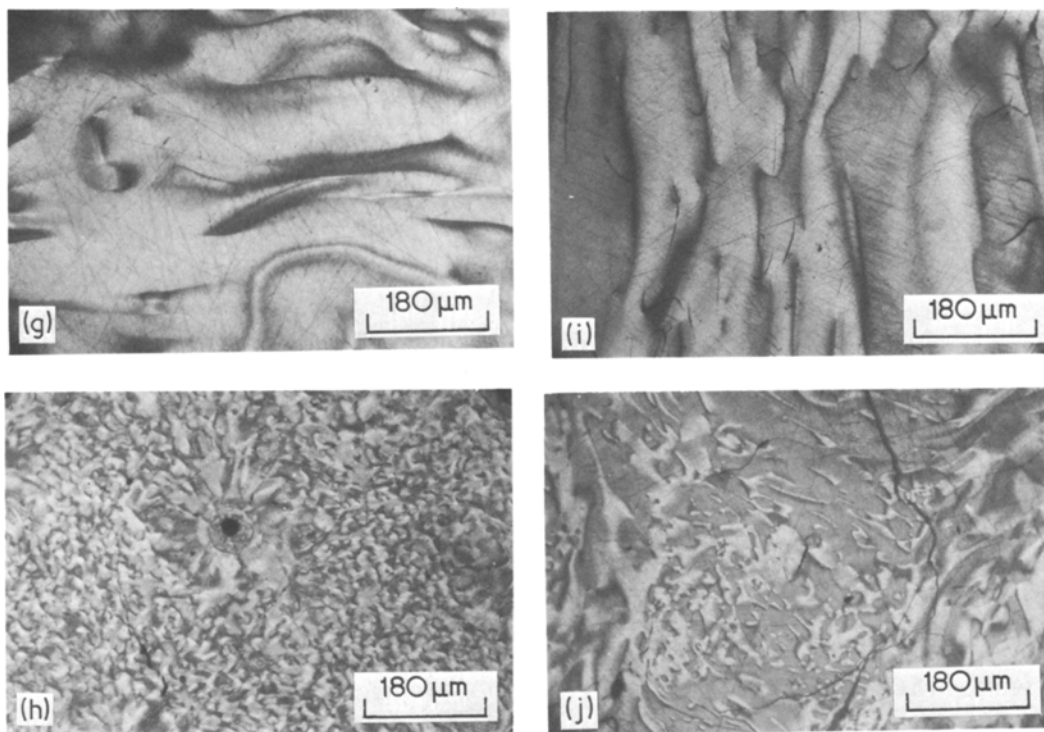
Figure 1 Continued.

saturate fraction is maintained sufficiently long during carbonization. From these results, we can expect that the nucleation and growth of meso-phase spheres in the saturate fraction heat treated under pressure would occure progressively with in-creasing residence time.

The saturate fraction of the vacuum residue was heat treated in an autoclave under a pressure of 20 kg cm^{-2} (gauge) at 450° C for various resi-dence times from 15 to 75 min and observed under cross nicols. The saturate fraction heat treated for 15 min was an isotropic liquid. From the compo-nent analysis of the bulk sample, f_a increased from 0.12 to 0.54 and the molecular weight de-creased from 880 to 490 during heat treatment for 15 min. By the component analysis of heat treated saturate fraction, decomposition and condensation-polymerization, which consist of

T A B L E III Microtexture of the cokes obtained from various fractions.

Sample		Description	Remarks[*]
Petroleum feedstocks	Type		
Vacuum residue	Original oil	Fine mosaic, fibrous	
	Saturates	Coarse fibrous	a, b
	Aromatics	Mosaic	c
	Resins	Fine mosaic	d
	Asphaltenes	Fine mosaic	e, f
Vacuum distillate	Original oil	Mosaic, fibrous	
	Saturates	Coarse fibrous	g
	Aromatics	Mosaic	h
Decant oil	Original oil	Mosaic, fibrous	
	Saturates	Coarse fibrous	i
	Aromatics	Mosaic, fibrous	j

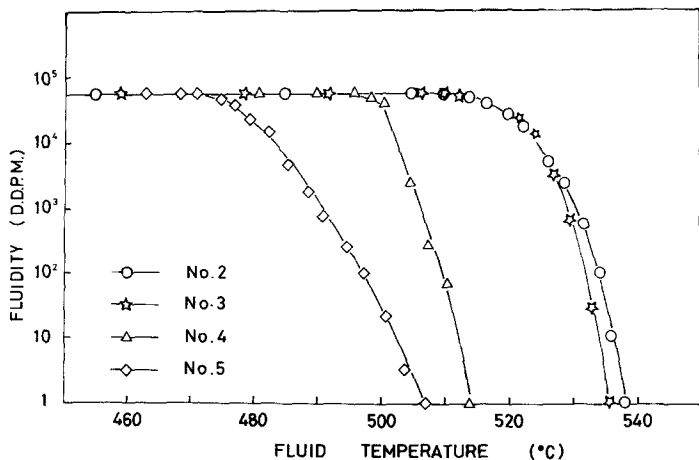[*] Symbols correspond to those of Fig. 1.

Figure 2 Fluidity curves for the fractions of the vacuum residues. No. 2: saturate fraction; No. 3: aromatic fraction; No. 4: resin fraction; No. 5: asphaltene fraction.

side-chains split off aromatic compounds, dehydrogenation of naphthenic compound and aromatization of paraffinic compound, may have occurred during the heat treatment.

The nucleation and growth of spheres occurred progressively with increasing residence time after 45 min heat treatment (Fig. 3). For the saturate fraction heat treated for 75 min in the mesophase system, a small amount of a fibrous microtexture showing flow pattern has been observed. On the basis of these observations it may be postulated that the mesophase system was converted into a needle-like coke by further heat treatment.
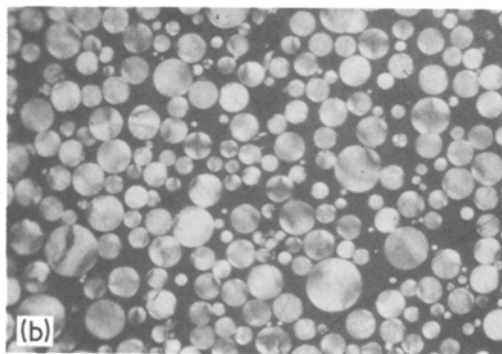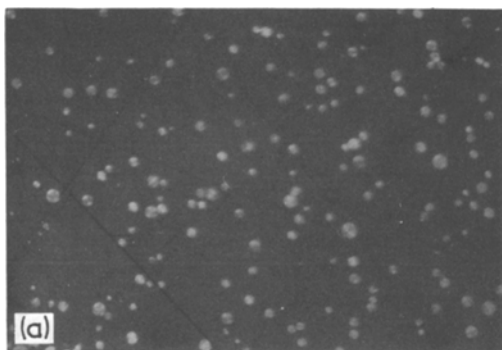
3.3. X-ray analysis of graphitized cokes

The relationship between the X-ray peak intensity of the (0 0 2) diffraction line $I(0\ 0\ 2)$ for each graphitized coke and the C/H atomic ratio of the starting fractions of the feedstocks are shown in Fig. 4. This figure shows that the degree of graphitization of the coke correlates closely with the C/H ratios of the starting fractions. The fraction with a low C/H ratio gives the coke with high graphitizability. For the vacuum residue, decreasing order of graphitizability was as follows: saturate fraction > parent residue > aromatic fraction > resin fraction > asphaltene fraction. For the vacuum distillate and decant oil, decreasing order of graphitizability was as follows: saturate fraction > parent oils > aromatic fraction. This tendency is similar to that of the fluidity behaviour previously shown in Fig. 2.

Figure 3 Polarized light micrographs of the saturate fraction of the vacuum residue (crossed nicols). (a) Heat-treated at 450° C for 45 min under 20 kg cm^{-2} (gauge). (b) Heat-treated at 450° C for 60 min under 20 kg cm^{-2} (gauge). (c) Heat-treated at 450° C for 75 min under 20 kg cm^{-2} (gauge).
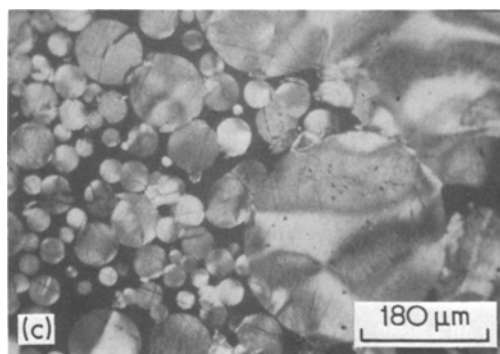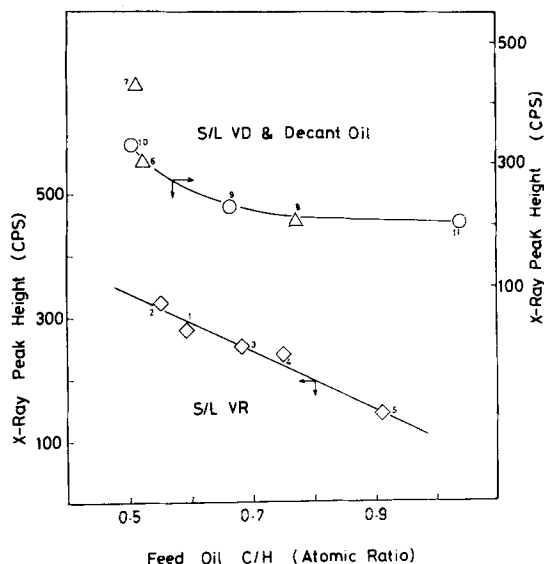
Figure 4 X-ray peak intensity $I(0\,0\,2)$ of the cokes after $2600°$ C treatment as a function of C/H ratio of the starting fractions.

In Fig. 5^{*}, the peak intensity $I(0\,0\,2)$ of the coke heat treated at $2600°$ C is plotted against the chemical structural parameters shown in Table II. It was generally found that the smaller the value of R (the number of aromatic rings) or the smaller the value of C_{al} (the number of alkyl side chains), the higher is the value of $I(0\,0\,2)$, as shown in Fig. 5. From these results, it may be hypothesized that if an aromatic ring has too many alkyl side chains, during condensation polymerization the product becomes cross-linked rather than stacked, thereby causing the degree of orientation of the crystallite to be poor.
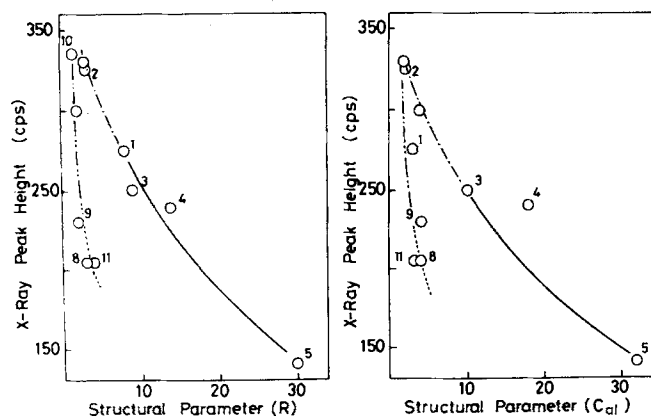
4. Conclusions

The coke, prepared under a pressure of $20\,kg\,cm^{-2}$ (gauge), from the saturate fraction with low aromaticity showed a fibrous texture, whereas resin and asphaltene fractions gave a mosaic texture. These microscopic textures of cokes are related to the fluidity behaviours during carbonization. The high value of solidification temperature, i.e. a long period in the fluid state during carbonization, for the saturate fraction resulted in the fibrous texture of the cokes. On the other hand, the asphaltene and resin fractions showed a relatively low solidification temperature and short duration in the liquid state; the resultant cokes had a mosaic texture.

Composition and characteristics of the feedstocks play important roles in determining coke quality. The coke quality measured using X-ray diffraction correlates with the number of aromatic rings (R) and the number of alkyl side chains (C_{al}), i.e. the smaller the value of R or the smaller the value of C_{al}, the higher the value of the peak intensity $I(0\,0\,2)$ gives.

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Figure 5 Relation between X-ray peak intensity $I(0\,0\,2)$ of the cokes after $2600°$ C treatment and structural parameters (the number of total rings; R and the number of alkyl side chains; C_{al}) of the fractions of the feedstocks.

*The structural parameters of the saturate fractions of petroleum feedstocks have not been obtained as shown in Table II. This is because by the multiplication effects of lower values of H_{a} and density, such parameters have been lost during the calculation procedures. These structural parameters were therefore calculated according to methods of Krevelen [15], and Brown and Ladner [16] and were plotted in Fig. 5..

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