

# Optimization of carbonization conditions for needle coke production from a low-sulphur petroleum vacuum residue

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The optimum carbonization conditions for converting a low-sulphur petroleum vacuum residue in a tube bomb in terms of pressure and temperature into better needle coke of low CTE, with less production of poor bottom coke, were studied by observation of the resultant cokes and sequential analyses of carbonization intermediates by means of solvent fractionation and gas evolution. Carbonization at 460°C under 15 kg cm<sup>-2</sup> G produced the best needle coke. The quality of the resultant needle coke was strongly influenced by viscosity changes of the system, the solidification range and gas evolution in the carbonization progress. The first two characteristics reflect the rates of condensation (such as QI formation) and devolatilization of soluble fractions, strongly influencing the growth of anisotropic units. The last characteristic reflects the pyrolytic cracking reaction to define the timing of gas evolution during carbonization, influencing the axial orientation of anisotropic texture as well as the porosity in the resultant coke. Both profiles varied very much, depending on the carbonization temperature. Finally, the formation of a bottom coke of fine mosaic texture is discussed from the viewpoint of the co-carbonization concept.

## 1. Introduction

The exploration of optimum carbonization conditions is one of most practically important areas of research for the production of the best needle coke from a given feedstock in a commercial delayed coker [1-4]. However, it is expensive and never feasible to operate a large coker for this purpose. It is most desirable to establish guidelines to approach this problem.

The present authors have succeeded in producing a lump of needle-like coke in a tube bomb by adjusting the carbonization pressure, temperature and heating rate [5]. The properties of the coke thus produced are comparable or sometimes superior to those of the commercial one from the same stock in terms of its coefficient of thermal expansion (CTE), optical anisotropy and bulk density [6]. The production scheme of needle coke has been elucidated by the sequential observation of the products in the bomb to define two major steps: the formation of bulk mesophase and the rearrangement of bulk mesophase into a flow texture parallel to the bomb axis by gas evolution just at the point of solidification [7].

In the present paper, optimum carbonization conditions for low-sulphur petroleum vacuum residue (LSVR) were explored by examining needle-like coke lumps produced in a tube bomb under a series of temperatures and pressures. The coke was evaluated in terms of optical texture, CTE and the amount of bottom mosaic coke [8]. Sequential analyses of carbonization intermediates by means of microscope

observation, solvent fractionation and gas analyses may reveal how the conditions influence the carbonization process, to lead to a needle coke. The correlation between the reactivity of the feedstock and the carbonization conditions is discussed briefly as a basis for the design of a needle coke production.

## 2. Experimental procedure

Some analytical data of LSVR are summarized in Table I. Weighed residue (ca. 40 g) in an aluminium foil tube was carbonized in a tube bomb of stainless steel which was heated in a sand bath at the prescribed temperature. The carbonization pressure was adjusted by the initial nitrogen pressure and adequate purging through a control valve during the carbonization. The amount of gas evolved was quantified during the carbonization by measuring the volume of purged gas. The carbonized product after a series of the prescribed times was quenched in cold water and the whole lump was recovered from the tube in the foil.

The coke lumps thus recovered were sectioned in a direction parallel to the bomb axis to examine the anisotropic development in its different parts under a reflected polarized microscope after conventional polishing. A montage was prepared from 100 micrographs of a lump to evaluate its texture.

Anisotropic units were evaluated by both  $l_{av}$  (average length of anisotropic unit vectors) and  $f_{av}$  (average length of vectors parallel to the CTE measurement axis) obtained using a point-counting method [9]:

TABLE I Some properties of low-sulphur vacuum residue

Microanalyses (wt %)				Composition (wt %)				Properties		
C	H	N	S	Saturated fraction	Aromatic fraction	Resin fraction	Asphaltene fraction	Specific gravity*	Viscosity at 100°C	Conradson carbon (wt %)
86.2	12.5	0.4	0.2	52	27	11	10	0.928	74.8	10.2

\*Oil at 15°C referred to water at 4°C.

$$l_{av.} = \frac{1}{n} \sum_{j=1}^n l_j$$

$$f_{av.} = \frac{1}{m} \sum_{i=1}^m \bar{f}_i$$

$$\bar{f}_i = \frac{1}{n} \sum_{j=1}^n f_j$$

$$f_j = l_j \cos \theta_j$$

where  $l_j$  = length of each anisotropic unit vector ( $j$ ),  $n$  = number of unit vectors in the  $i$ th column,  $m$  = number of column in the coke,  $\bar{f}_i$  = averaged  $f_j$  in the  $i$ th column parallel to the axis,  $f_j$  = axial component of an anisotropic unit vector in the  $i$ th column and  $\theta_j$  = angle of an anisotropic vector ( $j$ ) to the CTE axis.

The coke lumps were calcined at 1000°C to measure their CTE value (temperature range; room temperature to 500°C). Detailed procedures have been described in a previous paper [9].

The intermediate products remaining in the bomb before the completion of coking were extracted with benzene (B), hexane (H) and quinoline (Q) to estimate the extent of carbonization progress. <sup>1</sup>H nuclear magnetic resonance (NMR) of the hexane insoluble–benzene soluble (HI–BS) fraction in intermediate products was measured by Fourier transform NMR (FT-NMR) (Jeol FX-100). Carbon aromaticity was calculated according to the Brown–Ladner method [10].

### 3. Results

#### 3.1. Influences of carbonization temperature

Montage photographs of cokes produced under 15 kg cm<sup>-2</sup> G at various temperatures are shown in Fig. 1. The coke produced at 500°C had many pores of various shapes, exhibiting anisotropic fine mosaic textures in the major area of its bottom part, and anisotropic flow textures in its middle and upper parts. The flow textures in the latter areas were randomly oriented.

The coke produced at 480 and 460°C had fewer pores which were elongated in a direction parallel to the bomb axis. Their anisotropic texture was a well-developed flow type which was roughly oriented in a direction parallel to the bomb axis. The cokes, especially those produced at 460°C, exhibited very limited areas of fine mosaic texture in their bottom parts.

The temperature of 440°C provided a lump coke which had, surprisingly, a dominant area of anisotropic fine mosaic texture in the bottom. The flow texture, restricted to its middle and upper parts, was randomly oriented.

#### 3.2. The influence of carbonization pressure

Montage photographs of cokes produced under 7 and 40 kg cm<sup>-2</sup> G at various temperatures are shown in Fig. 2. Regardless of the pressure, the lower temperatures down to 460°C tended to provide better uniaxial orientation of flow texture and to decrease the area of fine mosaic texture in the bottom of the lump. The higher pressures emphasized this trend when optical textures were compared at the same carbonization temperatures, as reported in a previous paper [11].

Thus, the carbonization at 460°C produced the best coke in terms of optical anisotropy in the present study.

#### 3.3. Anisotropy and CTE of coke lump

Table II summarizes the anisotropic evaluation and CTE values of coke lumps produced at a series of temperatures under 15 kg cm<sup>-2</sup> G in the tube bomb. The values of  $f_{av.}$  and  $l_{av.}$ , which are indices for the degree of uniaxial orientation and the shape of anisotropy of the flow texture in the coke, respectively, were strongly dependent upon the carbonization temperature. The carbonization temperature of 460°C provided the largest values of both indices, and either higher or lower temperatures decreased the values. The CTE values of the cokes varied, again, depending significantly on the carbonization temperature just in the same manner as the optical anisotropy. The best CTE value of  $1.2 \times 10^{-6}$  (°C<sup>-1</sup>) obtained by carbonization at 460°C is comparable to that of the better commercial coke.

Another measure for the quality of the coke lump is its homogeneity. There was found to be a fine mosaic zone at the bottom of the lump, as Kakuta *et al.* had reported [8]. The thinner is the zone, the better is the coke. Table II summarizes results for the thickness of the zone. The carbonization temperature of 460°C provided the thinnest zone of 0.1 mm in a coke lump of 1 cm. Both higher and lower temperatures increased the thickness significantly. Thus, 460°C

TABLE II Quality of coke lumps produced from LSVR under 15 kg cm<sup>-2</sup> G in the tube bomb

Temperature (°C)	$f_{av.}^*$ (μm)	$l_{av.}^\dagger$ (μm)	$Z^\ddagger$ (mm)	CTE ( $\times 10^{-6}$ (°C) <sup>-1</sup> )
440	15.2	18.4	1.5	3.2
460	16.0	20.4	0.1	1.2
480	15.8	16.8	1.0	1.3
500	13.8	16.0	2.0	1.7

\*Average length of vectors parallel to the CTE axis.

†Average length of anisotropic unit vectors.

‡Thickness of fine mosaic zone.

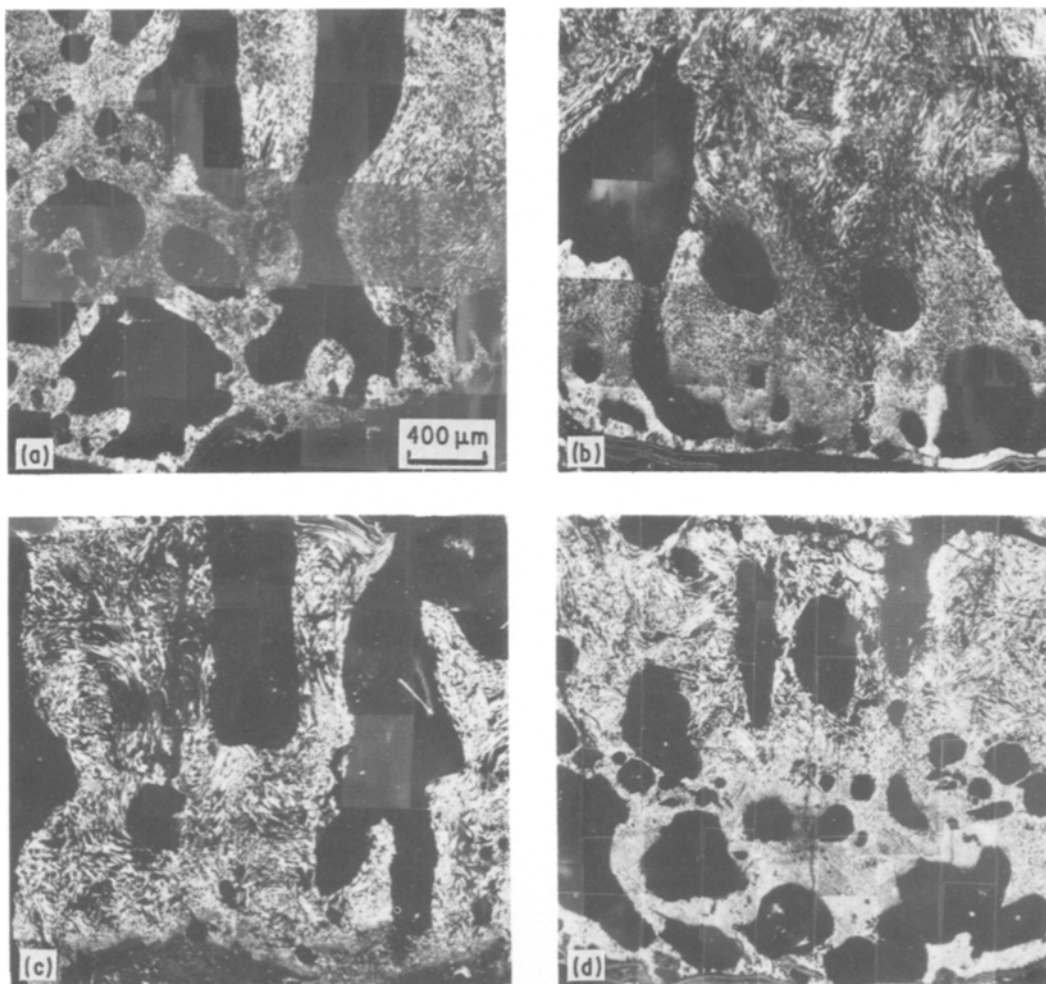


Figure 1 Montage photographs of coke lumps produced under  $15 \text{ kg cm}^{-2} \text{ G}$ : (a)  $500^\circ \text{C}$ ; (b)  $480^\circ \text{C}$ ; (c)  $460^\circ \text{C}$ ; (d)  $440^\circ \text{C}$ .

was the optimum temperature for the carbonization of LSVR into needle coke under  $15 \text{ kg cm}^{-2} \text{ G}$  in all aspects.

### 3.4. Carbonization progress at various temperatures

Fig. 3 summarizes the amount of remaining carbonization intermediate and its solubility in a carbonization time course at various temperatures under  $15 \text{ kg cm}^{-2} \text{ G}$ .

The residue, initially all soluble in hexane, was reduced to 40% of the starting amount within 30 min at  $500^\circ \text{C}$  under  $15 \text{ kg cm}^{-2} \text{ G}$ . The remaining intermediate in the tube at this time consisted of 16% HS, 7% HI-BSD, 5% BI-QS and 12% QI, (S = soluble, I = insoluble) on the feedstock basis. A longer carbonization time further decreased the amount of carbon remaining in the tube and increased the content of QI. These values reached 28% and 21%, respectively, at 90 min, when the carbonization was essentially completed because the amount of QI of this time was the same as that at 360 min, although some soluble fractions still remained in the tube.

The contents of the soluble fractions decreased from 8% HS, 4% HI-BS and 4% BI-QS at 60 min to 3% HS, 3% HI-BS and 1% BI-QS at 90 min. 2% of HS still remained on the top of the coke even at 360 min. Its reflux at the top of the tube may retain the fraction. A series of microscope observations revealed

at the major portion of the flow texture was fixed at  $500^\circ \text{C}$  between 30 and 60 min after the carbonization started, although the mosaic coke appeared to be produced at the bottom from a very early period ( $\sim 15 \text{ min}$ ).

A lower temperature reduced the rate of carbonization very much in terms of an increase of QI and a decrease of soluble fractions. The completion of carbonization was delayed to 120 to 150 min at  $480^\circ \text{C}$  and to 150 to 180 min at  $460^\circ \text{C}$ . It should be noted that more soluble fraction remained at the completion of the carbonization at lower temperatures. The QI increase was more gradual at its initial stage at lower temperatures, however rather rapid at its last stage, although the time of completion was much longer. The carbonization at lower temperatures may allow a longer time for mesophase growth and more rapid coalescence into the bulk mesophase.

Table II summarizes the carbon aromaticity ( $f_a$ ) of the HI-BS fraction in the intermediate product in the carbonization time courses at 480 and  $460^\circ \text{C}$ . The value of  $f_a$  increased from 0.26 in the starting residue to 0.72 in the last intermediate before solidification, regardless of the carbonization temperature. However, because it took a longer time to reach the value of 0.72 at the lower temperature, the increase of  $f_a$  was more gradual, giving intermediate values in the carbonization progress. It may be suggested that  $f_a$  for this fraction reaches at  $460^\circ \text{C}$  as high as 0.76 before

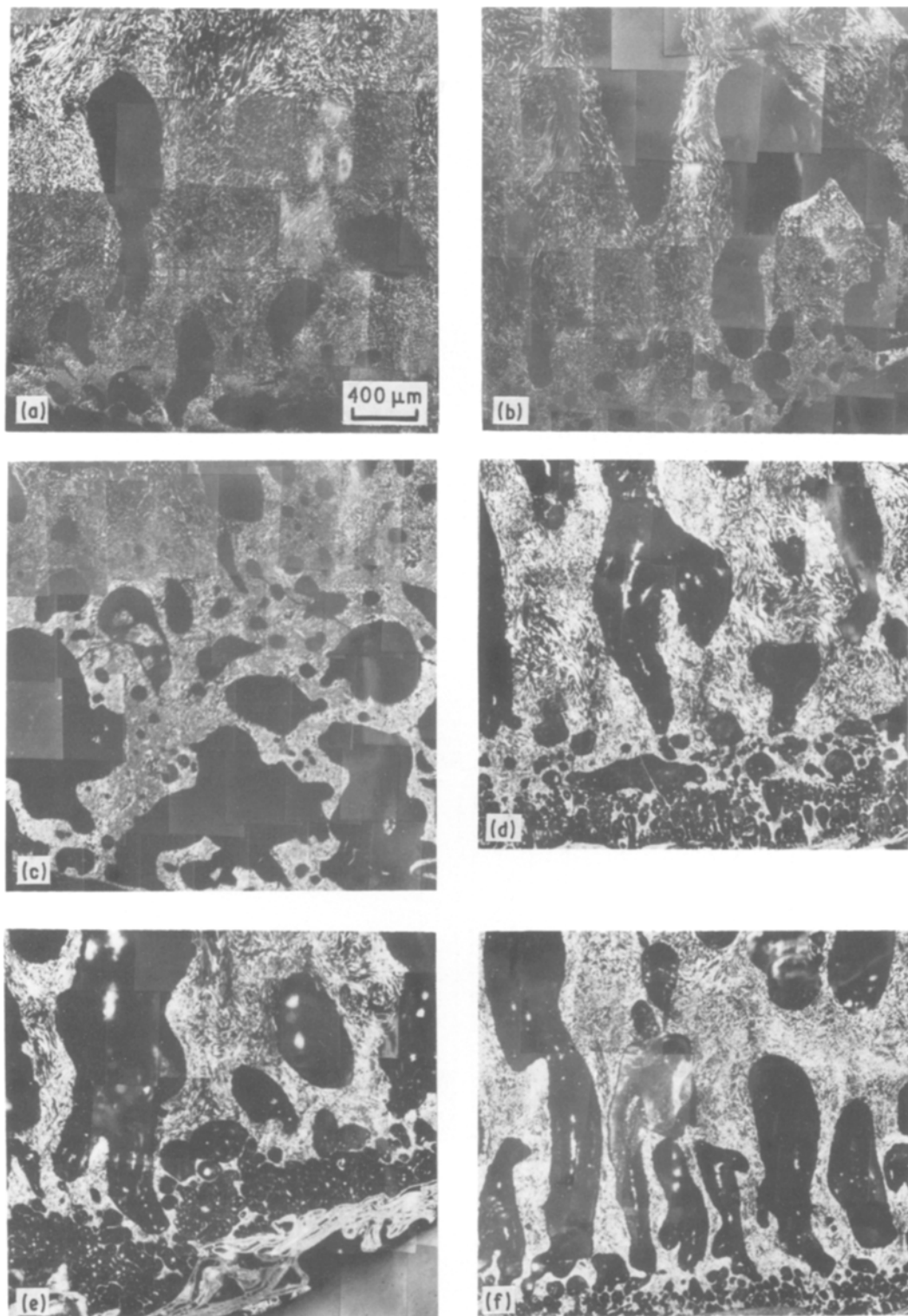


Figure 2 Montage photographs of coke lumps produced under 7 and 40 kg cm<sup>-2</sup> G: (a) 7 kg cm<sup>-2</sup> G, 460°C; (b) 7 kg cm<sup>-2</sup> G, 480°C; (c) 7 kg cm<sup>-2</sup> G, 500°C; (d) 40 kg cm<sup>-2</sup> G, 460°C; (e) 40 kg cm<sup>-2</sup> G, 480°C; (f) 40 kg cm<sup>-2</sup> G, 500°C.

the solidification, whereas the value was 0.76 at 480°C.

### 3.5. Gas evolution

Fig. 4 shows profiles of gas evolution during the carbonization of LSVR under 15 kg cm<sup>-2</sup> G at various temperatures. The regions of solidification while a solid lump was being produced are also included in Fig. 4. The gas evolution at 500°C increased rapidly to reach the maximum at 30 min, when the rate was as large as 97 ml in 10 min, and then decreased rapidly to

to zero at 60 min. The rate of gas evolution at the solidification region was 30 to 60 ml in 10 min.

At 480°C, the amounts of gas evolution increased sharply till 40 min to reach the maximum rate (82 ml

TABLE III The carbon aromaticity ( $f_a$ ) of the HI-BS fraction

Temperature (°C)	Time (h)				
	0	0.5	1.0	1.5	2.0
460	0.26	0.66	0.66	0.72	0.76
480	0.26	0.68	0.71	0.76	-

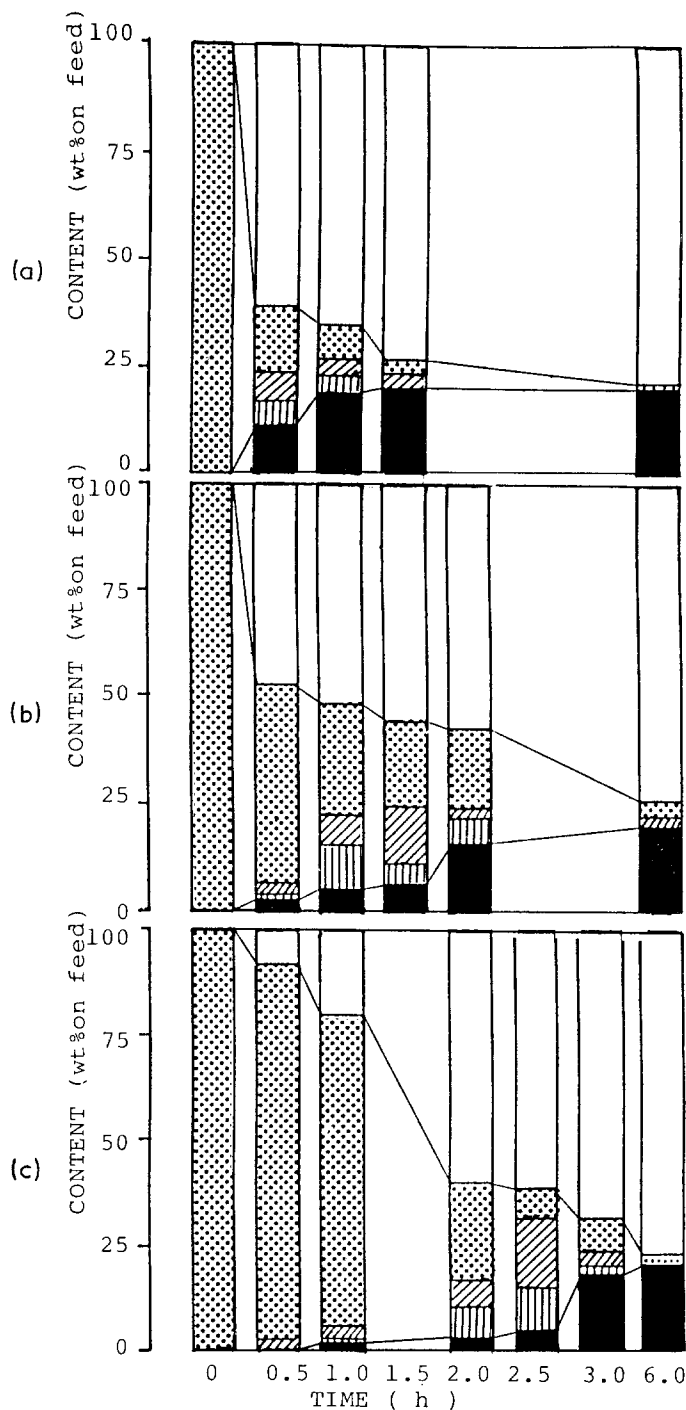


Figure 3 The solubility of intermediate products: (□) effluent, (▨) HS, (▩) HI-BS, (▧) BI-QS, (■) QI. Carbonization conditions; carbonization pressure and heating rate  $15 \text{ kg cm}^{-2}$  and  $250^\circ \text{C min}^{-1}$ , respectively. (a)  $500^\circ \text{C}$ , (b)  $480^\circ \text{C}$ , (c)  $460^\circ \text{C}$ .

in 10 min) and then decreased slowly to zero at 150 min. The rate of evolution decreased from 30 to 10 ml in 10 min between 90 and 120 min of the solidification region, while QI increased sharply from 7 to 17%.

The gas evolution at  $460^\circ \text{C}$  was similar to that at  $480^\circ \text{C}$  except for a slightly smaller amount in the initial 100 min, and it decreased much more slowly to reach zero at 200 min. The rate of gas evolution in the solidification region of 150 to 180 min was still  $\sim 10 \text{ ml}$  in 10 min, because the solidification was much delayed.

#### 4. Discussion

The present authors have proposed, based on the carbonization in a tube bomb, a scheme of carbonization leading to needle coke, which consists of two important steps; the formation of a bulk mesophase of

low viscosity through the growth and coalescence of anisotropic spheres at the first stage, and its rearrangement into a flow texture oriented parallel to the bomb axis by gas evolution at the solidification stage into a solid lump [7]. Both steps, mutually related, influence strongly the quality of the resultant coke.

The carbonization progress, which is defined by the rates of devolatilization and carbonization, and the structures of both carbonization intermediates and coexistent molecules during the carbonization, may be key factors in both steps. Hence, the optimum conditions in terms of the carbonization pressure and temperature for the best needle cokes are very characteristic of a particular feedstock since the respective feedstock has its own reactivity and starting structure.

The present study has revealed the optimum temperature of  $460^\circ \text{C}$  for a particular feedstock of low-sulphur petroleum vacuum residue to give the best

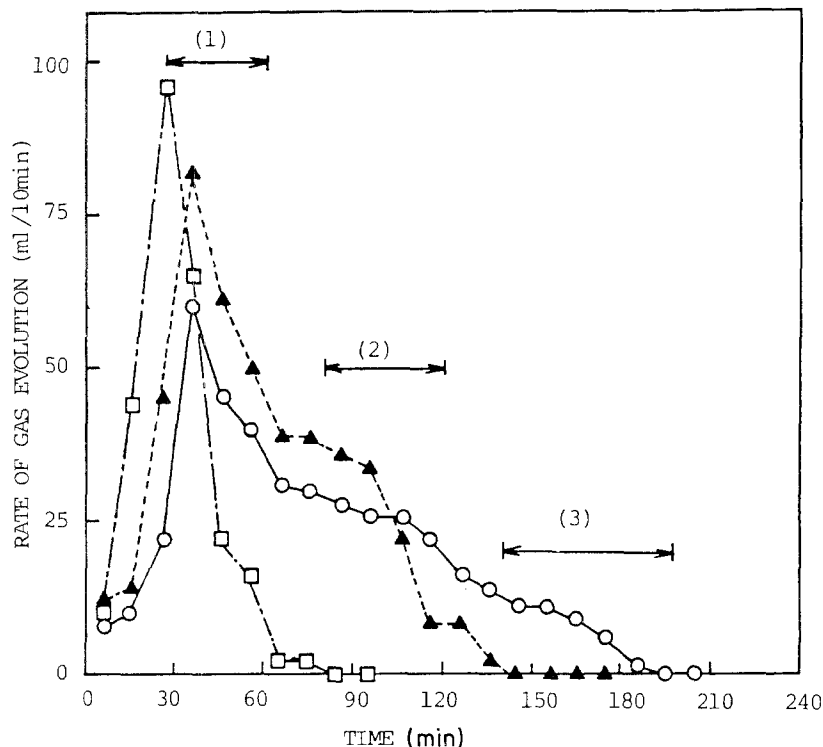


Figure 4 The profile of gas evolution during the carbonization: (□) 500°C, (▲) 480°C, (○) 460°C. Region of solidification under (1) 500°C, (2) 480°C, (3) 460°C.

needle coke under a particular gas pressure of  $15 \text{ kg cm}^{-2} \text{ G}$ , which is slightly higher than that of commercial operation. The coke lump produced from LSVR under these conditions exhibited a CTE value of  $1.2 \times 10^{-6} (\text{°C}^{-1})$  comparable to that of current commercial needle cokes, in spite of the fact that LSVR is not believed to be the best feedstock for commercial operation and that the commercial processes select or blend very carefully the feedstocks. The temperature is significantly lower than those for coal tar and FCC decant oil reported in previous papers [7, 11].

Fig. 5 illustrates models of carbonization progress at three representative temperatures in terms of viscosity changes of the carbonizing substance, its solidification range and the gas evolution. The first two characteristics may reflect the rates of condensation (e.g. QI formation) and devolatilization of the soluble fraction, strongly influencing the development of optical texture, while the last one reflects the pyrolytic cracking reaction to gaseous products during the carbonization, influencing the rearrangement of aniso-

tropic texture along with the axial porosity in the resultant coke.

The profiles may vary very much, depending strongly on the carbonization temperature. At the optimum temperature of 460°C, the increase of viscosity after its minimum is moderate, allowing sufficient growth and coalescence of mesophase to give a bulk mesophase of low viscosity since the increase of QI and disappearance of soluble fractions are moderate due to the moderate reaction temperatures. The aromaticity increase of the soluble fraction can follow the progress of carbonization to provide its high dissolving ability against heavier fractions of mesophase components, maintaining the viscosity low [12, 13].

The gas evolution is rather rapid in the initial 30 min of carbonization, while the system stays of low viscosity, leaving few traces of bubbles, and is considerable even at solidification, although its amount decreases gradually along with the carbonization progress. Because an adequate carbonization temperature assures high mutual solubility among the components of the feed, a major problem of the heavy asphaltene

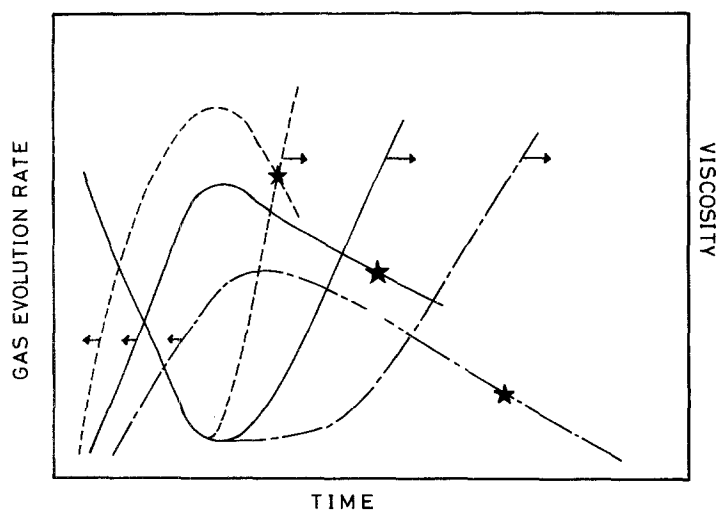


Figure 5 Carbonization scheme at three representative temperatures: (---) higher temperature, (—) optimum temperature, (-.-) lower temperature, (★) solidification zone.

of highest reactivity stays in the matrix to be co-carbonized to exhibit developed anisotropy without precipitating to the bottom, decreasing the formation of bottom mosaic coke. Thus, the best needle coke is produced at this temperature.

In contrast, at a higher temperatures, every change takes place much more rapidly. There is little time to allow the growth of an isochromatic area. The development of bulk mesophase and maximum evolution of turbulent gas are overlapped, so that the texture is arranged in a random manner. The rapid coking of the most reactive fraction may allow the precipitation of its condensed product to form the bottom mosaic coke. At a lower temperature, the carbonization progress is more moderate; however, the co-carbonization of the components may not work properly because of their different reactivities and lower mutual solubility at this temperature. Hence, a large amount of bottom coke is produced. The gas evolution is so much delayed as to miss the time of solidification, failing to force the uniaxial arrangement of bulk mesophase.

Carbonization for better needle coke of lower CTE and less production of poor bottom coke is an important operational target of the present delayed coking process [4]. The present study revealed the importance of exact control of the carbonization temperature to be neither too high nor too low. The carbonization pressure is found also to be very influential on the coke quality as well as its yield [11]. Hence, the authors can propose that a little higher pressure at the optimum temperature may solve the above problem at least partly.

It is suggested in the present study that the mutual solubility between carbonizing substances as well as

the volatile fractions play important roles in the carbonization to provide a low viscosity of mesophase. The latter substance can be a solvent, while they stay in the carbonization system. Hence, a co-carbonization technique with the use of appropriate additives is another procedure to be examined. Again optimum conditions should be carefully explored for the particular mixture of feedstocks, so that the components can do their best in co-carbonization.

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*Received 24 March  
and accepted 8 June 1987*