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Carbonization of coal-tar pitch into lump needle coke in a tube bomb

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The carbonization of coal-tar pitches and their QI (quinoline insoluble)-free fractions was studied by evaluating their lump cokes produced in a tube bomb at various temperatures (470 to 550° C) and pressures (0 to 75 kg cm^{-2} gauge). The lump coke from QI-free fractions had a comparable anisotropic development and coefficient of thermal expansion (CTE). The carbonization temperature and pressure were found to influence strongly the properties of the cokes. At the highest temperature of 550° C, the most appropriate pressure for the best needle coke was 15 kg cm^{-2} G (gauge). Either higher or lower pressure increased the CTE value of coke. In contrast, at a moderate temperature of 500° C, the higher pressure produced the better coke. At the lowest temperature of 470° C, it took 10 h to complete the carbonization, and the lowest pressure allowed the best extent of uniaxial arrangement. Among the cokes prepared under the present conditions, the carbonization at 500° C under 40 kg cm^{-2} G produced the best needle coke with a CTE value as low as 0.1 × 10^{-6} ° C^{-1}. The carbonization scheme leading into the needle coke is discussed for a better understanding of how the carbonization temperature and pressure cooperatively influence the quality of the resultant coke, in relation to the carbonization reactivity of coal-tar pitch.

1. Introduction

Since 1976, with the establishment of the anti-solvent technique for QI removal from coal-tar pitch [1], the pitch has been carbonized into excellent needle-cokes of low coefficient of thermal expansion (CTE) and high density [2, 3]. Recently, their puffing deterioration at the graphitization step has attracted studies to control carbonization and hence the micro- and macroscopic structure of the derived cokes [4, 5].

The present authors have reported that the carbonization of petroleum residues in a tube bomb produces lump cokes with properties similar to those of the needle coke produced in a commercial delayed coker from the same feedstocks [6]. The optical texture and pore structure of the cokes which define their CTE [7–9] were found to be strongly dependent on the carbonization conditions as well as feedstocks [6, 10].

The carbonization of some coal-tar pitches was studied, using a tube bomb to produce lump cokes under various carbonization temperatures and pressures. Resultant cokes were evaluated according to CTE measurement, coke yield and microscopic observation of the lump in terms of optical texture and porosity. The influences of the carbonization temperature and pressure which determine the reactivity of coal-tar pitches of highly aromatic constituents are studied in detail.

2. Experimental procedures

Two kinds of coal-tar pitches, by-products of blast furnace coke (from Nippon Steel Chemical) and foundry coke (from Osaka Gas) abbreviated as HT and FT, respectively, and their QI-free fractions (QIF) were selected. Their analyses are listed in Table I.

The weighed pitch (20 to 40 g) was put in a stainless pipe (tube bomb, 22 mm diameter, 150 mm height) which was equipped with swage locks at two ends. The tube bomb was inserted in a sand bath perpendicularly and heated rapidly (200 to 250° C min^{-1}) to the prescribed carbonization temperature and then soaked for 4 or 10 h. The carbonization pressure was adjusted by filling with nitrogen before carbonization, and occasional purging through a control valve during carbonization.

In order to describe the optical texture and porosity in the coke, montage photographs of lump green coke were prepared on the surface sectioned parallel to the axis of the tube bomb.

The lump coke was further calcined at 1000° C after carbonization. The CTE value of the calcined coke was measured in the direction parallel to the axis of the tube bomb at room temperature to 500° C. The CTE values of two pieces of coke were well reproduced within 10% of error.

3. Results

3.1. Carbonization of HT–QIF

Fig. 1 shows montage photographs and representative micrographs in higher magnification of lump cokes produced from HT–QIF at 550° C for 4 h under different pressures (0 to 75 kg cm^{-2} gauge). At atmospheric pressure, the coke exhibited flow texture of

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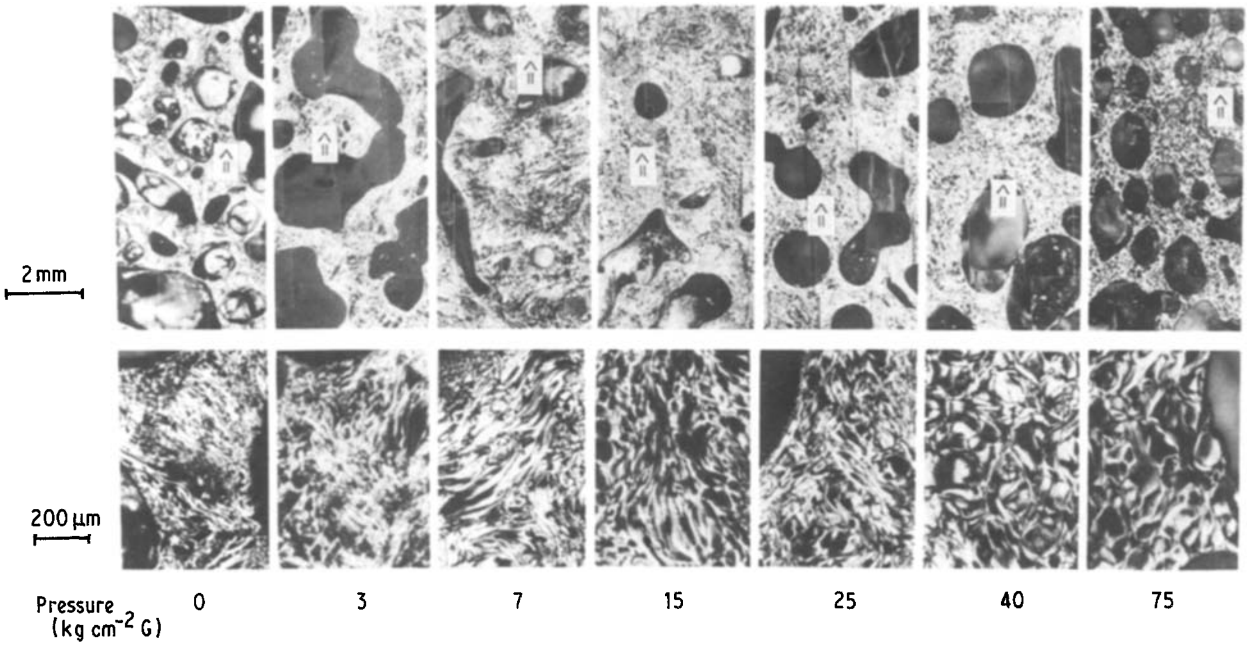

Figure 1 Optical texture of lump cokes prepared from HT–QIF at 550° C under various pressures. Top, montage photograph; bottom, microphotograph of a representative region.

small elongated units, many irregularly-shaped pores and thin walls. The increase of pressure to 15 kg cm^{-2} G (gauge) through 3 and 7 kg cm^{-2} G enlarged the optical units of the cokes and arranged them more uniaxially. The best needle-like coke was prepared at 15 kg cm^{-2} G since the pressure above 25 kg cm^{-2} G produced the anisotropic units of round shape. At 40 and 75 kg cm^{-2} G, a kind of super-domain unit (larger than 100 μm in diameter) was observed in the entire area. The pores tended to become smaller and spherical.

Fig. 2 shows montage photographs of lump cokes produced from the same feed at 500° C for 4 h under different pressures. As carbonization pressure increased from 0 to 75 kg cm^{-2} G, units of the anisotropic texture became not only longer and broader but also arranged uniaxially in a more perfect manner. High pressure above 15 kg cm^{-2} G enlarged anisotropic units, their width and length becoming larger than 40 and 1000 μm, respectively. The pores tended to take a round shape when the carbonization pressure became high at this temperature, too.

Fig. 3 shows montage photographs of lump cokes prepared from the same feed at 470° C for 10 h under 0, 7 and 15 kg cm^{-2} G. The carbonization was very slow at this temperature so that 10 h was required to produce a solid lump coke. Under atmospheric pressure, a coke with very narrow and long flow texture was formed, as observed in the coke of a delayed coker. Many pores were found in the coke. At this temperature, when higher carbonization pressure was applied, anisotropic units became larger again as observed at higher temperatures. However, the degree of uniaxial arrangement tended to become worse with increasing pressure, differing from that observed at higher temperatures.

Thus the anisotropic development of coke in terms of size and orientation of the units was delicately governed by the combination of carbonization temperature and pressure (Fig. 4). The coke yield increased with increasing carbonization pressure, the extent of increase depending on the carbonization temperature. At 550° C the coke yield was as low as 30% at atmospheric pressure. The increasing pressure up to 15 kg cm^{-2} G increased the yield to the maximum of 83%. No increase was achieved under higher pressure above 15 kg cm^{-2} G. The carbonization of the lower heating rate (in an autoclave) at the same temperature required much higher pressure, around 100 kg cm^{-2} G to achieve this level of yield [11]. At 500 and 470° C under atmospheric pressure, the coke yields were both 47%, which was definitely higher

TABLE I Properties of feedstocks

Samples	Elemental analyses (wt %)					C/H	fa§	Solubility¶ (wt %)			
	C	H	N	S	diff.			QI	BI–QS	HI–BS	HS
HT*–QIF‡	92.2	5.2	1.2	0.6	0.8	1.5	0.93	0	7	73	20
FT†–QIF‡	91.6	5.1	1.3	0.7	1.3	1.5	0.93	0	4	48	48
HT*	92.2	4.9	1.0	0.6	1.3	1.6	–	2	5	51	42

*By-product of blast furnace coke.
†By-product of foundry coke.
‡QI-free.
§Calculated according to *H-NMR.
¶BI–QS: benzene insoluble but quinoline soluble; HI–BS: hexane insoluble but benzene soluble; HS: hexane soluble.

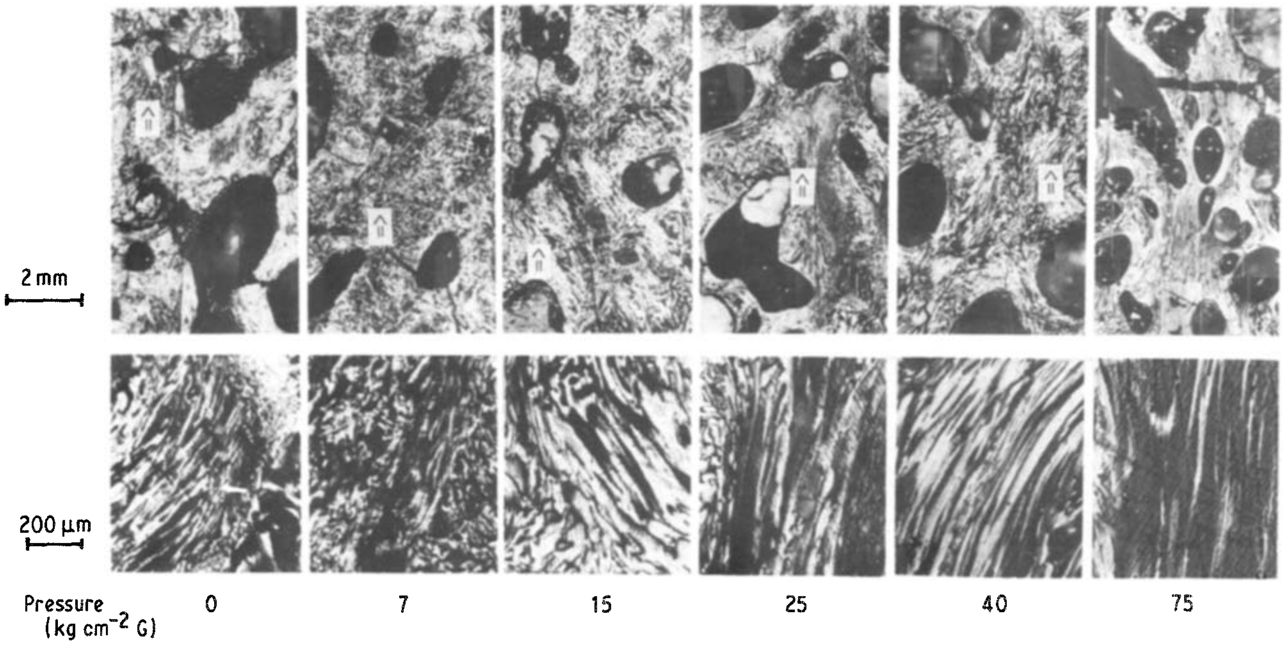

Figure 2 Optical texture of lump cokes prepared from HT–QIF at 500° C under various pressures. Top, montage photograph; bottom, microphotograph of a representative region.

than that at 550° C. The pressure of 7 kg cm^{-2} G increased it to 72 and 62%, respectively, at 500 and 470° C, almost no increase being observed under higher pressures. It is suggested that the substances of lower reactivity which stay in the tube bomb under pressurized conditions are carbonized to contribute to the increase of coke yield only at higher temperatures.

3.2. CTE values of lump cokes prepared from HT–QIF

The CTE values of lump cokes produced from HT–QIF are shown in Fig. 5. Firstly, cokes produced in the tube bomb have CTE values from 0.1 to 2.3 × 10^{-6}°C depending upon both carbonization temperature and pressure. These values are comparable to

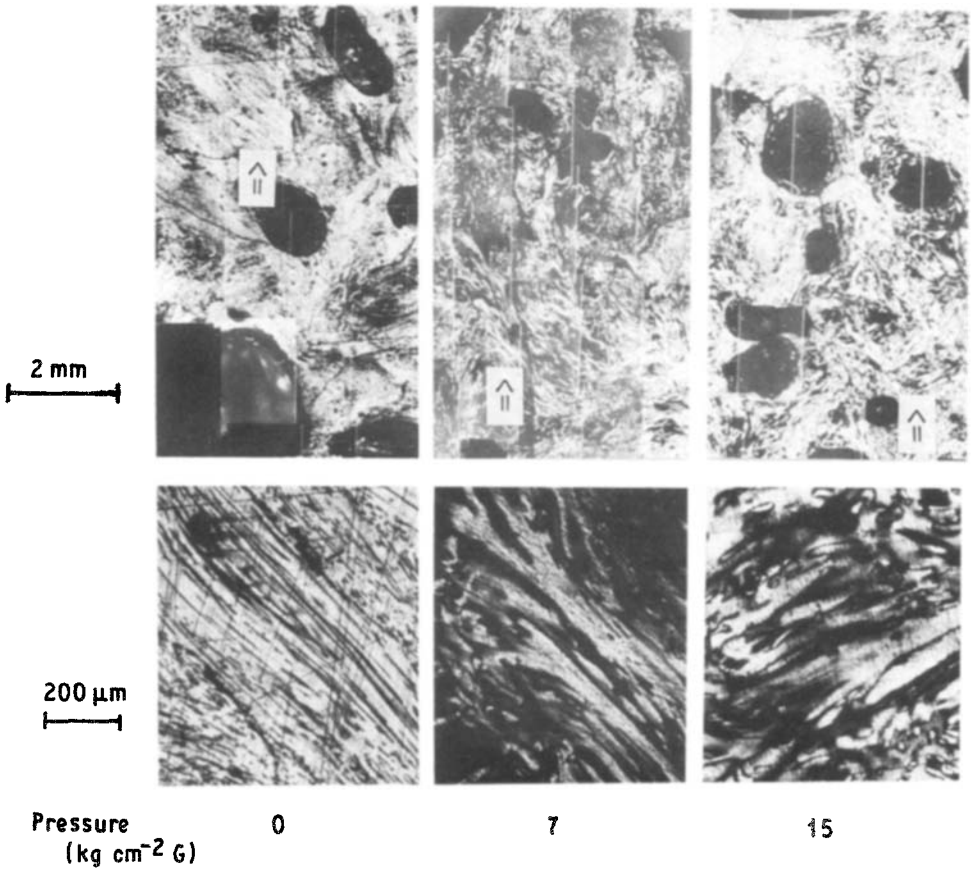

Figure 3 Optical texture of lump cokes produced from HT–QIF at 470° C under 0, 7 and 15 kg cm^{-2} G. Top, montage photograph; bottom, microphotograph of a representative region.

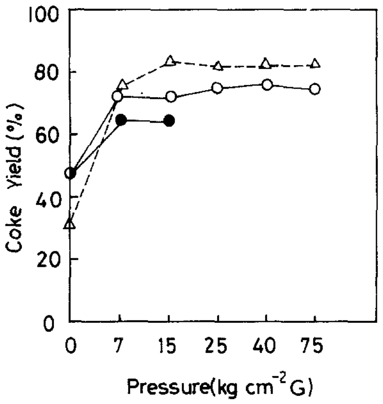

Figure 4 Dependence of coke yield on carbonization pressure. △ 550° C; ○ 500° C; ● 470° C.

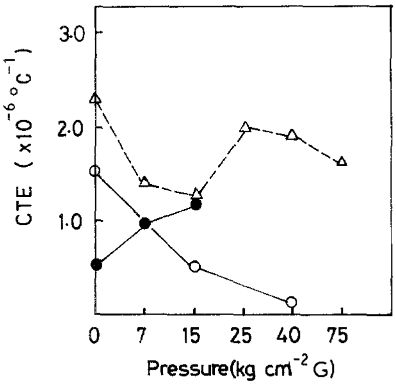

Figure 5 Dependence of CTE value on carbonization pressure. △ 550° C, ○ 500° C, ● 470° C.

those of commercial cokes produced from the same QI-free coal-tar pitch in the delayed coker.

The CTE values were delicately influenced by the carbonization conditions, temperature and pressure in this study, just as observed in the case of anisotropic development. The intimate correlation between CTE and anisotropy has been often observed [7, 8].

The CTE of cokes prepared at 550° C decreased first with the increasing pressure of carbonization until 15 kg cm^{-2} G where the value reached a minimum of 1.3×10^{-6} °C. The values of the cokes produced under pressures above 25 kg cm^{-2} G increased to about 2.0×10^{-6} °C. In contrast, CTE values of the cokes prepared at 500° C decreased with the increasing pressure to give the lowest value of 0.1×10^{-6} °C at 40 kg cm^{-2} G. The dependence of CTE on the pressure changed again at 470° C. The lowest pressure of 0 kg cm^{-2} G gave the best CTE value as low as 0.5×10^{-6} °C at these temperatures, although the coke was porous.

3.3. Cokes from other coal-tar derived feedstocks

Montage photographs, coke yields and CTE values of cokes prepared from FT–QIF are shown in Fig. 6 and Table II, respectively.

FT–QIF also gave needle-like lump cokes. The influences of carbonization temperature and pressure on the coke quality were similar to those in the case of HT–QIF.

QI containing pitch (HT) failed to produce needle-like cokes under the present experimental conditions, as often reported in the literature [12, 13]. Fig. 7 shows montage photographs of the lump cokes from HT, indicating the influences of carbonization conditions on coke properties. At 550° C, low pressures (e.g. 0 and 15 kg cm^{-2} G) produced cokes of mosaic texture with high CTE values of about 4.0×10^{-6} °C (Table II). It is of interest to note that the pressure of 40 kg cm^{-2} G also produced a very large round coke as observed in the coke produced from HT–QIF under the same conditions.

Carbonization at lower temperatures enlarged anisotropic texture to some extent as pressure increased. The CTE value of the coke produced at 470° C under 0 kg cm^{-2} G decreased to 2.0×10^{-6} °C, which is still considerably higher than the values of the cokes from QI free pitches.

4. Discussion

In a tube bomb the carbonization of the coal-tar pitch free from QI produced a lump coke with comparable properties to that produced commercially in a delayed coker. It is worthwhile to note that the coal-tar pitch can provide needle coke of better CTE in the tube bomb than that from petroleum residues as commercially observed [3, 14]. Therefore it is a facile way to investigate some details of carbonization chemistry on the needle-coke formation in terms of cooperative influences of carbonization temperature and pressure by using the tube bomb.

The carbonization of pitches into needle coke is thought to proceed through two major steps [15, 16]. The first is the development of bulk mesophase of low viscosity, and the second is the uniaxial arrangement of the developed bulk mesophase. In each step different chemistry is included. It has already been recognized

TABLE II Coke yield and CTE of the lump cokes from HT–QIF, FT–QIF and HT

Conditions (° C)	(kg cm^{-2} G)	Coke yield (%)		CTE ($\times 10^{-6}$ °C^{-1})		
		HT–QIF	FT–QIF	HT–QIF	FT–QIF	HT
550	0	31	37	2.3	2.1	3.9
	7	75	72	1.4	–	–
	15	83	85	1.3	1.1	4.1
500	0	47	–	1.5	–	–
	7	72	75	–	0.6	–
	15	72	83	0.5	0.5	3.5
470	0	47	–	0.5	–	2.2
	15	65	–	1.2	–	–

since Brooks and Taylor defined the mesophase sphere [17], that moderate viscosity during carbonization is essential for development of the bulk mesophase of a large isochromatic area [18, 19]. The moderate rate of carbonization, the adequate structure of the intermediate and the presence of solvent fraction are needed to satisfy this criterion [20].

On the other hand, sufficient gas evolution is required just at the point of solidification, because it is the gas bubble percolation that deforms the planar liquid-crystal components and arranges them into the uniaxial symmetry of a needle-coke precursor [21]. The timing of gas evolution against the final viscosity increase into a solid coke is, therefore, important. Evolution too early or too late is useless for the formation of needle coke. Too much evolution at solidification may lead to porous or flaky cokes [22].

The carbonization temperature and pressure control the rate of carbonization and gas-evolution as well as the amount of volatile matter which may stay for a while in the carbonization system as a kind of solvent. Thus they influence the carbonization scheme.

At a high temperature of 550° C, the pyrolysis is very rapid to make the gas evolve out at an early stage of carbonization. At a low pressure, the solidification takes place just at the major gas-evolution, giving a coke of low density and fine-flow texture. Much gas evolved in a turbulent rush may not allow the uniaxial arrangement of bulk mesophase. The moderate pressure increases the coke yield since it can retain a considerable amount of volatile matter to be carbonized in the bomb. Furthermore, this retained matter may

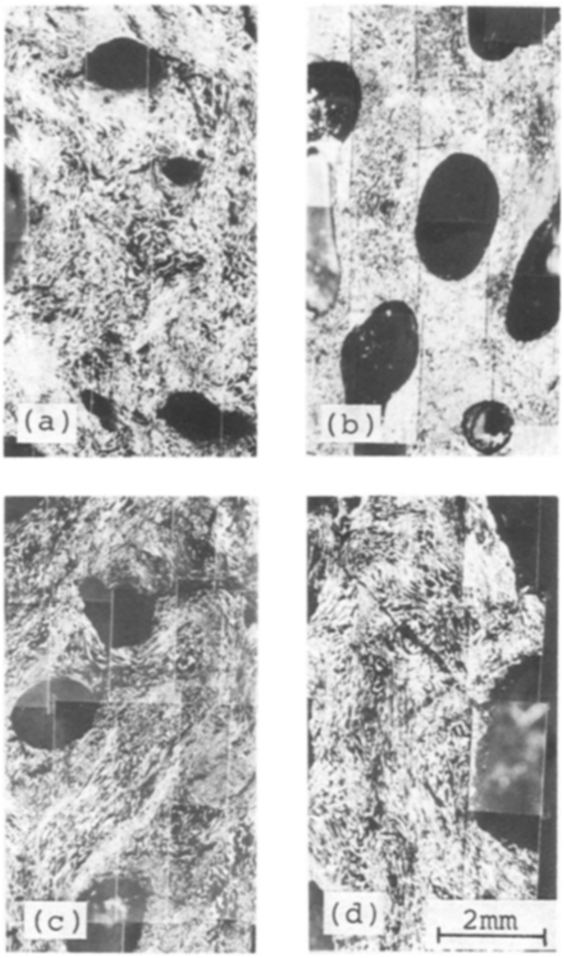

Figure 6 Montage photographs of lump cokes from FT-QIF. (a) 550° C, 7 kg cm^{-2} G; (b) 550° C, 15 kg cm^{-2} G; (c) 500° C, 7 kg cm^{-2} G; (d) 500° C, 15 kg cm^{-2} G.

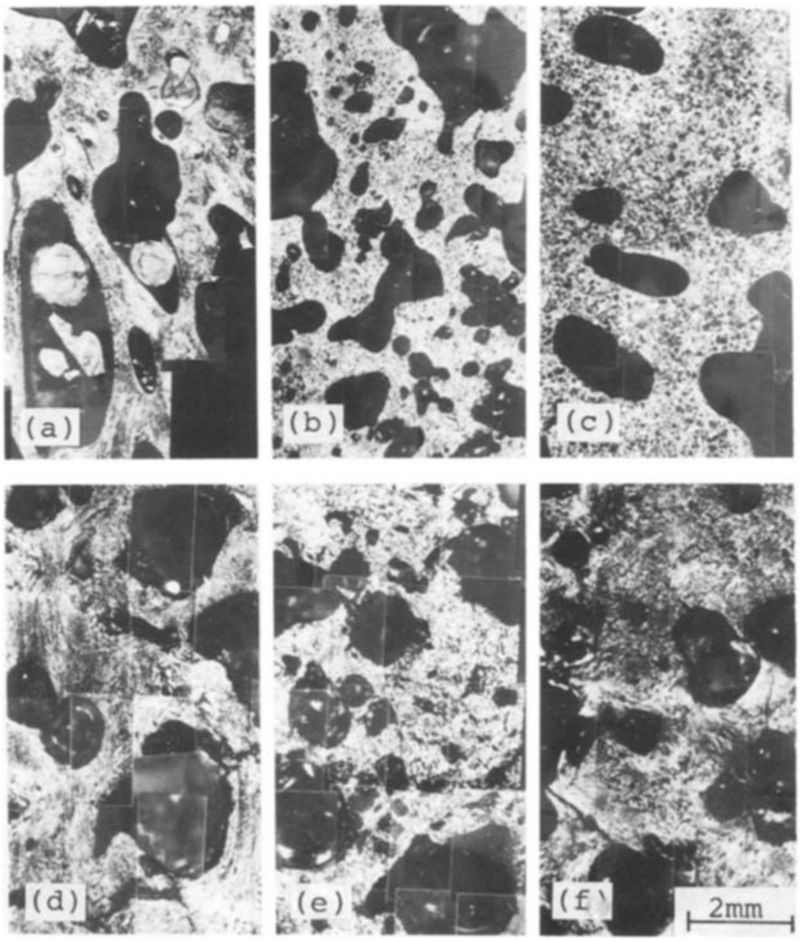

Figure 7 Montage photographs of lump cokes from HT. (a) 550° C, 0 kg cm^{-2} G; (b) 550° C, 15 kg cm^{-2} G; (c) 550° C, 40 kg cm^{-2} G; (d) 470° C, 0 kg cm^{-2} G; (e) 470° C, 15 kg cm^{-2} G; (f) 500° C 15 kg cm^{-2} G.

moderate the carbonization reaction at the beginning, acting as a solvent. Thus the higher pressure is favourable for enlarging the isochromatic area of mesophase and so the texture of the coke [23, 19]. Major gas may evolve while the carbonization system is still fluid, leading to fewer bubble pores. The last gas evolution will be sufficient to arrange the planar components of mesophase perfectly in an axial direction, leading to a good needle coke. Higher pressure is also favourable for enlarging the isochromatic area; however, it maintains a high fluidity until the last gas-evolution, therefore small sphere-like bubbles are left in the solidified mesophase or coke. No uniaxial arrangement is expected under this situation. The porosity may increase because of the retention of many spherical bubbles.

At the moderate temperature of 500° C, the pyrolysis is much slower than at 550° C due to the fair thermal-stability of coal tar pitch of well developed aromaticity; however it can provide sufficient gas to make the bulk mesophase elongated and rearranged uniaxially. The last gas evolution is extended to match the carbonization under higher pressure, giving an excellent needle coke since higher pressure is favourable for the development of a large isochromatic area.

At a low temperature of 470° C the carbonization is very slow, and a longer time (10 h) was required for the completion of the carbonization. The slow pyrolysis tends to produce a little gas available to rearrangement at the solidification stage. The increasing pressure, therefore, slows down the pyrolysis further, deteriorating the uniaxial arrangement. The gas evolution and mesophase development occur at the same time under atmospheric pressure at this temperature to give a porous coke.

Thus the strong influences of both carbonization temperature and pressure on the coke quality are intimately correlated. It should be also noted that the optimum conditions are variable due to the feedstocks which have their own reactivity and temperature dependence.

The comparison of HT–QIF and FT–QIF may be of value since the natures of pitch feedstocks are known to be influential on the coke properties. It is believed that a lower temperature of coal carbonization tends to deteriorate the carbonization properties of the resultant pitch [24, 25]. FT is certainly produced at a lower temperature than HT [26]. Nevertheless FT–QIF produced comparable cokes to those from HT–QIF. Although their preliminary analyses tell little about their differences, more HS fraction in the latter feedstock may be favourable for anisotropic development and sufficient gas generation under pressure.

The carbonization temperature and pressure are also found to be influential on the anisotropic development from the QI containing pitch. Their suitable combination enlarged the anisotropic units and improved their orientation to decrease CTE. However, the entire flow-texture of typical needle coke was not obtained.

5. Acknowledgement

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