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The co-carbonization behaviour of Chinese coals with pitch additives

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Five Chinese coals, of rank (NCB No.) 602-204, have been carbonized singly, in coal blends and with four pitch additives. Changes in optical texture of resultant cokes are quantitatively assessed using a point-counting method. The pitches are more able than the coals to act as modifiers and bridging agents to up-grade the optical texture of cokes from the low rank and high rank coals. The modifying ability of the pitches can be separately assessed using the extents of conversion of 9,10-dihydroanthracene to anthracene as an index. The Chinese coals are essentially similar to European coals with respect to modifying ability.

1. Introduction

1.1. Chinese coals

The extensive coal reserves of China are mostly located in basins along the eastern side of the country. Apart from tilting of the strata and minor faulting, the coal fields (except for Hupek) are generally free from tectonic disturbance [1]. This quiet structural environment is reflected by very long-periods during which coal was deposited in particular areas, for example in Shansi and Liaoning. In China, coal was deposited more or less continuously, except for the Triassic Period, from Carboniferous to Tertiary times. The reason for this almost uninterrupted deposition of coal may be related to plate tectonics.

From Carboniferous to Tertiary times China was either surrounded totally by sea, (before about 225 million years ago) or on two sides by an ocean to the east and the Tethys sea to the west, (after about 225 million years ago). China has varied in position with time, but has probably always been between 70°N and 15°N [2, 3]. Given these fluctuations some part of China has been in an ideal situation for the formation of peat for a long stretch of geologic time, because of the warm wet south westerly winds blowing inland from the sea.

In the late Carboniferous, China and Indo-China formed a continent completely separated from other land masses [2]. The coals of this age are found in the coal fields of Liaoning, Shansi, Hopeh, Shensi, Shautung and were deposited between 35°N and 55°N [2].

Caking coal constitutes about 37% of Chinese coal resources. Of these caking coals more than 50% are low rank bituminous coals. The distribution of coal in different districts is not economically balanced either in quantity or in coal rank. The utilization of low rank coal in maximum amounts to produce metallurgical coke is therefore an attractive objective in the economy of China. This paper examines possibilities of such use of low rank coals.

1.2. Coal co-carbonization

The process of coal carbonization can be modified by co-carbonization with model organic compounds [4, 5], petroleum pitches [6–10], coal-tar pitch and solvent refined coals [11]. Modification is interpreted in terms of extent of change in

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TABLE I Analyses of coals

Coal	Ash % (dry)	VM% (d.a.f.)	C% (d.a.f.)	H% (d.a.f.)	Reflectance (mean, max)	FSI	Dilatometer					Giesler plastometer				Rank	
							T_1 (°C)	T_2 (°C)	T_3 (°C)	a%	b%	T_P (°C)	T_M (°C)	T_K (°C)	α_{max} (° min^{-1})	NCB	CC*
Fu Shun	5.41	42.83	83.63	5.92	0.705	$4\frac{1}{2}$	360	418	446	33	27	372	428	453	935	602	G_2
Shuang Ya	9.02	36.52	84.98	5.46	0.782	$7\frac{1}{2}$	372	427	460	30.8	25	375	438	464	3400	502	FG
Kai Lan	12.12	26.46	88.36	5.31	1.162	$7\frac{1}{2}$	366	415	483	28.3	107	364	453	493	2.34×10^4	301a	F
Ji Xi	13.68	24.48	89.56	5.23	1.261	8	408	448	485	29	43	398	466	493	587	301a	K
Ben Xi	11.64	15.21	90.17	4.97	1.663	1	483		515	5	C.O.	481	497	505	1	202	L

*CC Chinese coal classification.
G_2 Gas coal group 2.
FG Fat-gas coal.
F Fat coal.
K Prime coking coal.
L Lean coal.

optical texture of resultant cokes. Optical texture can be considered as one possible criterion for acceptability as a metallurgical coke. Resultant coke may be acceptable if it is anisotropic with, e.g. a fine-grained optical texture, ~ 1.5 μm diameter.

Mochida *et al.* [5] have summarized the mechanism of the co-carbonization of coals with organic additives. The process of solvation or solvolysis enables the additive to penetrate and depolymerize coal substance [12].

The phenomena of formation of anisotropic carbon in coke via nematic liquid crystals and mesophase are dependent on the extent of fluidity, the temperature range of maximum fluidity and chemical stability of the fluid phase [13]. It has been proposed by Marsh and Neavel [14] that hydrogen donor and acceptor mechanisms could be involved in carbonization processes with particular relevance to formation and stability of the nematic liquid crystals. Petrakis and Grandy [15] studied the structure and role of free radicals in coals using electron spin resonance spectroscopy (ESR). Pyrolized coals show a marked increase in free radical concentration especially around 673° C. Yokono and Marsh [16] co-carbonized pitch with anthracene and acenaphthylene to explain the concept of "hydrogen shuttling". It is presumed that the hydrogen may cap the reactive free-radicals produced in pyrolysis. This prevents the formation of isotropic carbon in a relatively early stage of carbonization and so minimizes the viscosity of fluid phase (maximizes fluidity) which enhances the formation of mesophase so leading to the anisotropic carbon.

1.3. Objectives of study

The objectives of this study are as follows:

1. To investigate the modification of optical texture of cokes from low-rank and high-rank Chinese coals by blending of coals and by additions of pitch to coal systems.
2. To search for correlations between the modifying ability of a pitch and its action as a hydrogen shuttle "vehicle" in pyrolysis reactions.
3. To assess the bridging effect of cokes from caking coal or pitch between "cokes" from weakly caking low-rank and high-rank coals.

2. Experimental procedures

2.1. Materials used

Five coals of different rank from the Liaoning Province of North Eastern China are used. The analyses of coals are listed in Table I. Table II contains the analyses of the pitch additives. CTP pitch is a coal-tar pitch from a Chinese coking plant. SRC pitch is a product from SRC-I process. AHA pitch is from residual oil after steam cracking and prepared by the Anshan Research Institute of Thermo-energy on a laboratory scale. A240 pitch from Ashland Petroleum Company is used as a comparison. The 9,10-dihydroanthracene was of 98% purity.

TABLE II Analyses of pitches (wt %)

Pitch	C	H	N
AHA	87.63	8.37	1.84
SRC	89.10	5.12	1.14
CTP	92.25	4.36	0.81
A240	91.36	5.69	0.20

2.2. Carbonization and examination

The carbonizations were carried out under nitrogen to a maximum temperature of 1273 K, at 4 K min^{-1}, with a soak period of 30 min. The size of samples is < 250 μm (< 60 mesh).

In co-carbonizations, the blends were mixed thoroughly in the ratio 50:50 (for coal blends), 70:30 (coal to pitch) and 40:40:20 (low rank coal:high rank coal:pitch). A reference metallurgical coke was made from the blend of 22.4% Fu Shun coal, 17.6% Shuang Ya coal, 21.6% Kai Lau coal, 26.6% Ji Xi coal and 11.8% Ben Xi coal.

Resultant cokes from the carbonizations were mounted in resin and polished surfaces examined using a Vickers M41 polarized light optical microscope with a half-wave retarder plate. Using a Swift semi-automatic point counter, quantitative assessments based on 800 points were made according to the classification of the size of optical texture in Table III. The data are presented as histograms.

2.3. Assessment of hydrogen shuttling ability of pitch

Each pitch was co-carbonized with 9,10-dihydroanthracene (1:1) in a sealed glass tube to 673 K at 5 K min^{-1}, no soak time. The resultant product was thoroughly extracted by chloroform and the chloroform subsequently removed in a rotary evaporator under vacuum. The residue matter was then dissolved in $CDCl_3$. Spectra were acquired using a 60 MHz ^1H NMR spectrometer. The peak areas at 8.3 and 3.85 ppm indicate relative con-

TABLE III Nomenclature to describe optical texture in polished surfaces of cokes

Isotropic (I)	No optical activity
Very fine-grained mosaics (VMF)	$< 0.5\ \mu m$ in diameter
Fine-grained mosaics (Mf)	0.5 to $1.5\ \mu m$ in diameter
Medium-grained mosaics (Mm)	1.5 to $5.0\ \mu m$ in diameter
Coarse-grained mosaics (Mc)	5.0 to $10.0\ \mu m$ in diameter
Supra mosaics (SM)	Mosaics of anisotropic carbon orientated in the same direction to give a mosaic area of isochromatic colour
Medium-flow anisotropy elongated (MFA)	$< 30\ \mu m$ in length; $< 5\ \mu m$ in width
Coarse-flow anisotropy elongated (CF)	30 to $60\ \mu m$ in length; 5 to $10\ \mu m$ in width
Acicular flow domain anisotropy (AFD)	$> 60\ \mu m$ in length; $< 5\ \mu m$ in width
Flow domain anistropy elongated (FD)	$> 60\ \mu m$ in length; $> 10\ \mu m$ in width
Small domains, isochromatic (SD)	10 to $60\ \mu m$ in diameter
Domains, ~ isometric (D)	$> 60\ \mu m$ in diameter

D_b is from basic anisotropy of low-volatile coking vitrains and anthracite.

D_m is by growth of mesophase from fluid phase.

Ribbons (R) Strands of mosaics inserted into an isotropic texture.

centrations of formed anthracene and residual 9,10-dihydroanthracene. The hydrogen shuttling ability of pitch is monitored as the extent of formation of anthracene from 9,10-dihydroanthracene during the co-carbonization.

3. Results

Figs. 1 to 6 are optical micrographs to illustrate the optical textures of cokes. Table IV describes the changes in optical texture of cokes brought about by use of blending of additives.

TABLE IV Optical texture of cokes from co-carbonizations

Coke from coal or coal blend	% Component within optical texture										
	I	Mf	Mm	Mc	SM	MFA	CFA	SD	FD	D	D_b
Fu Shun (602) I	97	3	–	–	–	–	–	–	–	–	–
Shuang Ya (502) II	70	29	1	–	–	–	–	–	–	–	–
Ben Xi (202) III	–	–	3	2	–	–	2	–	3	–	90
Kai Lan (301a) IV	11	26	32	25	4	–	–	2	–	–	–
Ji Xi (301a) V	8	18	10	4	52	2	5	–	–	–	1
I plus IV (1:1)	46	42	6	4	1	1	–	–	–	–	–
II plus IV (1:1)	34	36	19	8	2	–	–	1	–	–	–
I plus V (1:1)	50	30	1	1	16	1	–	–	–	–	1
AHA pitch VI	2	25	34	38	1	–	–	–	–	–	–
I plus VI (7:3)	60	18	19	3	–	–	–	–	–	–	–
II plus VI (7:3)	37	47	8	8	–	–	–	–	–	–	–
III plus VI (7:3)	–	2	7	24	2	3	–	3	1	–	58
SRC pitch VII	3	2	4	8	–	4	6	–	–	–	–
I plus VII (1:1)	29	66	4	1	–	–	–	–	–	–	–
II plus VII (1:1)	29	64	5	1	1	–	–	–	–	–	–
III plus VII (1:1)	–	1	8	29	3	–	1	6	–	–	52
CTP pitch VIII	–	17	1	1	–	–	4	72	3	2	–
I plus VIII (7:3)	12	88	–	–	–	–	–	–	–	–	–
II plus VIII (7:3)	12	78	3	1	6	–	–	–	–	–	–
III plus VIII (7:3)	–	19	10	10	9	–	–	1	1	–	50
A240 pitch IX	–	–	–	–	–	–	1	27	37	45	–
I plus IX (7:3)	5	93	–	–	2	–	–	–	–	–	–
II plus IX (7:3)	3	93	–	–	3	–	–	–	–	–	1
III plus IX (7:3)	–	–	32	36	–	–	–	21	1	8	32
I plus III (1:1)	48	–	1	1	–	–	–	2	1	–	47
I plus III, VIII (4:4:2)	35	14	2	4	3	2	–	7	1	–	32
I plus III, IX (4:4:2)	10	50	3	7	3	1	–	4	–	1	19

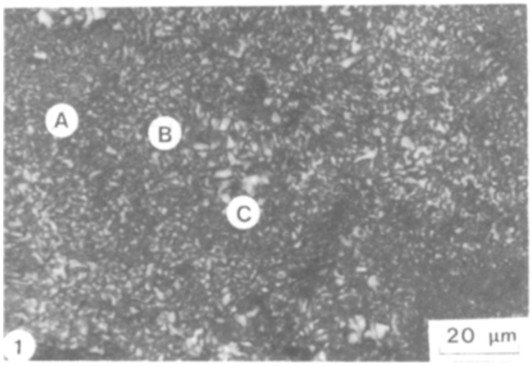

Figure 1 Optical micrograph of coke from AHA pitch showing fine-grained, medium-grained and coarse-grained mosaics, positions A, B and C, respectively.

4. Discussion

4.1. Coal blends

Table IV shows that the sizes of optical texture of cokes from coals increase with increasing rank of coal. The optical textures range from isotropic through to mosaics and domains. Domains in cokes from Bex Xi coal (202) developed from the basic anisotropy of the original coal, are different in origin from the domains formed from mesophase via liquid crystals.

Kai Lan coal and Ji Xi coal (301a) both can slightly modify the optical texture of coke from Fu Shun coal, the modification by Kai Lan coal being somewhat better than that by Ji Xi coal. This may be due to the fluidity of Kai Lan coal being higher than that of Ji Xi coal (Table I Giesler plastometer data).

Co-carbonization of coal blends from Shuan Ya coal (502) with Kai Lan or Ji Xi coal gave similar results.

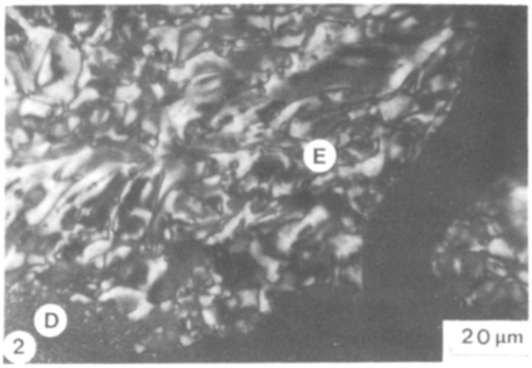

Figure 2 Optical micrograph of coke from CTP pitch showing fine-grained mosaics and small domains, positions D and E, respectively.

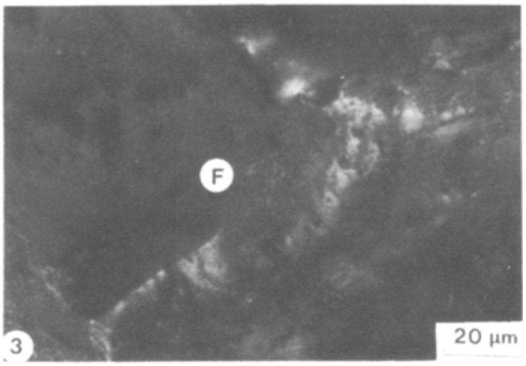

Figure 3 Optical micrograph of metallurgical coke (Fu Shun coal 22.4%, Shuang Ya coal 17.6%, Kai Lan coal 21.6%, Ji Xi coal 26.6%, Ben Xi coal 11.8%). Position F is coke from Fu Shun coal.

Little or no interaction occurred between Ben Xi coal (202) and Kai Lan or Ji Xi coal. There is a sharp boundary between the two cokes.

4.2. Coal pitch co-carbonizations

4.2.1. Pitch carbonizations

Optical textures of cokes from pitches are shown in selected micrographs of Figs. 1 and 2. The AHA pitch produces a coke having fine-grained, medium-grained and coarse-grained mosaics, Fig. 1. The SRC pitch produces a coke mainly containing coarse-grained mosaics, Fig. 2. The CTP pitch produces a coke with small domains and fine-grained mosaics. A240 pitch produces a coke possessing domains and flow domains, i.e. the largest of optical textures.

Following co-carbonizations of coals and coals with pitch, some optical textures of resultant cokes are shown in Figs. 3 to 5; the quantitative

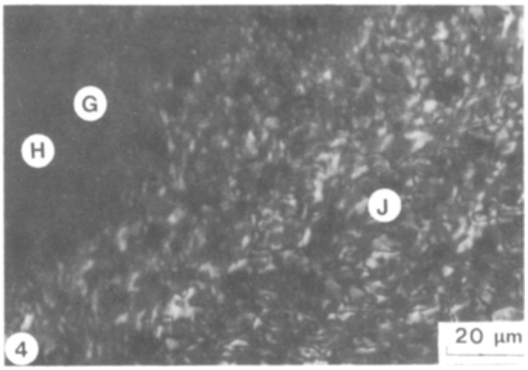

Figure 4 Optical micrograph of coke from Shuang Ya coal + AHA pitch (70:30). Position G shows the diffuse zone of change of optical texture between Shuang Ya coke, position H and AHA coke, position J.

analyses are in Table IV. Figure 3 is an optical micrograph of a metallurgical coke from a blend of Chinese coals.

4.2.2. Fu Shun (602) coal

There is a little interaction between Fu Shun coal (602) and AHA pitch. Sharp boundaries occur at the interface between the pitch coke and coal coke. Quantitative analysis shows that 61% of isotropic carbon still remains (Table IV). Here, AHA pitch mainly acts as a binder. In the co-carbonization of Fu Shun coal with SRC pitch, there is a diffusion zone at the interface with isotropic coke indicating that the pitch partly penetrates into coal. About 29% of isotropic carbon remains and the coarse-grained mosaics of pitch coke have mostly disappeared, Table IV. When Fu Shun coal is co-carbonized with CTP pitch or A240 pitch, the isotropic carbon is almost entirely replaced by fine-grained mosaics. About 12% of isotropic carbon is left for CTP pitch and ~ 4.4% for A240 pitch. No unmodified pitch coke occurs in the resultant optical texture. This resultant optical texture must be formed from a homogeneous fluid phase of dissolved pitch and coal substance.

4.2.3. Shuang Ya coal (502)

The modification of the optical texture by pitches is more marked for Shuang Ya coal than for the Fu Shun coal; Table IV. Even in co-carbonizations of Shuang Ya coal with the least effective AHA pitch there is a diffusion zone with progressive decrease in size of anisotropic coke occurring at the interface, Fig. 4, position G. Quantitative results are in Table IV.

4.2.4. Ben Xi coal (202)

AHA pitch and SRC pitch seem unable to modify the optical texture of coke from this higher-rank Ben Xi coal. There are sharp boundaries between the coal coke and the pitch coke; hence, the resultant coke has two distinct anisotropic cokes. One is the basic anisotropy from coal of which ~ 58% still remains and the other is the optical texture from unmodified pitch. Addition of CTP pitch to Ben Xi coal causes limited interaction between the coal and pitch, but sharp boundaries also occur, Fig. 5, position K. When A240 pitch is used, the interface is irregular showing some limited degree of penetration of the pitch into the coal. The largest size of optical texture from A240 pitch is absent. The quantitative results of adding CTP pitch and A240 pitch to Ben Xi coal are in Table IV.

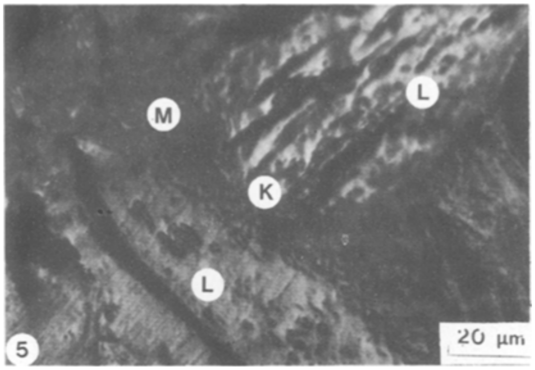

Figure 5 Optical micrograph of coke from Ben Xi coal + CTP pitch (70:30). Position K shows sharp boundaries between Ben Xi coke, position L and CTP coke, position M.

4.3. Hydrogen transfer from pitches

The modifying ability of coals in coal blends are quite limited. The pitches, except AHA, are much more effective. Firstly, this can be attributed to the low softening point of pitch (normally before the softening of low rank coal). This creates a wide temperature range of fluidity so preventing chemical cross-linking to form isotropic coke from low rank coal at an early stage of carbonization. Secondly, it can also be attributed to the much greater fluidity of pitch compared with that of coal.

The results show that not all pitches behave similarly. To explain the difference between them, the modifying ability of pitch in terms of its hydrogen shuttling ability has been examined. The results are given in Table V. The percentage of isotropic component remaining in the resultant coke of Fu Shun coal (602) with pitch (as an example) is used as an index of the modifying ability of the pitch. The ratio of amounts of

TABLE V Correlation between modifying ability and hydrogen "shuttling"

Pitch	Isotropic component in coke*	A/DHA
A240	4.4	0.75
CTP	12.3	0.66
SRC	28.6	0.40
AHA	61.0	0.37

*Coke from Fu Shun coal + pitch (7:3).
A = Anthracene.
DHA = 9,10-dihydroanthracene.

anthracene (A), which are formed by co-carbonizing pitch with dihydroanthracene, to remaining dihydroanthracene (DHA) represents the hydrogen accepting ability of pitch. Table V shows that the modifying ability of pitch is related to its hydrogen shuttling ability. This implies that pitch molecules transfer hydrogen from one coal molecule to another coal molecule so behaving as a hydrogen shuttling vehicle. Hydrogen may cap certain of the free radicals formed from coal. Such capping stabilizes the system for a period of time so preventing or delaying the repolymerization of coal to anisotropic coke. This process provides the necessary lower fluidity over a wider temperature range and consequently enhances the extent of modification to create a larger sized optical texture.

4.4. Coal–coal pitch co-carbonizations

Metallurgical coke is usually produced from a multi-coal blend (Fig. 3). Coals in blends can generally be divided into three groups. Low-rank coals are responsible for the production of gas and chemical products. In co-carbonization of Fu Shun coal (low-rank) with Ben Xi coal (high-rank), they are carbonized individually without any interaction and coalescence so the resultant coke is granular without sufficient strength. The quantitative data (Table IV) show that each coke retains its original optical texture. Hence, it is necessary to have some bridging agent such as prime coking coal, strongly caking coal, or pitch to link these granules together. The bridging ability is due to the development of the new optical texture which incorporates the coal into coke composite.

To observe the bridging effect, coal blends from low-rank coal and high-rank coal were co-carbonized with CTP pitch. The CTP pitch interacts with low-rank coal to develop intermediate texture (defined by Ragan and Marsh [6]), of fine-grained mosaics which is bonded to the basic anisotropy from high-rank coal. The quantitative data, Table IV, confirms that the isotropic component from low-rank coal has been reduced and that the basic anisotropy from high-rank coal is hardly affected.

Addition of A240 pitch to the coal blend causes penetration not only into the coke from low-rank coal, but also into the coke from high-rank coal. In Fig. 6, position N is isotropic carbon from Fu Shun coal; positions P and Q are the intermediate texture formed by the interaction with Fu Shun coal, (position P), and with Ben Xi coal (position Q). Position R is basic anisotropy from Ben Xi coal. The quantitative analyses, Table IV, show that the isotropic and basic domain components are reduced in extent.

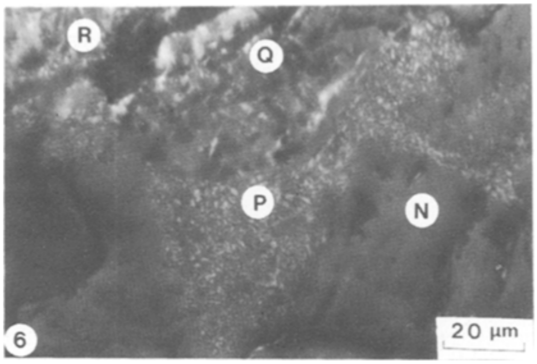

Figure 6 Optical micrograph of coke from Fu Shun coal + Ben Xi coal + A240 pitch (40:40:20). Position N = isotropic carbon from Fu Shun coal. Positions P and Q = intermediate optical texture. Position R = basic anisotropy from Ben Xi coal.

5. Conclusions

Fu Shun (602) and Shuang Ya (502) coals are easier to modify than Ben Xi (202) coal. Ji Xi and Kai Lan coals can be modifiers but their modifying ability is limited. The pitches, except AHA are much more effective as modifiers.

The extent of modification of a pitch is related to its original optical texture. The different modifying abilities of pitch increase with increasing ability to shuttle hydrogen.

The additive can form a bridging coke with cokes from low-rank coal and high-rank coal in the coal blend. Only the most effective of pitches, such as A240 can interact with both the low-rank and high-rank coals to result in significant bonding and modification.

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