INFLUENCE OF COKE STRUCTURE ON GASIFICATION KINETICS AND SELECTIVE GASIFICATION

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1. INTRODUCTION Coals, carbons, cokes and graphites, industrially, are mostly used in oxidative atmospheres resulting in gasification of the carbonaceous material. This gasification is often the required process as in steam gasification of coals and chars and in the electrolytic reduction of bauxite to aluminium where carbon anodes are consumed. The major part of the world's energy requirements are met by combustion of coal in electrical power stations. On the other hand, it is undesirable that metallurgical coke in the blast furnace should undergo gasification to carbon monoxide whilst in the stack of the blast furnace. The purpose of arc-electrodes in steel making is to transmit electrical energy to the crucible. Here gasification of the arc-electrode is detrimental to performance.

The literature of carbon gasification is dominantly concerned with the kinetics of gasification reactions using oxygen, steam, nitrous oxide, sulphur dioxide, carbon dioxide and hydrogen (1-5). An aspect of gasification reactions which has received much less attention is the role of the structure of the carbon and the influence of gasification reactions upon the properties of the solid carbon as the reactions proceed (6-8). The purpose of this paper is to discuss further the role of carbon structure during gasification reactions.

1.1. Solid carbons The term 'solid carbon' covers all natural and synthetic substances consisting mainly of atoms of the element carbon and with the structure of graphite or at least with two-dimensionally ordered layers of carbon atoms (9). Solid carbons (referred to as 'carbons') exist as non-graphitic non-graphitizable forms, as non-graphitic graphitizable forms or as graphitic forms. Non-graphitic carbons have two-dimensional long range order of carbon atoms in planar hexagonal networks but without measurable crystallographic order in the third direction. On heat treatment to above 2500 K the graphitizable carbons adopt a more or less perfect three-dimensional crystalline order as graphitic carbon, whereas the non-graphitizable carbons retain only two-dimensional order.

1.2. Formation of solid carbons The non-graphitizable carbons are mostly derived from parent substances which do not pass through a fluid phase on carbonization. They are therefore structural pseudomorphs of the parent material, examples being charcoal from wood, chars from low rank coals and carbonized anthracite. They have usually surface areas $>>100\ m^2g^{-1}$, are microporous and are isotropic in polished section in plane polarized light optical microscopy. The graphitizable carbons are mostly derived from parent substances which pass through a fluid phase on carbonization. Here the resultant solid carbon is formed via an intermediate phase, the MESOPHASE, of aromatic lamellar nematic liquid crystals (10). The graphitizable carbons have, usually, surface areas $<5\ m^2g^{-1}$, they contain little or no microporosity and are anisotropic in polished section in plane polarized light optical microscopy (11). Thus, the term 'solid carbon' is a generic term and contains many quite diverse materials.

1.3. Anisotropic carbons These materials exhibit a wide range of structure best characterized by optical microscopy (11). The liquid crystals of the carbonization process exhibit a size range, observable in optical microscopy, between ~1 μm and 200 μm diameter. The liquid crystals, as carbonization temperatures increase, can either (a) fuse together without loss of identity or (b) coalesce into each other with loss of identity to give larger crystals. The structure of the resultant anisotropic carbon (coke) is a consequence of this fusing or coalescing and is made up of the 'macrocrystals' from the liquid crystals. The size range of this macrocrystallinity is described as the optical texture of the carbon and a nomenclature

exists (12) covering from the very fine-grained mosaics (<0.5 μm dia.) to domains (~200 μm dia.). Thus, within anisotropic carbons alone wide variations in structure exist and need to be specified.

1.4. Influences upon gasification It has to be emphasized that rarely (if ever) does a solid carbon exist in the pure form, i.e. containing only the element carbon. It is always associated with hydrogen and oxygen, other heteroatoms and mineral impurities. These other elements significantly affect rates of gasification reactions, i.e. CATALYTIC effects exist (3, 4). Gasification reactions of carbon are heterogeneous processes and a complete specification of the solid carbon of the study is desirable (if not essential). This specification should include (a) for anisotropic carbons, the heat treatment temperature (HTT) and size/shape of optical texture (b) an indication of the impurity content of the carbon, heteroatoms and mineral matter (c) surface area. The surface area of carbons varies from ~2000 m^2g^{-1} to ~0.01 m^2g^{-1} (13, 14). Rates of gasification will accordingly vary considerably, carbon to carbon, simply on the basis of surface availability alone, i.e. total surface area (TSA). However, some twenty years ago, the concept of Active Surface Area (ASA) was introduced and has recently been developed (5). This concept states that surfaces of carbons of equal surface area do not necessarily have the same 'reactivity' under standardized conditions, but can have different surface concentrations of active sites. These must be related to structure (i.e. defects and heteroatom content) within the planar hexagonal network of carbon atoms which make up the structure within carbons.

1.5. Selective gasification Solid carbons are essentially non-homogeneous materials (glassy carbons being one of the more homogeneous forms). The non-graphitizing isotropic carbons contain the diverse structures of the parent material and manufactured carbons are mostly composite materials made up of several carbon forms each of which is heterogeneous with a range of size/shape of optical texture. As a consequence of this, during gasification reactions, it is observed that surfaces of carbons exhibit areas of selective preferential gasification, resulting in pitting and fissuring (6, 7). Thus, during gasification, the composition of the carbon material is itself changing. Likewise, physical properties also change such as strength and crack resistance (15). This process of selective gasification can thus influence the 'shift-life' of industrial carbon artifacts, e.g. the aluminium anode and metallurgical coke.

1.6. The reactivity of carbons Rate expressions have been developed to describe gasification processes by e.g. steam and carbon dioxide (16). Studies which encompass 'families' of carbons into kinetic data are limited (17) but indicate a spread of reactivities, partly due to lack of ASA data to correct the TSA. The concept that a carbon has a given 'reactivity' which can place it in a given 'pecking-order' could be useful. The limited evidence available suggests that even for a single gasifying gas, e.g. carbon dioxide, 'pecking-orders' depend upon experimental conditions. When several gases are considered the concept of a reactivity pecking-order for all gases is virtually unstudied.

2. OBJECTIVES The objectives of this paper are (a) to prepare carbons, with a size range of optical texture, made from pure model organic compounds and Ashland A240 petroleum pitch containing chemical and inert additives; (b) to study the gasification of these carbons by carbon dioxide and relating rates to optical texture and topographical features of pitting etc. using scanning electron microscopy (SEM); (c) to study the relative reactivities of pitch cokes of different optical textures to N_2O, O_2 and CO_2 as well as spontaneous ignition temperatures (SIT) in air; (d) to study the relative efficacies of catalysts in equal concentrations, in carbons of different optical textures from the Ashland A240 pitch.

3. EXPERIMENTAL AND RESULTS

3.1. Use of model compounds (18) Carbons were prepared by carbonization under nitrogen, in tube furnaces to 1273 K (1000°C) at 5 K min^{-1} of acenaphthylene (I), acridine (II), anthrone (III), thianthrone (IV) as well as 9:1 and 1:1 mixtures of acenaphthylene with II to IV and cellulose (V). Optical textures were assessed by optical microscopy (11) and rates of gasification in carbon dioxide were measured gravimetrically using a Stanton Redcroft STA 780 with microbalance facility (DTG)

CO_2 flow rate of 50 $cm^3 min^{-1}$, particle size 250-500 μm, between 1073 and 1273 K. Results are summarized in Table 1.

Table 1.

Carbon	Dominant Size of Optical Texture/μm	Rate at 1240 K/ $s^{-1} \times 10^{-6}$	Activation Energy/ kJ mol^{-1}
I	>60	8	140
II	10-60	20	186
III	<1	28	170
IV	Isotropic	56	180
9:1 (1:II)	>60	19	88
1:1 (1:II)	>60	22	-
9:1 (1:III)	5-30	13	160
1:1 (1:III)	<5-30	185	-
9:1 (1:IV)	5-30	12	-
1:1 (1:IV)	<5-30	17	120
9:1 (1:V)	5-30	23	170
1:1 (1:V)	1.5-5.0	92	200

Rates of gasification are expressed on a g $g^{-1}s^{-1}$ (i.e. s^{-1}) basis. Surface areas are not measured. The pure carbon (without heteroatoms) (I) has the lowest reactivity (8×10^{-6} s^{-1}) and largest optical texture. The three carbons of smallest optical texture from (IV), (1:1 (I:III)) (1:1(I:V)) have the highest reactivity i.e. 56, 185 and 92×10^{-6} s^{-1} respectively. Certainly, the presence of heteroatoms within the carbon, i.e. nitrogen (II), oxygen (III and V) and sulphur enhance reaction rates, the oxygen being the most effective. As the size of optical texture decreased, the topographical features of gasification changed from fissures to pitting.

3.2. Use of Ashland A240 petroleum pitch (18) Carbons were prepared from Ashland A240 pitch, singly and with additions of cellulose and sulphur, as described above. Reactivities were measured 1073-1273 K and surface areas measured volumetrically at 77 K using krypton as adsorbate. Results are summarized in Table 2.

Table 2.

Carbon	Dominant Size of Optical Texture/μm	Rate at 1240 K/ $s^{-1} \times 10^{-6}$	Activation Energy/ kJ mol^{-1}	Surface Area/ $m^2 g^{-1}$	Rate at 1240 K $g\ s^{-1} m^{-2} \times 10^{-6}$
A240	>60	5	205	0.14	37
A240+V 6:4	30-60	15	205	0.52	29
A240+V 1:1	1.5-5.0	19	185	1.21	16
A240+S 9:1	5-10	5	185	0.48	11
A240+S 6:1	Isotropic	8	155	2.04	4

Compared with the data of Table 1, carbons from A240 pitch are less reactive than carbons from acenaphthylene (units of s^{-1}). In these units the addition of oxygen in cellulose (more so) and sulphur (less so) enhances the rates of gasification. But when expressed in units of $g\ s^{-1} m^{-2}$, the rates of gasification decrease with addition of cellulose and sulphur, i.e. the ASA apparently decreases. Activation energies also decrease.

3.3 Addition of TK800 silica to A240 pitch Additions of 'inert' solids, <1 μm diameter, to pitch materials influence the carbonization process by restricting coalescence of mesophase (19, 20). Consequently, the progressive additions of such solids (often referred to as QI material) to a pitch can reduce the size of optical texture of resultant carbon from domains (>60 μm dia) to isotropic (<0.5 μm dia). This 'mechanical' modification to optical texture is distinct from that brought about by 'chemical' additions, as in Tables 1, 2. Experimentally, carbons were prepared from A240 pitch containing known dispersions of TK800 silica (particle dia ~10 nm; surface area ~150 $m^2 g^{-1}$). Rates of gasification and surface areas were measured as described above. Results are summarized in Table 3. Rates are corrected for silica content.

Table 3.

Carbon	Dominant Size of Optical Texture/μm	Rate at 1240 K/ $s^{-1}x10^{-6}$	Activation Energy/ $kJ\ mol^{-1}$	Surface Area/ m^2g^{-1}	Rate at 1240 K $g\ s^{-1}m^{-2}x10^{-6}$
A240	>60	6	205	0.14	43
+5%	3-20	9	175	0.001	$9x10^3$
10%	0.5-1.5	26	220	0.09	290
15%	0.5-1.5	83	145	0.22	380
25% of TK800	0.5-1.5	130	190	12	11

Additions of 'inert' silica have significant effects on the rates of gasification when expressed in units of $g\ s^{-1}m^{-2}$, rates varying by three orders of magnitude. The 'inert' material should not be considered as being chemically inert. Its addition to the pitch and its presence in the liquid crystal phase of carbonization must influence the chemistry of conversion of pitch to carbon such that major changes result in the ASA of the carbon, more than observed by chemical additions. In a separate experiment of mechanical mixing of carbon with the TK 800 silica, the latter was not observed to be a catalyst to gasification reactions.

3.4. Relative reactivities of pitch cokes (21) Cokes were prepared from 21 pitch materials and examined by optical microscopy with rates of gasification being measured using oxygen, nitrous oxide and carbon dioxide. Spontaneous ignition temperatures (SIT) (21) were determined in static air. Table 4 lists the pitch cokes in increasing SIT values, i.e.of decreasing reactivity (1 to 21) together with an optical texture index (OTI) a measure of average size of optical texture (12), QI content of pitch and k_{CO_2} (1240 K) in units of s^{-1}. Table 5 lists the pecking-order of pitch cokes relative to the order established based on SIT. The data within these two Tables suggest broad correlations between SIT and OTI and QI content as well as k_{CO_2} (1240 K). It is seen that the pecking-orders of reactivities in different gases change with the gasifying gas being used. The pecking-order, when using a single gas, i.e. carbon dioxide, depends upon the temperature of measurement of the rate of gasification. There is an identifiable correlation between SIT and k_{O_2} and k_{N_2O}. However, at the higher temperatures needed to determine k_{CO_2} some major displacements of position occur. This suggests that the ASA of carbons could be a function of the gas used as well as being a function of the structure of the carbon. An unknown factor in this particular study is the lack of knowledge of possible catalytic mineral impurities within the pitch coke and derived from the pitch. Catalysis is sensitive to the reacting gas (4) and the temperature of gasification and this factor may account for displacements in the pecking-order.

3.5. Catalyst efficacies in pitch carbon The A240 pitch and pitches No. 16 and 14 were doped with nickel acetylacetonate and sodium chloride according to the ratios in Table 6 and carbonized as described. Reactivities of resultant carbons to carbon dioxide were assessed to give a rate at 1240 K (k_{CO_2}). Relevant details and results are in Table 6. These are preliminary data and suggest that the catalysts may be more effective in carbons of medium sized optical texture, as for pitch carbons (No. 16). Comparison of Table 4 with 6, using k_{CO_2} (1240 K) data, suggest that the carbons of high reactivity, e.g. Nos. 1, 3, 5, 6, 14 may contain catalytically active mineral impurities.

4. CAUSES OF SELECTIVE GASIFICATION Examination of surfaces of carbons, after gasification, by scanning electron microscopy indicates the formation of fissures within carbons of largest size optical texture and of pitting within carbons of smallest size of optical texture. This implies a heterogeneity of structural components within the carbon. In discussing gasification mechanisms the (e.g.) carbon dioxide molecule reacts specifically with only ONE carbon atom in the available surface. The existence of preferential selective gasification to produce (e.g.) pitting implies either that a volume element within the carbon is more 'reactive' than the surrounding carbon, or that the removal of a single carbon atom or even a planar hexagonal network of carbon atoms may induce or create a

Table 4.

Pecking-Order for 21 Pitch-Cokes

Based on SIT values (low to high)	Optical Texture Index	QI Content/ wt. %	k_{CO_2} at 1240 K $s^{-1} x10^{-6}$
1	7.3	8.1	68
2	3.2	17.6	36
3	7.6	10.9	42
4	3.6	24.7	25
5	6.4	7.7	67
6	7.2	8.5	49
7	5.7	8.0	14
8	12.8	0.8	33
9	3.6	20.3	31
10	7.4	8.4	29
11	4.7	15.6	19
12	10.2	5.7	26
13	5.2	11.0	21
14	2.9	17.7	42
15	8.7	0.8	27
16	4.6	18.0	11
17	10.8	0.3	35
18	7.0	10.6	14
19	12.8	3.1	11
20	11.4	0.1	10
21	14.0	0.2	7

Table 5.

Pecking-Order for 21 Pitch Cokes
(Most Reactive to Least Reactive)

Based on SIT values (low to high)	Based on k_{O_2}:900 K (high to low)	Based on k_{N_2O}:900 K (high to low)	Based on k_{CO_2} 1173 K (high to low)	1273 K	1423 K
1	3	1	1	14	14
2	1	11	5	1	5
3	2	3	3	5	13
4	6	5	8	3	4
5	7	6	2	10	3
6	10	7	6	9	1
7	11	8	14	20	6
8	8	4	10	6	2
9	5	10	13	4	7
10	4	2	17	13	10
11	12	9	16	8	18
12	13	15	7	17	19
13	9	12	20	2	20
14	14	14	12	12	15
15	16	19	11	15	12
16	18	13	15	18	8
17	15	17	4	11	11
18	19	18	9	7	17
19	17	16	19	19	16
20	20	20	21	16	19
21	21	21	18	21	21
Average displaced position	1.91	1.95	3.82	4.38	4.10

Table 6.

Carbon	k_{CO_2} at 1240 K $s^{-1} x10^{-6}$	OTI	QI Content/ wt. %
A240	7	14	0
A240 + 0.01 mol Ni	11		
A240 + 0.01 mol Na	39		
A240 + 0.034 mol Na	57		
Pitch No. 16	15	4.6	0.8
+ 0.01 mol Ni	155		
+ 0.01 mol Na	38		
0.034 mol Na	270		
Pitch No. 14	44	2.9	17.7
+ 0.01 mol Ni	120		
+ 0.01 mol Na	100		
0.034 mol Na	140		

more reactive position. The data of Table 3 suggest that carbons of different optical texture can have markedly different reactivities, particularly if optical texture is influenced by the presence of 'inert' (QI) material within the pitch. In carbon composites or even in single carbons, the existence of a range of size of optical texture is common experience. The differences in reactivities between these 'macro-crystals' of optical texture may account for selective gasification processes.

However, the reason why certain 'macrocrystals' are more reactive has to be considered specifically. During gasification, (e.g.) carbon dioxide probably reacts preferentially with carbon atoms at prismatic edge presentations or at defects within the basal planes of the planar networks (22). A study of shape and size of these planar networks (within carbons of several optical textures) by phase contrast high resolution electron microscopy (23) suggests that as the size of optical texture decreases so the size and planarity of the networks of carbon atoms also decreases. This suggests that the ASA of a carbon surface is dependent upon the size and perfection of the networks which make up that plane and that these factors are not independent of optical texture. Variations of 'reactivity' between carbon atoms in different positions within a network have recently been reported (24). However, the presence of catalytic mineral impurities within the carbon can override the above deliberations.

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