INTRINSIC REACTIVITY OF COKE AND CHAR TO CARBON DIOXIDE

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INTRODUCTION

Petroleum coke and coal derived cokes and chars find widespread use in metallurgical and gasification processes. During aluminium smelting, carbon electrodes are consumed not only by the desired electrolytic reactions but also by undesirable means, such as gasification by carbon dioxide and oxygen from the surrounding air. In ferrous and non-ferrous blast furnace processes, metallurgical coke is often excessively consumed by reaction with carbon dioxide which may lead to degradation of coke strength, and hence reduce furnace permeability. Further, due to the endothermic nature of the reaction, excessive reaction of coke with CO_2 may lead to disturbance of the desired blast furnace temperature profile and heat balance. Coal chars find widespread use as a source material in gasification processes and in activated carbon manufacture. Chars derived from Australian brown coals are particularly suited to the latter application as they contain only very small quantities of mineral matter.

In order to devise means of suppressing wasteful consumption of carbon and energy in metallurgical processes and to optimise the utilisation of coal chars in other processes it is necessary to have a quantitative understanding of the factors which control the rate of carbon gasification. The rate of reaction of coke or char with CO_2, in common with other gas-solid reactions, is controlled by three main factors [1]: (a) the rate of reactant gas transport to the coke or char surface; (b) the combined effects of the rate of diffusion of the gas through the pore structure of the material and the rate of chemical reaction of the gas with the carbonaceous components of the coke or char; and (c) the rate of chemical reaction alone.

The reaction conditions selected for the present study were such that any significant influences of factors (a) and (b) were eliminated in order to allow the intrinsic chemical reactivity of the selected materials to the reaction $C_{(s)} + CO_{2(g)} = 2CO_{(g)}$ to be evaluated.

EXPERIMENTAL

Three materials were considered in this study. They were (1) an experimental metallurgical coke produced from Queensland coking coal in a small scale (7 kg) laboratory coke oven; (2) a sample of petroleum coke used in the production of anodes for a commercial aluminium smelter and previously studied in this laboratory [2], and (3) a sample of char produced from a Victorian brown coal. Chemical analyses of these materials are given in Table 1.

The experimental apparatus is illustrated in Figure 1. This apparatus and the procedures adopted are a modification of a system previously developed at CSIRO [2,3]. It allows the reaction rate, order in CO_2 concentration and activation energy to be determined from a single experiment.

The rate of carbon loss (dW/dt) was determined directly from the flow-rate and carbon monoxide content of the reactor exit gas stream which was continuously measured with a non-dispersive infra-red CO analyser. The specific reaction rate, ρ [g/min.g], was then calculated according to Equation (1):

$$\rho = \frac{1}{W}\left(\frac{dW}{dt}\right) \qquad [g/min.g] \qquad (1)$$

where W is the weight of sample remaining at any time, t.

It is known that the product carbon monoxide can have a retarding effect on the rate of reaction [4]. The present investigation was carried out with carbon monoxide levels always below 1% v/v, at which value the retardation effect can be ignored [5].

During an experiment, step changes were made in the concentration of carbon dioxide in the reactant gas stream. This was achieved by alternating between the two reactant streams indicated as streams A and B in Figure 1. Hence the reaction rate of individual samples was determined at several carbon dioxide concentrations (approximately 30, 50, 75 and 100% v/v) in a single experiment. The reaction order thus determined was corrected, using the experimentally determined activation energy (see below), for any temperature variation brought about by the change in gas composition and is independent of changes in the pore structure of the sample.

At the conclusion of a test, the furnace was switched off and the activation energy of the reaction calculated from an Arrhenius plot of the rate data obtained during cooling of the reaction system. The weight loss of the materials was very small (less than 1%), and the pore structure therefore assumed to remain unchanged, during this period.

The total surface area, A_g, of the sample residue was then measured and the intrinsic reaction rate, ρ_s, calculated according to Equation (2).

$$\rho_s = \frac{\rho}{A_g} \qquad [\,g/m^2.min] \qquad (2)$$

The kinetic data, obtained at a common extent of reaction, are expressed as

$$\rho = A_g\ C_g^{\,m} B \exp\,(-E/RT) \qquad [g/min.g] \qquad (3)$$

where R is the gas constant, m is the order of reaction in CO_2 concentration, C_g, E is the activation energy, and B is a pre-exponential or frequency factor.

The observed values of E and m in Equation (3) only represent their respective true values when neither external transport nor pore diffusion effects have any significant effect on the observed reaction rate. Preliminary experiments revealed that the reaction rate, ρ, was independent of the reactant gas flowrate (between 500 and 1000 ml/min) and of coke or char particle size (between 0.2 and 1.7 mm) and that particle density decreased linearly during gasification. These observations confirm that mass transfer processes do not exercise a significant influence on the reaction rate under the conditions selected for the present work.

RESULTS

The results of a typical experiment are shown in Figures 2 and 3. In Figure 2, the reaction rate, ρ, at 890°C, of a bed of 0.9 mm metallurgical coke particles is plotted as a function of the fractional weight loss of the coke. The response to sudden changes in the inlet gas composition can be clearly seen. The reaction order, m, was calculated at these step changes and is shown, in the upper portion of Figure 2, to remain approximately constant during reaction (average value = 0.68). The activation energy, E (239 kJ/mol), was determined from the Arrhenius diagram of Figure 3, a plot of the data over the declining temperature period depicted in the final portion of Figure 2.

The results of a series of experiments using all three materials are summarised in Table 2 and Figure 4. The overall activation energy of the reaction is similar for all three materials examined here and values in the range 185-245 kJ/mol were found. The kinetic data determined for the petroleum coke in this study are in general agreement with the results of a previous investigation using this material [2].

It appears that E increases during reaction of the brown coal char, however the range of this variation is not large and further work is required to determine the significance of this trend. Similar behaviour was not apparent for the other materials where variations in E between experiments are not considered significant given the heterogeneous nature of the materials (particularly the metallurgical coke).

The order of reaction with respect to CO_2 partial pressure was approximately constant for all of the materials as the extent of gasification increased. The average values of m for the three materials are summarised in Table 2. Similar values of m (0.65-0.68) were found for the petroleum and metallurgical cokes while reaction of the brown coal char showed a slightly lower dependence on CO_2 partial pressure (m = 0.57). Values of m in the range 0.55-0.60 were also found during a number of experiments using different particle sizes of brown coal char.

It is apparent in Figures 2 and 4 that the rate of reaction of the metallurgical and petroleum cokes increases during reaction. The brown coal char demonstrated an apparent decline in reaction rate in the initial period of reaction, up to approximately 6% weight loss (Figure 5), beyond which the rate increased strongly with further gasification (Figure 6). The reasons for the initial decrease in the observed reaction rate of this material are not yet explained but it is possible that this initial evolution of CO is the result of desorption of oxygen containing species which are present initially on the char surface and were not dislodged by heating to reaction temperature in nitrogen.

The subsequent increase in the reaction rate of the char and the increase in ρ during reaction of the two cokes is thought to be due, at least in part, to alteration of the surface area of the materials. The relatively high initial surface area of the brown coal char (Table 2) may also account for its high values of ρ relative to the coke samples (Fig. 4).

Surface areas of coke and char residues at various extents of gasification are presented in Table 2 and Figure 7. The surface areas of the brown coal char and metallurgical coke increase greatly during reaction with CO_2 while that of petroleum coke, despite a measurable increase, remains very low.

The intrinsic reaction rate of each of the materials was calculated from the rate and surface area data of Figures 4 and 7 respectively, according to Equation (3) and is shown in Figure 8. The main features of Figure 4 remain evident, however the relative reactivities of the materials change greatly when allowance is made for the changing surface area of the materials. Despite their vastly different total surface areas, the brown coal char and the metallurgical coke are seen to display similar reactivities per unit surface area (Figure 8). At all temperatures, the petroleum coke was far more reactive, per unit surface area, to CO_2 than the coal derived materials. As the reaction proceeds and the surface area increases, the intrinsic reactivity, ρ_s, of all the materials decreases. This behaviour has not yet been explained and will be considered in future work. An attempt to determine the reasons for the high intrinsic reactivity of petroleum coke relative to the coal derived materials will also be made.

CONCLUSIONS

Measurements have been made of the intrinsic reactivity of a petroleum coke, a metallurgical coke and a brown coal char to carbon dioxide over the temperature range 650-900°C and at carbon dioxide partial pressures between 0.3 and 1 atm.

The order of reaction with respect to carbon dioxide concentration remained constant during reaction up to 42% weight loss at approximately 0.65 for petroleum coke and metallurgical coke and 0.55-0.60 for brown coal char. The activation energy of reaction was similar for all materials and was in the range 185-245 kJ/mol. The surface area of the materials varied widely and increased during reaction (up to 42% weight loss) by factors of approximately 5, 100 and 25

for the petroleum coke, metallurgical coke and brown coal char respectively. The intrinsic reaction rate per unit surface area decreased during gasification of each of the materials.

REFERENCES

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3. Tyler, R.J., Wouterlood, H.J. and Mulcahy, M.F.R., Carbon, 14, 271 (1976).

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TABLE 1: Chemical Analysis of Cokes and Char (% w/w)

Material	Ash	C	H	N	S	O
Metallurgical Coke	12.1	85.0	0.4	1.9	0.6	0.0
Petroleum Coke	0.5	96.7	0.2	1.6	1.0	0.0
Brown Coal Char	2.4	94.9	0.6	0.5	0.1	1.5

TABLE 2: Summary of Reactivity Data for 0.9 mm Particles

Material	weight loss (%)	E (kJ/mol)	m (average)	A_g (m^2/g)
Petroleum coke	0	-	-	0.6
	6	231	nd	0.9
	31	214	0.65	3.1
	42	218	0.65	2.4
Metallurgical coke	0	-	-	0.9
	9	239	0.68	54.9
	38	216	0.66	98.6
Brown coal char	0	-	-	39.1
	6	185	0.57	358.7
	18	214	nd	464.4
	41	244	nd	986.9

nd = not determined

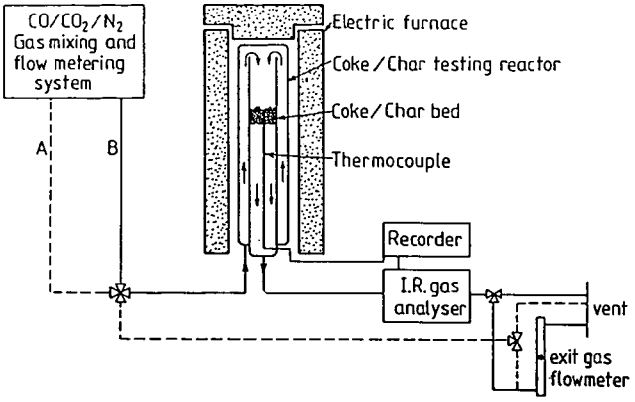
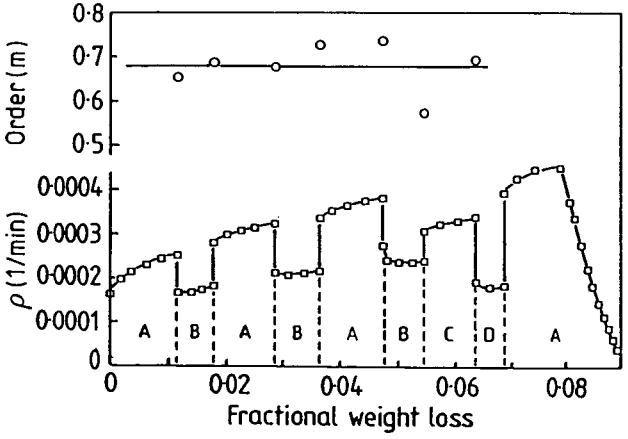


Figure 1 Schematic representation of experimental apparatus



	A	B	C	D
CO_2(%)	100	50	77	30

Figure 2 Reaction rate (▫) and order (o) for metallurgical coke (0.9 mm) reacted in CO_2/N_2 mixtures at 890°C.

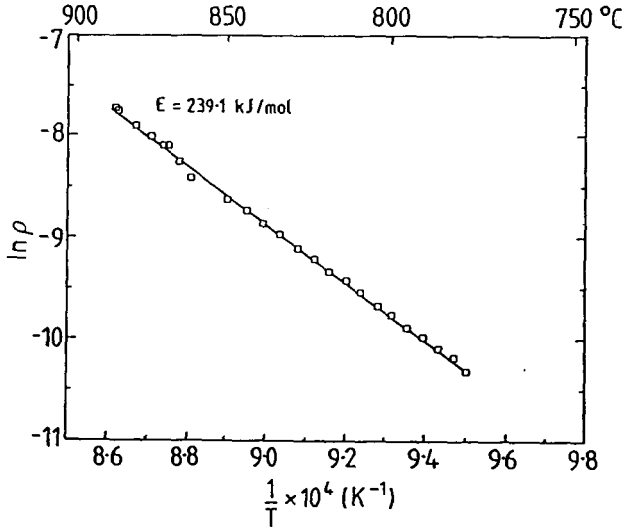


Figure 3 Reaction rate, ρ (g/min.g), during cooling of coke sample as depicted in final portion of Figure 2.

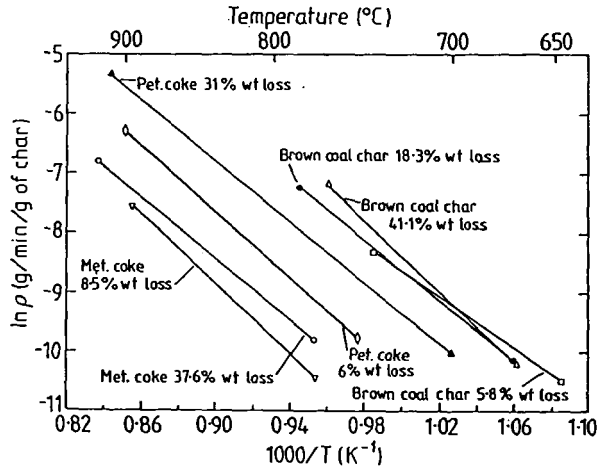


Figure 4 Relation between reaction rate, ρ (g/min.g), and temperature for brown coal char, metallurgical coke and petroleum coke. (p_{CO_2} = 1 atm).

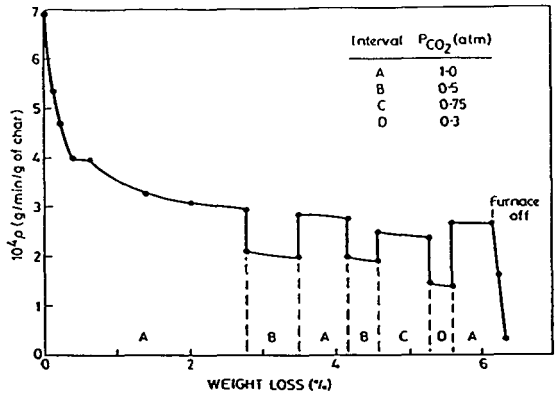


Figure 5 Reaction rate of brown coal char (0.9 mm) during the initial period of reaction at 740°C.

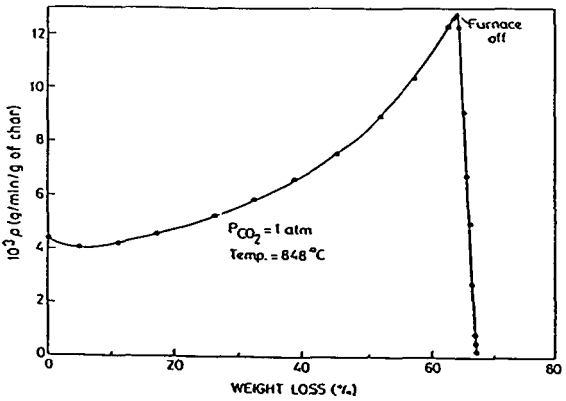


Figure 6 Reaction rate as a function of the extent of gasification of char at 848°C.

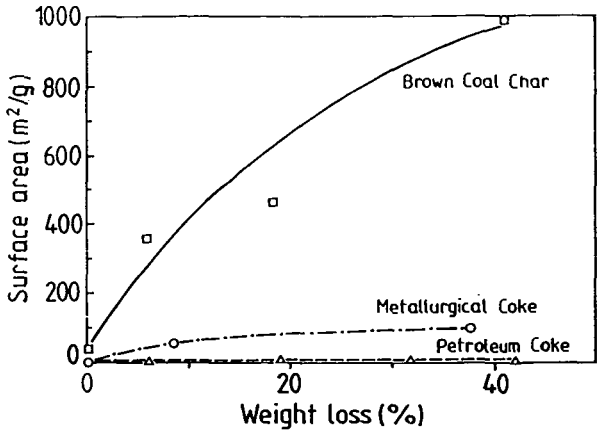


Figure 7 Effect of reaction on total (N_2, BET) surface area.

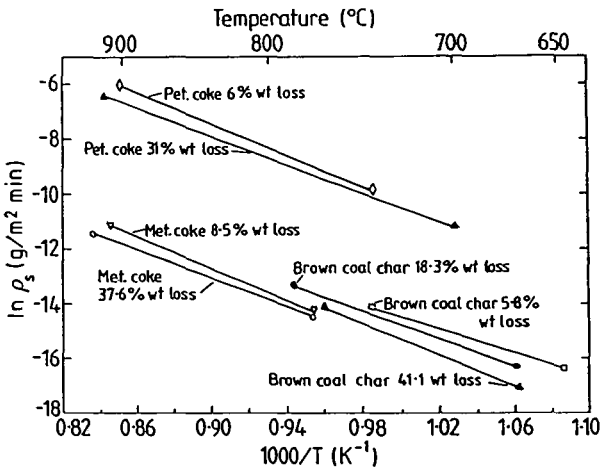


Figure 8 Intrinsic reaction rate, ρ_s (g/min.m^2) of brown coal char, metallurgical coke and petroleum coke. (p_{CO_2} = 1 atm).