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# Reactivity of heat-treated coals in steam

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Reactivities of seventeen 40 × 100 mesh (U.S.) coals charred to 1000°C have been measured at 910°C in 0.1 MPa of a N<sub>2</sub>-H<sub>2</sub>O mixture containing water vapour at a partial pressure of 2.27 kPa. Char reactivity decreases, in general, with increasing rank of the parent coal. The chars show a 250-fold difference in their reactivities. Results suggest that gasification of chars in air, CO<sub>2</sub> and steam involves essentially the same mechanism and that relative gasification rates are controlled by the same intermediate oxygen-transfer step. Removal of inorganic matter from raw coals prior to their charring or from chars produced from raw coals decreases the reactivities of lower-rank chars, whereas reactivities of higher-rank chars increase. Addition of H<sub>2</sub> to steam has a marked retarding effect on char reactivity in most cases. However, in a few cases H<sub>2</sub> acts as an accelerator for gasification. The effect of particle size, reaction temperature and water-vapour pressure on char reactivity is considered

Because of the current interest in coal-conversion processes for producing liquid and gaseous fuels, the char-steam reaction has assumed a unique importance. The major products of this reaction, namely CO and H<sub>2</sub>, can be used not only as a medium-heating-value gas but also as precursors for catalytic synthesis of a wide range of products, namely Fischer-Tropsch synthesis for oil, gasoline, LPG; methanol and ammonia synthesis; oxo compounds; as well as for the production of substitute natural gas by catalytic methanation. In the future, economic considerations may necessitate the use of coals of all ranks as feedstock for the production of chars for subsequent gasification in steam. Therefore, it is desirable to study relative gasification rates in steam of a number of chars prepared under fixed conditions of charring from coals of different rank. This paper describes the results of such a study. The variables chosen for investigation were rank of the parent coals, inorganic matter content, particle size, reaction temperature and pressure. Effect of addition of H<sub>2</sub> to steam on char reactivity has also been studied.

## EXPERIMENTAL

### Char preparation

Seventeen char samples produced from coals varying in rank from anthracite to lignite were used in the investigation. These chars were available from a previous study<sup>1</sup>. The analyses of coals used for the preparation of chars are given in Table 1. The chars were prepared from 40 × 100 mesh fractions of coals in N<sub>2</sub> at 1000°C in the manner described previously<sup>1</sup>. In order to study the effect of inorganic matter removal on char reactivity, selected coals, prior to charring, or chars produced from raw coals were acid-washed with 10 volume per cent HCl. Chars produced from acid-washed coals are referred to as AW in the text whereas the acid-washed chars are referred to as AW\*. The inorganic matter content of some of the acid-washed coals was fur-

ther reduced by treatment with a 1:1 HCl-HF mixture. Chars prepared from such coals are referred to as demineralized (Dem) samples in the text.

A relatively unreactive low-volatile bituminous char (PSOC-127) and a highly reactive lignite char (PSOC-87) were chosen for investigating the effect of particle size on reactivity. Chars produced from raw coals of 40 × 100 and 200 × 325 U.S. mesh size were studied. Experimental details for the preparation of acid-washed and demineralized chars, as well as chars with different particle sizes, are described elsewhere<sup>1,2</sup>.

### Surface area

Nitrogen and CO<sub>2</sub> surface areas of most chars were available from a previous study<sup>1</sup>. In the case of chars for which the areas were not available, they were determined from N<sub>2</sub> adsorption at -196°C using the BET equation and from CO<sub>2</sub> adsorption at 25°C using the Polanyi-Dubinin equation. Experimental details are described elsewhere<sup>1,3</sup>. Walker and co-workers<sup>3,4</sup> have concluded that the N<sub>2</sub> surface area is a measure of transitional and macroporosity, whereas adsorption of CO<sub>2</sub> at 25°C measures essentially the total surface area of microporous coals and chars.

### Reactivity measurements

Reactivities of chars were measured at 910°C in 0.1 MPa of a N<sub>2</sub>-H<sub>2</sub>O mixture containing water vapour at a partial pressure of 2.27 kPa. This water-vapour pressure was generated by bubbling prepurified N<sub>2</sub> through deaerated distilled water thermostated at 20°C. Reactivities were also measured on selected samples in a 20% H<sub>2</sub>-80% N<sub>2</sub> mixture which contained 2.27 kPa of water vapour.

A Fisher TGA unit, Model 442, was used for reactivity measurements. About 3 mg of char contained in a platinum pan was heated in N<sub>2</sub> (300 cm<sup>3</sup>/min) up to 1000°C at a rate of 20°C/min. Heating at 1000°C was continued until the char weight became constant. The sample was then cooled to reaction temperature (910°C) and held at this temperature for 20 min for temperature stabilization.

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Table 1 Analyses of coals

PSOC Sample No.	ASTM rank	State	Ash (wt %, dry basis)	(wt %, daf)				O (by diff.)
				C	H	N	S <sup>a</sup>	
91	Lignite	Mont.	7.7	70.7	4.9	0.80	0.30	22.3
87	Lignite	N.D.	8.2	71.2	5.3	0.56	0.46	22.5
140	Lignite	Tex.	9.4	71.7	5.2	1.3	0.72	21.1
138	Lignite	Tex.	10.3	74.3	5.0	0.37	0.51	19.8
98	Sbb-A	Wyo.	8.4	74.3	5.8	1.2	1.1	17.7
101	Sbb-C	Wyo.	6.1	74.8	5.1	0.89	0.30	18.9
26	HVB	Ill.	10.8	77.3	5.6	1.1	2.3	13.6
22	HVC	Ill.	10.1	78.8	5.8	1.6	1.8	12.1
24	HVB	Ill.	11.8	80.1	5.5	1.1	2.3	11.1
67	HVB	Ut.	4.8	80.4	6.1	1.3	0.38	11.9
171	HVA	W.Va.	7.6	82.3	5.7	1.4	1.8	8.9
4	HVA	Ky.	2.1	83.8	5.8	1.6	0.66	8.2
137	MV	Ala.	7.1	86.9	4.8	1.5	0.81	5.9
114	LV	Pa.	9.8	88.2	4.8	1.2	0.62	5.2
127	LV	Pa.	5.7	89.6	5.0	1.0	0.52	3.9
81	Anthracite	Pa.	7.8	91.9	2.6	0.78	0.54	4.2
177	Anthracite	Pa.	4.3	93.5	2.7	0.24	0.64	2.9

<sup>a</sup> Organic sulphur

Table 2 Reactivities of coal chars in steam

Parent coal PSOC No.	Reactivity (mg h <sup>-1</sup> mg <sup>-1</sup> )
91	2.9
87	2.8
140	1.5
138	1.2
98	1.0
101	2.5
26	0.25
22	0.45
24	0.52
67	0.22
171	0.15
4	0.30
137	0.10
114	0.07
127	0.011
81	0.13
177	0.11

Nitrogen was then replaced by the N<sub>2</sub>-H<sub>2</sub>O mixture. The weight of the sample was recorded continuously as a function of time. It was ascertained in a few exploratory runs that for starting sample weights up to 3 mg, mass-transport resistance to diffusion of reactant gas molecules down through the bed was negligible.

Burn-off versus time curves for different chars usually had a slow induction period followed by a rate increase. Following the suggestion of Jenkins *et al.*<sup>5</sup> the reactivity parameter was calculated by the following equation:

$$R = \frac{1}{w_0} \cdot \frac{dw}{dt}$$

where  $w_0$  is the starting weight of the char on a dry-ash-free (daf) basis and  $dw/dt$  is the maximum rectilinear weight loss rate (mg h<sup>-1</sup>).

It was calculated that under the experimental conditions used in the present study the amount of water vapour contained in the N<sub>2</sub>-H<sub>2</sub>O mixture was far in excess of that needed for the maximum gasification rate of even the most reactive char (PSOC-91).

For the char produced from coal PSOC-140, ten reactivity runs were made in the N<sub>2</sub>-H<sub>2</sub>O mixture. For the ten determinations, a 95% confidence interval on the mean value of  $R$  was  $1.53 \pm 0.021$  mg h<sup>-1</sup> mg<sup>-1</sup>.

## RESULTS AND DISCUSSION

### Correlation of char reactivity with coal rank

Reactivity results for various chars are given in Table 2. It is seen that the reactivity parameter decreases, in general, with increase in the rank of the parent coal. The LV bituminous char, PSOC-127, is the least reactive; whereas the Montana lignite char, PSOC-91, is the most reactive, its reactivity being about 250 times that of the PSOC-127 char. The higher reactivities of chars derived from lower-rank coals compared to those produced from higher-rank coals is consistent with the three major factors governing gasification rates. That is, the lower-rank chars have a higher concentration of active sites, a higher concentration of feeder (transitional and macro) porosity and hence a greater utilization of active sites located in micropores, and a higher degree of dispersion of inorganic catalytic impurities<sup>1,6</sup>.

We have previously studied the reactivities of a number of chars in air (0.1 MPa) at 500°C<sup>5</sup>, CO<sub>2</sub> (0.1 MPa) at 900°C<sup>2</sup>, and H<sub>2</sub> (2.7 MPa) at 980°C<sup>1</sup>. Reactivities of various chars in steam (Table 2) show more or less the same kind of spread as well as dependence on rank of the precursor coal as do the corresponding reactivities in air<sup>5</sup> and CO<sub>2</sub><sup>2</sup>. In contrast, reactivities in H<sub>2</sub> show a random variation with rank; and the spread in reactivities of different chars is much less than that in air, CO<sub>2</sub> and steam<sup>1</sup>. These results thus suggest that the gasification of chars in air, CO<sub>2</sub> and steam involves essentially the same mechanism, that is an oxygen transfer step followed by a gasification step<sup>6</sup>. These can be written as follows:

### Oxygen transfer

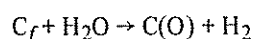
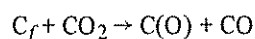
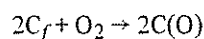
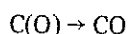




Table 3 Effect of inorganic-matter removal on reactivities of chars in steam

Parent coal PSOC No.	Surface area (m <sup>2</sup> /g)		Ash (wt %, dry basis)	Reactivity (mg h <sup>-1</sup> mg <sup>-1</sup> )
	N <sub>2</sub>	CO <sub>2</sub>		
91	31	420	10.9	2.9
91 AW*	17	470	7.2	1.8
91 AW	88	912	1.3	0.43
87	93	260	13.1	2.8
87 AW*	106	500	6.0	1.1
87 AW	11	610	2.6	0.33
87 Dem	1	600	0.0	0.38
138	120	560	16.0	1.2
138 AW*	11	497	11.6	0.88
138 AW	4	680	9.6	0.34
138 Dem	47	115	0.9	0.19
101	62	400	8.2	2.5
101 AW*	17	359	5.4	1.6
101 AW	3	670	1.1	0.35
127	2	12	6.7	0.011
127 Dem	4	37	0.0	0.14
81	1	39	6.4	0.13
81 AW*	<1	47	6.1	0.14
81 AW	<1	40	5.8	0.14
81 Dem	<1	56	0.9	0.19

### Gasification



where  $C_f$  is a carbon-free (active) site and  $C(O)$  is a fleeting oxygen complex<sup>6</sup>.

#### Effect of removal of inorganic matter on char reactivity

Most inorganic impurities catalyse gasification rates of carbons<sup>6,7</sup>. The specific catalytic activity of an impurity is determined by its chemical form and degree of dispersion (particle size) as well as the gaseous atmosphere used<sup>6,7</sup>. We have previously reported that upon partial or complete removal of inorganic impurities from coals by acid-washing with HCl or demineralizing with an HCl-HF mixture, prior to charring, gasification rates of lower-rank chars in air, CO<sub>2</sub> and H<sub>2</sub> generally decrease, whereas those of chars produced from higher-rank coals increase<sup>1,2</sup>. Demineralization produced a greater change in subsequent char reactivity than did acid washing. An explanation for these results was offered earlier<sup>1,2,5</sup>.

The same general effect of inorganic-matter removal on subsequent char reactivity has also been observed for reaction in steam (Table 3). However, in the present study we have investigated, as we failed to do in the previous reactivity studies in air, CO<sub>2</sub> and H<sub>2</sub>, the effect of inorganic-matter removal not only from the coal precursor but also from the raw char on subsequent char reactivity. Results show (Table 3) that the magnitude of the effect of mineral-matter removal on reactivities of lower-rank chars is markedly dependent upon the manner in which the inorganic constituents are removed. In the case of chars produced from lignite (PSOC-91, 87 and 138) and sub-bituminous (PSOC-101) coals, reactivities of the AW samples are significantly lower than those of the corresponding AW\* samples. This result parallels the fact that ash yields of the chars produced from these acid-washed coals were lower than those produced from the acid-washed chars.

As previously reported, a lowering of the inorganic impurity content in chars produced from the high-rank coals resulted in increases in reactivity<sup>2</sup>. The effect was pre-

viously attributed to the presence of additional macropores and transitional pores (feeder pores) in these chars as a result of the removal of inorganic constituents. That is, accessibility to active carbon sites was enhanced.

It is interesting that acid washing of either the precursor coals or the chars produced from the raw coals leads to N<sub>2</sub> and CO<sub>2</sub> surface areas for product chars which are markedly different from the values for the chars produced from the process which involves no acid treatment. These results will be considered more fully in a future publication. It can simply be said at this point that no relation is found between N<sub>2</sub> and CO<sub>2</sub> surface areas of the chars prior to their gasification and their maximum reactivities.

#### Effect of H<sub>2</sub> addition to steam on reactivity

A study of the effect of H<sub>2</sub> on the reactivity of coal chars to steam shows, on the one hand, the complexity that mixed reactant atmospheres can introduce to the understanding of gasification and, on the other hand, the fascinating roles which physical phenomena like chemisorption and catalysis can play in heterogeneous gas-solid reactions. To understand the effect of H<sub>2</sub>, it is important to distinguish between the 'catalysed' and 'uncatalysed' reactions. In the former, dissociation of steam, in the oxygen transfer step, occurs predominantly at impurity (catalyst) sites, the oxygen species then attaching itself to an active carbon site. In the latter, the dissociation of steam occurs predominantly at active carbon sites†. Whether the uncatalysed or catalysed gasification reaction is dominant depends upon a number of variables, including temperature and the concentration and specific activity of inorganic impurities present.

It has been shown by a number of workers that hydrogen is a strong inhibitor of the 'uncatalysed' reaction<sup>6</sup>. It is generally agreed that this inhibition is caused by the strong dissociative chemisorption of hydrogen onto active carbon sites, thus blocking them for the oxygen transfer reaction with steam. The inhibition of the 'uncatalysed'

† In this latter case, some reaction can also proceed via the catalysed route since all carbons contain at least traces of inorganic impurities, but the uncatalysed route is dominant

Table 4 Effect of hydrogen addition to steam on char reactivity

Parent coal PSOC No.	Pyrite in coal (wt %, dry basis)	Reactivity (mg h <sup>-1</sup> mg <sup>-1</sup> )	
		Steam	Steam-H <sub>2</sub>
91	0.19	2.9	0.63
91 AW*	—	1.8	0.51
87	0.41	2.8	1.0
138	0.34	1.2	1.3
138 AW*	—	0.88	0.63
26	7.9	0.25	0.24
22	1.7	0.45	0.40
24	3.6	0.52	0.59
127	0.54	0.011	0.20

carbon-steam reaction by hydrogen is also consistent with the finding that the rate of carbon gasification in hydrogen is about three orders of magnitude slower than the rate of gasification in steam<sup>6</sup>.

By contrast, McKee<sup>8</sup> has more recently shown that H<sub>2</sub> can be an accelerator for the 'catalysed' carbon-steam reaction when appreciable amounts of iron are present. In the absence of added H<sub>2</sub>, the steam converts the iron to an oxide; in this chemical state it is a poor catalyst. At a sufficiently high H<sub>2</sub>/H<sub>2</sub>O ratio, the iron is maintained in a reduced (high catalytic) state; and the rate of the 'catalysed' carbon-steam reaction is considerable. Whether H<sub>2</sub> acts as an accelerator or inhibitor in the carbon-steam reaction in the presence of potential catalytic impurities depends upon the chemical state(s) in which the particular impurities are active catalysts. For example, iron, cobalt, and nickel are active catalysts for the carbon-steam reaction when in the reduced state<sup>7,8</sup>. On the other hand, impurities like vanadium, molybdenum, potassium, and sodium are active catalysts in an oxidized state<sup>7</sup>.

With this introduction, results on the effect of H<sub>2</sub> addition to the reactivity of coal chars to steam can now be considered. Results on selected chars reacted in a 20% H<sub>2</sub>-80% N<sub>2</sub> mixture containing 2.27 kPa of water vapour are presented in Table 4. Effects of H<sub>2</sub> addition are presented more graphically for selected chars in Figure 1. As perhaps expected from the previous discussion, the effect of hydrogen is mixed. It is an inhibitor to gasification for the low-rank chars, has little effect for chars produced from coals of intermediate rank, and is a marked accelerator to gasification in the case of the char produced from the low-volatile bituminous coal.

Hydrogen inhibition of gasification for the low-rank coal chars would have been predicted. That is, their high gasification rates are attributed primarily to the high concentration of well dispersed calcium (an active catalyst) associated with the carboxyl groups in the original coals. Hippo, who studied catalysis of gasification of char derived from PSOC-140 in steam, showed that the catalytic activity of ion-exchanged calcium was fully maintained during gasification to high burn-offs<sup>9</sup>. That is, steam does not deactivate calcium as a catalyst as it does iron, for example. Thus the main role of hydrogen during steam gasification of the low-rank coal chars is expected to be that of blocking a fraction of the active carbon sites.

Acceleration by hydrogen of gasification of the high-rank coal char in steam would have also been predicted. First, low-volatile bituminous coals have a negligible concentration of carboxyl groups and, hence, well dispersed calcium. Secondly, recent studies from this laboratory have shown

that none of the major minerals found in coal are significant catalysts for the oxygen-transfer reaction — in the absence of H<sub>2</sub><sup>10</sup>. On the other hand, in the presence of sufficient H<sub>2</sub>, pyrite is reduced to metallic iron and can thus become a precursor of an active catalyst. Figure 1 shows the strong accelerating effect of H<sub>2</sub> addition on the rate of gasification of PSOC-127 char in steam. Catalysis is attributed to iron derived from pyrite in this coal; that is, the H<sub>2</sub>/H<sub>2</sub>O ratio used in the present study was sufficient to maintain iron in its metallic state at 910°C<sup>11</sup>. In this case, reduced iron is also seen to have a significant catalytic activity for char gasification in H<sub>2</sub> to produce methane.

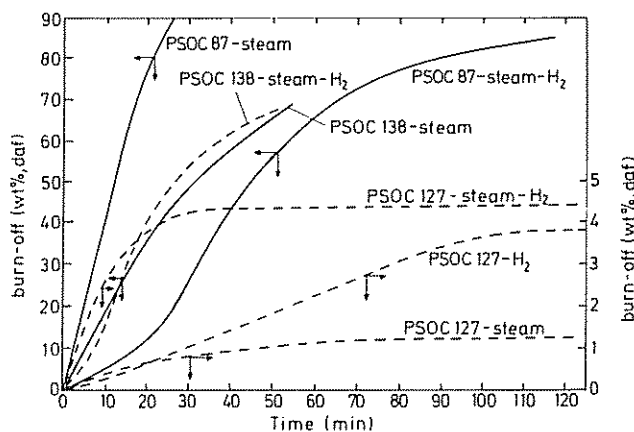
The fact that the gasification of PSOC-127 char in both the steam-H<sub>2</sub> and H<sub>2</sub> atmospheres essentially stops at very low burn-offs (that is about 3.8 to 4.3%) is another interesting feature of the system. It suggests that the iron catalyst has become deactivated and that the 'uncatalysed' reaction of PSOC-127 char proceeds at a very low rate in these atmospheres at 910°C. As previously suggested by King and Jones while studying catalysis of the coal char-CO<sub>2</sub> reaction by iron, deactivation of the iron is attributed to its reaction (combination) with silica, titania, and alumina present in the char<sup>12</sup>. PSOC-127 has a high concentration of kaolinite in its mineral matter. O'Gorman and Walker have shown (by DTA studies) that kaolinite converts to metakaolin below 600°C and metakaolin converts to either a spinel-like form of alumina, known as  $\gamma$ -alumina, or mullite between 950–1000°C<sup>13</sup>. Thus the incorporation of iron into  $\gamma$ -alumina and/or mullite (present as a result of the initial charring of the coal at 1000°C) at reaction temperature is suggested as being responsible for catalyst deactivation.

It was surprising to the authors that H<sub>2</sub> addition had little effect on the rates of reaction of the high-volatile-bituminous coal chars in steam, since all the coals contained significant amounts of pyrite, as seen in Table 4. These results point up the complexities which make it difficult to unify our understanding of the gasification of coal chars.

#### Other effects on reactivity

Selected experiments were also run to look at the effect of particle size, temperature, and water-vapour pressure on reactivity. These results are considered briefly, not because they give a complete story but because they serve to point out effects about which anyone concerned with the gasification of coal chars should be aware.

Results considered so far were generated from studies on chars produced from coals of 40 × 100 mesh size. If


 Figure 1 Effect of H<sub>2</sub> addition to steam on burn-off versus time plots for selected coal chars

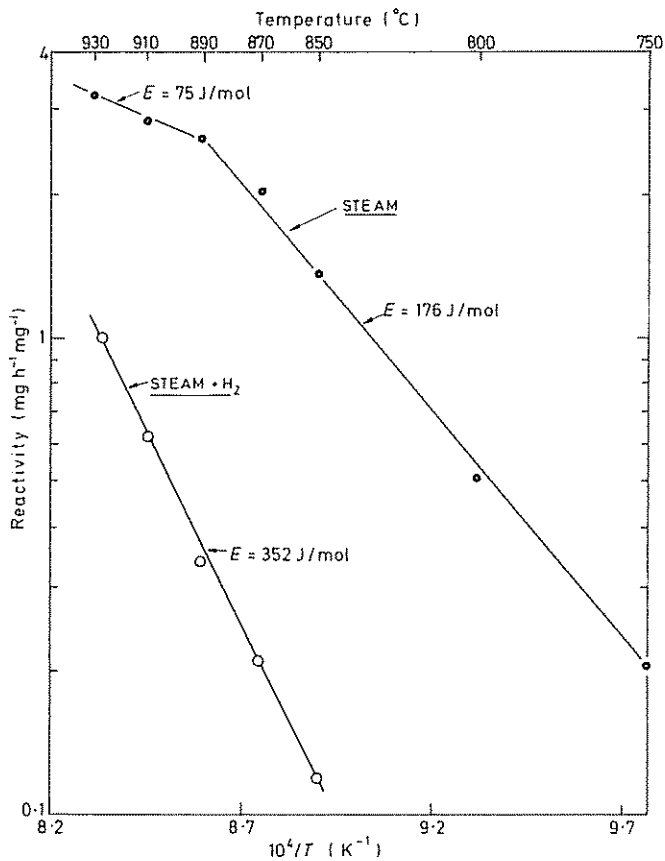


Figure 2 Arrhenius plots for gasification of PSOC-91 char in steam and a steam-H<sub>2</sub> mixture

diffusional resistance of reactant into the particles or products out of the particles is similar to the resistance of the slowest chemical step in gasification, reactivities will increase with decreasing size of char particles being gasified. For chars produced from 40 × 100 and 200 × 325 mesh sizes of PSOC-87, reactivities in steam were unaffected by particle size, that is 2.8 mg h<sup>-1</sup> mg<sup>-1</sup>. For chars produced from these sizes of PSOC-127, the reactivity was increased from 0.011 to 0.043 mg h<sup>-1</sup> mg<sup>-1</sup>. Generally, the higher the gasification rate the more apt is the system to be affected by diffusional resistance. However, these results show that this is not necessarily true when considering reactivities of chars produced from coals of widely different rank. That is, even though the reactivity of PSOC-87 char is orders of magnitude greater than that of PSOC-127 char at 910°C, its reactivity is not diffusion-limited since it has a large supply of macropores and transitional pores (feeder pores) through which diffusion to the reacting micropores is relatively rapid<sup>3</sup>. Low-volatile bituminous coals and their chars, however, do not have this large concentration of feeder pores<sup>3</sup>.

Figure 2 summarizes results on the reactivity of PSOC-91 lignite char in steam and a steam-H<sub>2</sub> mixture over a range of temperatures. It is concluded that for this char, reactivity in steam is not diffusion-limited up to a reaction temperature of about 890°C or a reaction rate of about 2.5 mg h<sup>-1</sup> mg<sup>-1</sup>. The apparent activation energy in the low-temperature regime (176 kJ/mol) is substantially less than the values reported for the 'uncatalysed' carbon-steam reaction<sup>6</sup>, because the reaction is strongly catalysed by calcium contained in the char<sup>7,9</sup>. The addition of H<sub>2</sub> to steam not only markedly lowered the char gasification rate but also markedly raised the activation energy for

gasification. This is as expected on the basis of the overall rate expression for carbon gasification in the presence of steam and hydrogen<sup>6</sup>, that is

$$\text{Rate} = \frac{k_1 P_{H_2O}}{1 + k_2 P_{H_2} + k_3 P_{H_2O}} \quad (1)$$

where  $k_1$ ,  $k_2$ , and  $k_3$  are rate constants. The rate constant  $k_2^\dagger$  has a negative activation energy, and thus the retarding effect of hydrogen decreases with increasing temperature<sup>14</sup>.

Figure 3 summarizes results on the reactivity of PSOC-91 char in varying partial pressures of steam both in the absence and presence of added H<sub>2</sub>. Clearly the reaction order

†The rate constant  $k_2$  is really an equilibrium constant for the dissociative chemisorption of hydrogen on active carbon sites<sup>14</sup>

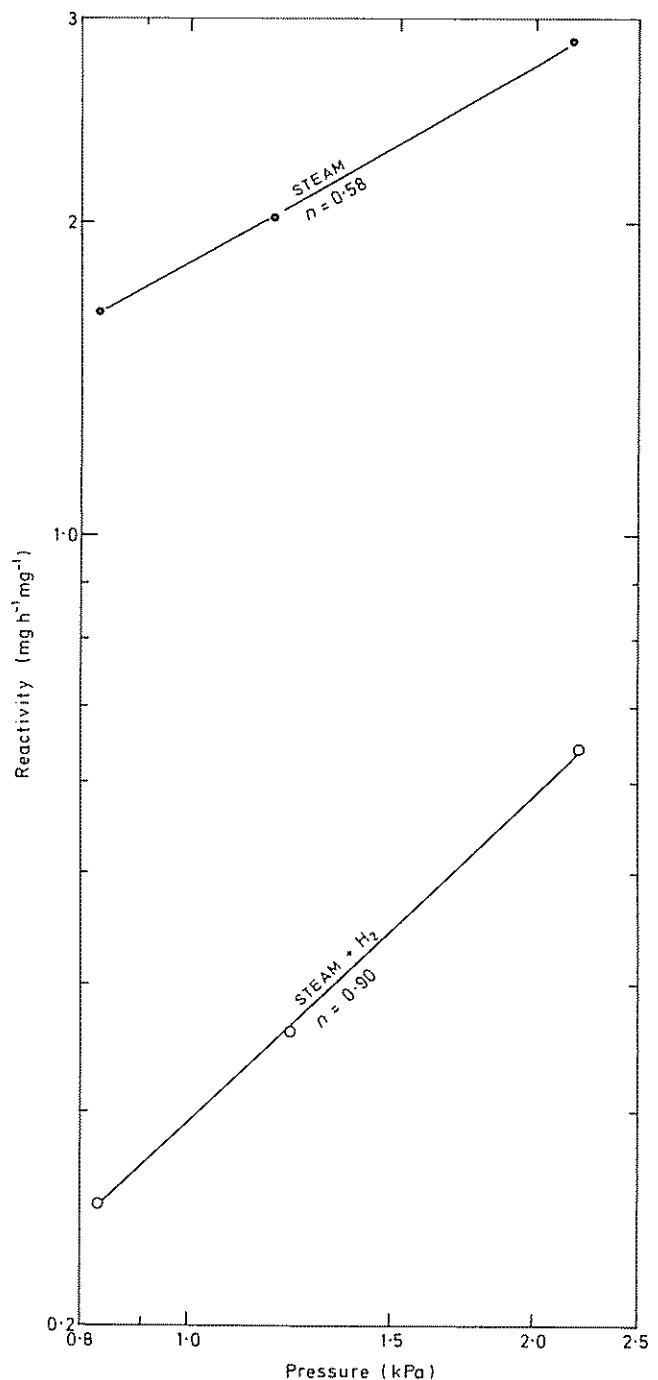


Figure 3 Effect of pressure of water vapour on reactivity of PSOC-91 char in steam and steam-H<sub>2</sub> mixtures

in steam ( $n$ ) is a function of whether  $H_2$  has been added. An increase in order with addition of  $H_2$  is expected on the basis of equation (1). That is, in the limit at high  $H_2$  pressures, the denominator can be approximated by  $k_2 P_{H_2}$  and the order of the reaction in pressure of steam will be one. At the other limit, in a high steam pressure the rate can be approximated by  $k_1$ ; thus the reaction order in steam will be zero. The orders found reflect intermediate situations between the two limits.

#### ACKNOWLEDGEMENTS

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