

*File Copy #832*

# FUEL

the science and technology of Fuel and Energy



Published by Butterworths



# Preface

In recent years there has been a revival of interest in coal science, including coal conversion processes. At present we are probably on the threshold of the large-scale introduction of coal gasification. A promising development in this field is catalysed coal gasification.

However, much basic knowledge of the processes taking place is lacking. In fact, many groups have only just initiated their research on catalytic coal gasification. This implies, amongst other things, that throughout the world these groups are relatively unaware of each others' activities and advances, which impedes the exchange of knowledge and ideas.

Hence our initiative to organize an international symposium on the fundamentals of catalytic coal and carbon gasification.

It was the aim of the organizing committee to bring together scientists active in catalytic carbon and coal gasification. It was a pleasure to notice the enthusiastic response of the scientific community to our call for papers and the spontaneous reaction of organizations asked for sponsoring.

This special issue of *Fuel* contains the plenary lectures and the accepted papers presented at the symposium. The topic areas the organizing committee decided upon were:

1. Fundamentals of gasification reactions of  $H_2O$ ,  $H_2$ ,  $CO_2$ ,  $O_2$  and other gases with coal and related solids in the presence of catalytic materials or mineral matter: mechanisms, kinetics, thermodynamics.
2. Influence of catalytic materials on the pyrolysis of coal.
3. Interaction of carbon and catalysts; electronic properties, dispersion and sintering.
4. Chemical state of the catalyst under gasification conditions.
5. Methanation and water gas shift under gasification conditions.
6. Practice of catalytic coal gasification as far as it concerns fundamentals.
7. Experimental methods and techniques in relation to catalytic coal and carbon gasification.

The papers in this issue deal in detail with most of these topics, except for the influence of catalysts on pyrolysis and methanation, and water gas shift reactions under gasification conditions. The papers show that the major emphasis of present research applies to the transition metals Fe and Ni, the earth alkali metal Ca and the alkali metals K and Na.

For carbon-steam gasification the transition metals are active only in the metallic state. The mechanism probably is C-C bond breaking followed by dissolution of carbon

in the metal. Practical application is strongly hindered by the fact that sulphur is a poison.

Calcium is an interesting cheap non-corrosive catalyst. The major problem is to achieve a high dispersion.

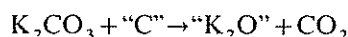
Alkali metal catalysis appears to be very complicated. The great number of contributions on this subject showed that the important parameters include type of alkali metal, type of anion, concentration of the catalyst, initial dispersion, properties of the carbon (impurities, surface area, porosity), mineral matter, history of the sample (pre-treatment temperature), temperature, and gas phase composition.

The chemical state of the alkali metal during gasification is still subject to debate. The following suggestions have been made:

K	surface salt
$K_2O$	$K_2CO_3$
KH	chemisorbed K
intercalate	physisorbed K
$\rho-O^-K^+$	

The discussion is further complicated by the fact that some evidence for cluster formation was presented.

There appears to be consensus that during heat treatment  $K_2CO_3$  dissociates:



The status of " $K_2O$ " is subject to debate. The results suggest that during both steam and carbon dioxide gasification an oxygen transfer mechanism is operative. This might imply a redox mechanism, but a cycle between two complexes with potassium in the ionic form has certainly not been ruled out. The major problems for practical applications are: additional cost for catalyst, corrosion, catalyst recovery, reaction with mineral matter, caking, environmental impact and, perhaps, restriction to a limited number of coals.

Many novel techniques have been demonstrated, including *in situ* i.r. spectroscopy, a packed bed balance reactor, solid state n.m.r. and Temperature Programmed Desorption.

Summarizing it can be concluded that the papers in this issue of *Fuel* give a good description of the 'state of art' of the fundamentals of catalytic carbon and coal gasification and, hopefully, they will stimulate further research.

There will be a follow-up symposium in 1984 which will be organized by: Bergbau Forschung GmbH, D-4300 Essen 13/B.R.D., Franz Fischer Weg 61, GFR.

Jacob A. Moulijn  
Chairman of the organizing committee

# Catalysis of gasification of coal-derived cokes and chars\*

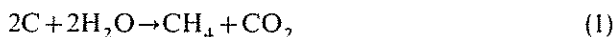
Philip L. Walker, Jr., Shiro Matsumoto, Tamotsu Hanzawa,\*  
Takatoshi Muira,† and Ismail M. K. Ismail‡

The Pennsylvania State University, Department of Materials Science and Engineering,  
University Park, PA 16802, USA

Calcium is the most important *in-situ* catalyst for gasification of US coal chars in O<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>O. It is a poor catalyst for gasification of chars by H<sub>2</sub>. Potassium and sodium added to low-rank coals by ion exchange and high-rank coals by impregnation are excellent catalysts for char gasification in O<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>O. Carbon monoxide inhibits catalysis of the C-H<sub>2</sub>O reaction by calcium, potassium and sodium; H<sub>2</sub> inhibits catalysis by calcium. Thus injection of synthesis gas into the gasifier will inhibit the C-H<sub>2</sub>O reaction. Iron is not an important catalyst for the gasification of chars in O<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>O, because it is invariably in the oxidized state. Carbon monoxide disproportionates to deposit carbon from a dry synthesis gas mixture (3 vol H<sub>2</sub> + 1 vol CO) over potassium-, sodium- and iron-loaded lignite char and a raw bituminous coal char, high in pyrite, at 1123 K and 0.1 MPa pressure. The carbon is highly reactive, with the injection of 2.7 kPa H<sub>2</sub>O to the synthesis gas resulting in net carbon gasification. The effect of traces of sulphur in the gas stream on catalysis of gasification or carbon-forming reactions by calcium, potassium, or sodium is not well understood at present. Traces of sulphur do, however, inhibit catalysis by iron.

(Keywords: catalysis; gasification; coal chars; cokes)

The potential of carrying out the reaction:



in a coal gasifier for the production of CH<sub>4</sub> has intrigued workers for years since it is essentially thermoneutral. This overall reaction is a combination of the endothermic carbon gasification reaction:



and the exothermic water-gas shift and methanation reactions



All three reactions are slow in the absence of a catalyst, although rates can be increased, up to a point, by increasing pressure. However, at higher pressures the rate of carbon gasification by steam tends to zero order,<sup>1</sup> further equilibrium conversion is reduced with increasing pressure. The rate of carbon gasification by steam increases sharply with increasing temperature,<sup>1</sup> but increasing temperature severely limits the equilibrium production of CH<sub>4</sub>. The accepted solution is to operate the gasifier at an intermediate temperature (around 1000 K), where equilibrium presents minimal problems, and to rely on catalysts to accelerate reaction rates. Since catalysts which are active for the gasification of carbon by steam are invariably even more active for the water-gas-

shift reaction,<sup>1,2</sup> it is catalysis of reactions (2) and (4) which is of primary concern.

In this Paper we will consider catalysis of carbon gasification by oxygen-containing gases for the most part. Catalysis of the methanation reaction will also be considered, along with two other reactions which can occur in the gasifier once coal char and steam react:



## EXPERIMENTAL

Reactivity of chars, derived from coals varying in rank from anthracite to lignite, to air, CO<sub>2</sub>, H<sub>2</sub>, and H<sub>2</sub>O have been studied in this laboratory.<sup>3-15</sup> In addition to starting with raw coals, we have also used coals first treated with HCl and HF to reduce the exchangeable cation and/or the mineral matter content. In some cases the acid treated coals have been loaded with potential catalysts by ion exchange or impregnation, using metal acetate solutions of varying concentrations.

Coals were converted to chars by heating in 0.1 MPa of N<sub>2</sub> at a slow heating rate (10–20 K min<sup>-1</sup>) in a thermogravimetric analysis (t.g.a.) apparatus or in a tube furnace.

Reactivities were measured in a t.g.a. apparatus, where the char was bathed in N<sub>2</sub> at reaction temperature from between 30 and 60 min before introducing the reactive atmosphere. In some cases, the effluent gas stream was analysed for CH<sub>4</sub> concentration using an i.r. detector. Experimental details have been considered in previous publications.

\* Present address: Gunma University, Gunma, Japan

† Present address: Tohoku University, Sendai, Japan

‡ Present address: Allis-Chalmers Corp., Milwaukee, WI, USA

\* Presented at International Symposium, 'Fundamentals of Catalytic Coal and Carbon Gasification', held at Amsterdam, The Netherlands, 27–29 September 1982

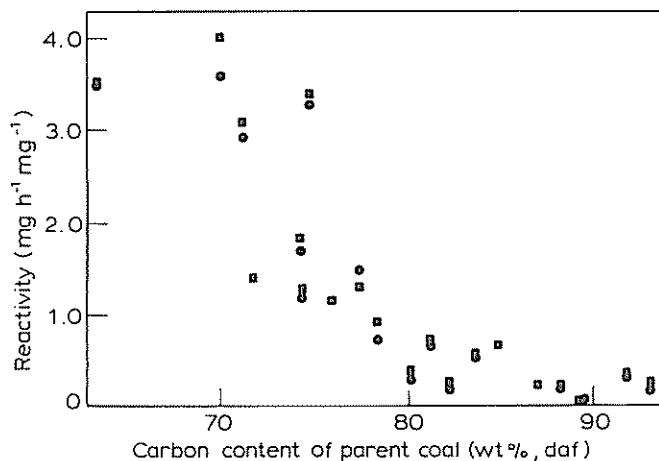


Figure 1 Variation of reactivity of 1273 K chars produced from US coals of different rank<sup>4</sup>. ●, 0.1 MPa CO<sub>2</sub> at 1173 K; ■, 0.1 MPa air at 773 K

## RESULTS AND DISCUSSION

### Reactivity of raw coal chars

We studied the reactivities of chars produced upon heating raw coals varying in rank from anthracite to lignite to 1273 K. Reaction conditions were air (0.1 MPa) at 773 K,<sup>3</sup> CO<sub>2</sub> (0.1 MPa) at 1173 K,<sup>4</sup> wet N<sub>2</sub> (2.3 kPa) at 1183 K,<sup>10</sup> and H<sub>2</sub> (2.7 MPa) at 1273 K.<sup>5</sup> Reactivities, *R*, were calculated from:

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

where *w*<sub>0</sub> is the starting weight of char on a daf basis and *dw/dt* is the maximum rectilinear weight loss. They show more or less the same kind of spread as well as dependence on rank of the precursor coal for the air, CO<sub>2</sub> and H<sub>2</sub>O reactions. Results for air and CO<sub>2</sub> are summarized in Figure 1. In all cases, reactivity is highest for the char produced from the Montana lignite (PSOC-91) and lowest for the char (coke) produced from the Pennsylvania low volatile bituminous coal (PSOC-127). A maximum ratio in reactivity for these two coals of 263 is found for the C-H<sub>2</sub>O reaction. In contrast, reactivities in H<sub>2</sub> show a random variation in rank and the spread in reactivities of different chars is much less than that in air, CO<sub>2</sub> and H<sub>2</sub>O. For example, the ratio of reactivities in H<sub>2</sub> for PSOC-91 and PSOC-127 chars is only 19.

Major differences in reactivity of US coal chars can be attributed to three primary factors: catalysis of gasification, active site concentration, and accessibility of the reacting gas to the active sites. It is concluded that the most important catalyst for gasification of chars derived from raw US coals in air, CO<sub>2</sub> and H<sub>2</sub>O is calcium. In the low-rank lignite and subbituminous coals, calcium is the most abundant cation associated with carboxyl groups. It is highly dispersed on the char surface, following decomposition of the carboxyl groups and liberation of CO<sub>2</sub> upon coal pyrolysis.

In contrast, the calcium content of bituminous coals is much lower, and the CaO derived from the decomposition of calcite upon coal pyrolysis is poorly dispersed. Figure 2 shows the correlation between reactivity of US coal chars in air and CO<sub>2</sub> and CaO content in the chars. No other inorganic constituent has been found to give such a good correlation.

The high reactivity of lignitic chars can also be attributed to a high concentration of carbon active sites and excellent accessibility to the active sites. Figure 3 shows data for N<sub>2</sub> surface areas (77 K) of chars prepared at 1273 K as a function of carbon content of the starting coal. Lignitic chars have high surface areas (and, therefore, high concentrations of active sites) as a result of lignites having high volatile matter contents and behaving as thermosetting precursors during their pyrolysis. Conversely, bituminous coals have lower volatile matter

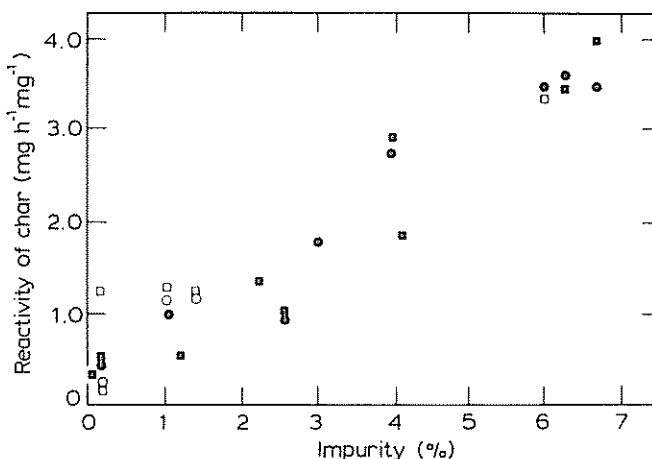


Figure 2 Plots of CO<sub>2</sub> and air reactivities of 1273 K chars versus wt% CaO present in the chars<sup>4</sup>. Closed and open symbols represent chars from original and acid-washed coals, respectively. ○, ●: 0.1 MPa CO<sub>2</sub> at 1173 K; □, ■: 0.1 MPa air at 773 K

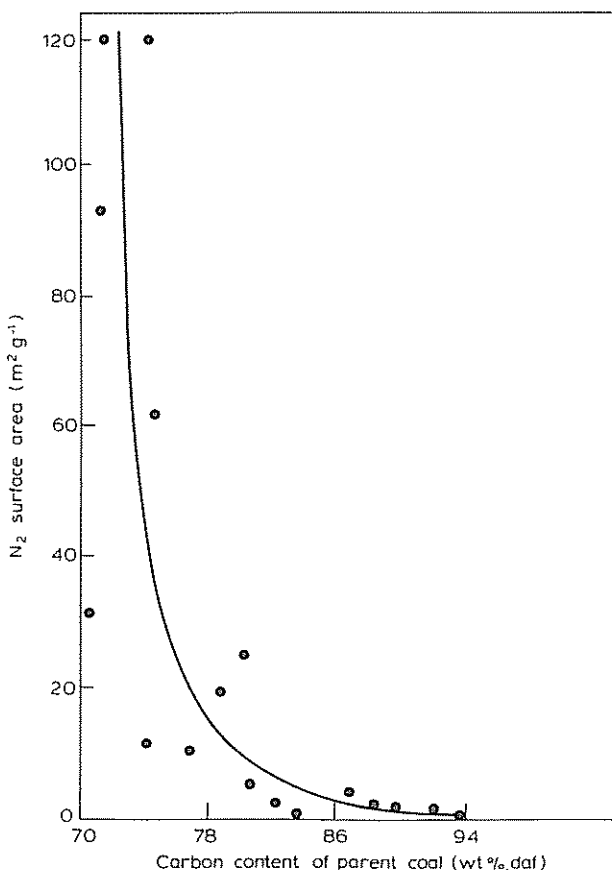


Figure 3 Correlation between the N<sub>2</sub> surface areas of US chars (1273 K) and the carbon content of the parent coals

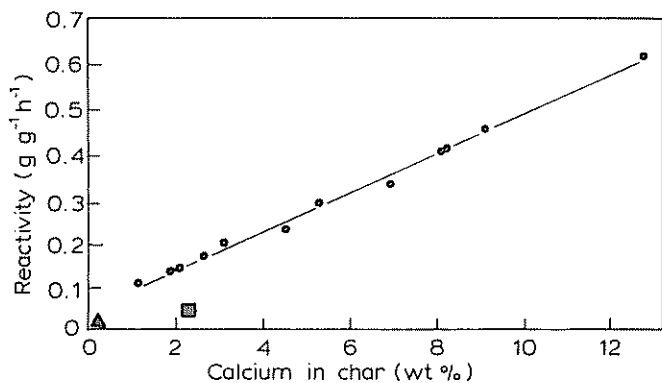


Figure 4 Reactivities in 0.1 MPa steam at 923 K of 1073 K chars prepared from  $\square$ , raw;  $\triangle$ , demineralized; and  $\odot$ , various Ca-exchanged lignites<sup>11</sup>

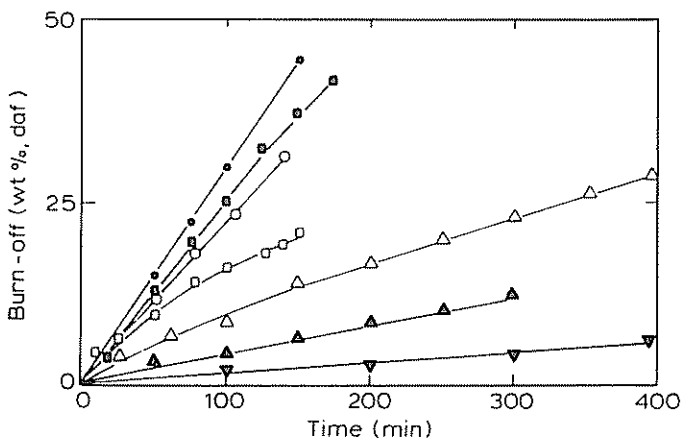


Figure 5 Reactivity plots at 923 K in 0.1 MPa of steam for 1073 K chars prepared from raw, demineralized, and various metal-exchanged lignites. Metal loading on lignites  $\approx 0.3 \text{ mmol g}^{-1}$ .  $\triangle$ , raw;  $\nabla$ , demineralized;  $\odot$ , K;  $\circ$ , Na;  $\blacksquare$ , Ca;  $\square$ , Fe; and  $\blacktriangle$ , Mg<sup>11</sup>

contents and, more importantly, exhibit some degree of plasticity upon pyrolysis. It has been shown that if PSOC-127, the low volatile bituminous coal, is pre-oxidized in air (0.1 MPa) between 393 and 523 K its fluidity can be sharply reduced on subsequent pyrolysis, leading to a char of higher surface area and a substantially higher reactivity.<sup>12</sup>

The presence of active catalysts and the possession of a high concentration of carbon active sites are necessary but not sufficient conditions for the high reactivity of coal chars. The active sites, found primarily in micropores in the chars, must be well connected to the exterior surface of the particles by transitional and macropores (the feeder pores) through which the reactant gas can rapidly diffuse; otherwise they will not be well utilized. It has previously been shown that lignites contain a substantial concentration of feeder pores; conversely, anthracites have a negligible concentration of larger pores.<sup>16</sup>

Enhancement of char reactivity by addition of catalysts

**Lignite.** We have shown that US lignites contain from about 2 to 3 meq  $\text{g}^{-1}$  of carboxyl groups and that roughly half of these carboxyl groups have undergone exchange of their hydrogen by metal cations.<sup>17</sup> The major cation exchanged is calcium, which is an excellent gasification catalyst; but the next most exchanged cation is magnesium, a poor catalyst. Therefore, it should be

possible to enhance the reactivity of lignitic chars by converting all carboxyl groups to the hydrogen form by treating the raw lignite with HCl, followed by back exchange of the desired cation. Most of the mineral matter can also be removed by treatment in HF prior to loading.

Hippo and co-workers<sup>11</sup> carried out this treatment on a Texas lignite (PSOC-140) before producing chars by heating in  $\text{N}_2$  at  $10 \text{ K min}^{-1}$  to 1073 K. The desired amount of cation loading could be achieved by immersing the acid-treated lignite in metal acetate solutions of appropriate concentration. For example, 10 levels of calcium, ranging from 0.10 to 2.14 mmol of cation  $\text{g}^{-1}$  of coal (daf), were added by exposing the lignite for 24 h to acetate solutions ranging in concentration from 0.04 to 2.0 M. The acid treated lignite was also exchanged in 0.10 M solutions of other cations for 24 h to add approximately 0.3 mmol of cation  $\text{g}^{-1}$  of coal.

Figure 4 shows that reactivity of the char in 0.1 MPa of steam at 923 K increases monotonically with increasing calcium loading. The reactivity of the char containing 12.9 wt% Ca was roughly 13 times higher than that of the char produced from the raw lignite. Figure 5 shows reactivity plots in 0.1 MPa of steam for chars loaded to essentially the same molar extent with different cations. Potassium, calcium and sodium are the best catalysts in that order. At low burn-offs, iron is a good catalyst, but its catalytic activity diminishes with reaction time as it becomes oxidized.<sup>2</sup> Magnesium is a poor catalyst.

Reactivity of the char loaded with various cations was also studied in air (0.1 MPa) at 663 K, in  $\text{CO}_2$  (0.1 MPa) at 1033 K, and in  $\text{H}_2$  (0.1 MPa) at 1063 K. Results for the air reaction are shown in Figure 6. Potassium, sodium and calcium are again the best catalysts, but sodium is in this instance a better catalyst than potassium. The order of reactivity in  $\text{CO}_2$  is the same as in air. In contrast, there is a major difference in the order of reactivity in  $\text{H}_2$ , as seen in Figure 7. Iron and sodium are good catalysts, while the catalytic activities of calcium and potassium are negligible.

In the Exxon catalytic gasification process for the production of  $\text{CH}_4$  through the use of overall equation (1),  $\text{CO}$  and  $\text{H}_2$  leaving the gasifier are separated from  $\text{CH}_4$  and  $\text{CO}_2$  and reinjected into the gasifier.<sup>18</sup> Potassium is added to the coal as a catalyst for the  $\text{C-H}_2\text{O}$  reaction.

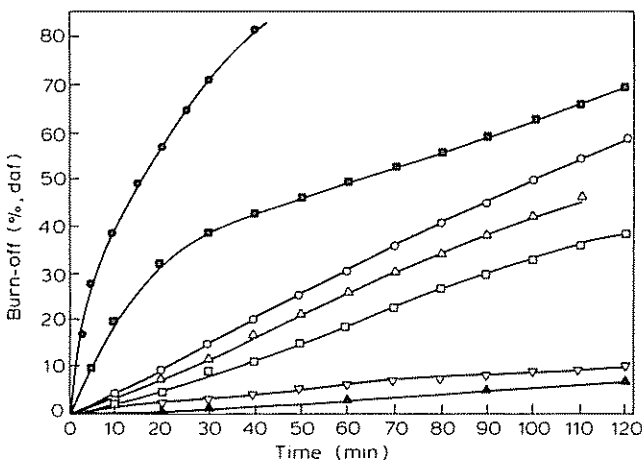


Figure 6 Reactivity plots at 663 K in 0.1 MPa of air for 1073 K chars prepared from raw, demineralized, and various metal-exchanged lignites. Metal loading on lignites  $\approx 0.3 \text{ mmol g}^{-1}$ .  $\odot$ , Na;  $\circ$ , K;  $\triangle$ , Ca;  $\nabla$ , raw;  $\square$ , Fe;  $\nabla$ , Mg;  $\blacktriangle$ , demineralized

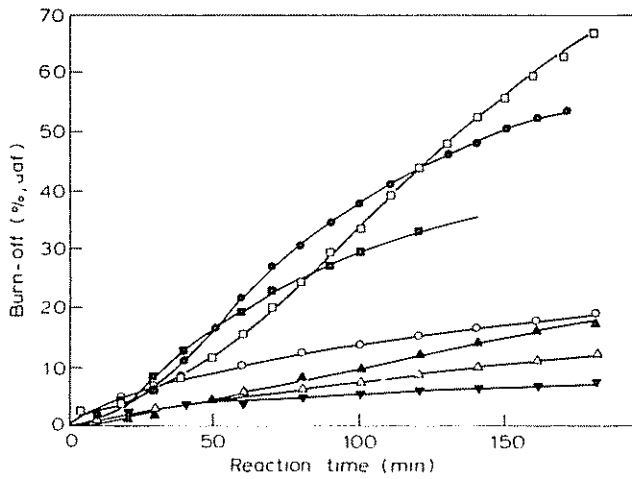


Figure 7 Reactivity plots at 1063 K in 0.1 MPa of  $H_2$  for 1073 K chars prepared from raw, demineralized, and various metal-exchanged lignites. Metal loading on lignites  $\approx 0.3 \text{ mmol g}^{-1}$ .  $\square$ , Fe;  $\bullet$ , Na;  $\blacksquare$ , raw;  $\circ$ , Ca;  $\blacktriangle$ , demineralized;  $\triangle$ , K;  $\blacktriangledown$ , Mg

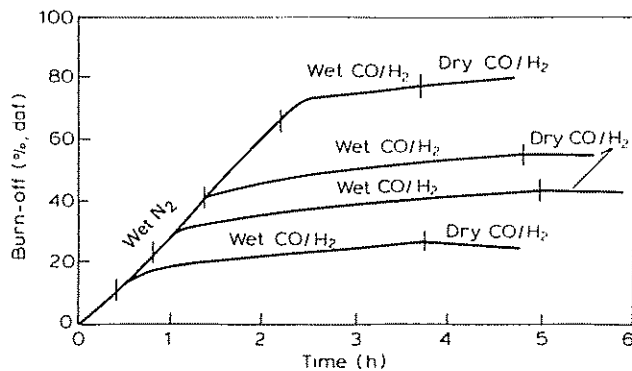


Figure 8 Reactivity plots of K-loaded 1123 K lignite char in 2.3 kPa of steam at 1123 K, showing inhibiting effect of  $H_2/CO$  mixture

Therefore, it is of interest to determine the effect of  $H_2$  and CO on the rate of char gasification by steam. A Texas lignite (PSOC-623) was loaded with 4.0 wt% potassium before converting it to a char by heating in  $N_2$  at  $20 \text{ K min}^{-1}$  to 1123 K and holding for 30 min. Char gasification in 0.1 MPa of wet  $N_2$  ( $H_2O$  partial pressure of 2.3 kPa) was then followed at 1123 K.

As seen in Figure 8, burn-off was essentially constant over the first 2 h or up to a burn-off of about 70%. However, if at different levels of burn-off a  $H_2/CO$  mixture (3 vol  $H_2$  + 1 vol CO is used throughout this Paper) was substituted for  $N_2$ , the rate of gasification was sharply reduced. If at a longer time in the run, dry  $H_2/CO$  was substituted for wet  $H_2/CO$ , in some cases a weight gain was observed, suggesting that disproportionation of CO was occurring. Gasification of chars, loaded with sodium and calcium, in steam was also strongly inhibited by the presence of a  $H_2/CO$  mixture. Therefore, it is clear that a price is being paid in the Exxon catalytic gasification process, as a result of reinjecting a  $H_2/CO$  mixture into the gasifier.

It is of interest to separate the effects of  $H_2$  and CO on char gasification by steam. Results for the Texas lignite char, loaded with different metals, are summarized in Figures 9 and 10. Gasification was conducted at 1123 K at a total pressure of 0.1 MPa and a water partial pressure of

2.3 kPa. For the potassium and sodium-loaded chars, gasification rates are similar in wet  $N_2$  and wet  $H_2$ ; CO, however, is a strong inhibitor of the C- $H_2O$  reaction. For the calcium-loaded char, both  $H_2$  and CO are strong inhibitors of the C- $H_2O$  reaction. For the iron-loaded char,  $H_2$  is a strong promoter of the C- $H_2O$  reaction once iron oxide is reduced to metallic iron.

Note that the behaviour of the char produced from the raw lignite resembles that found for the calcium-loaded char. This is to be expected since calcium is the predominant inorganic species in the raw lignite. On the

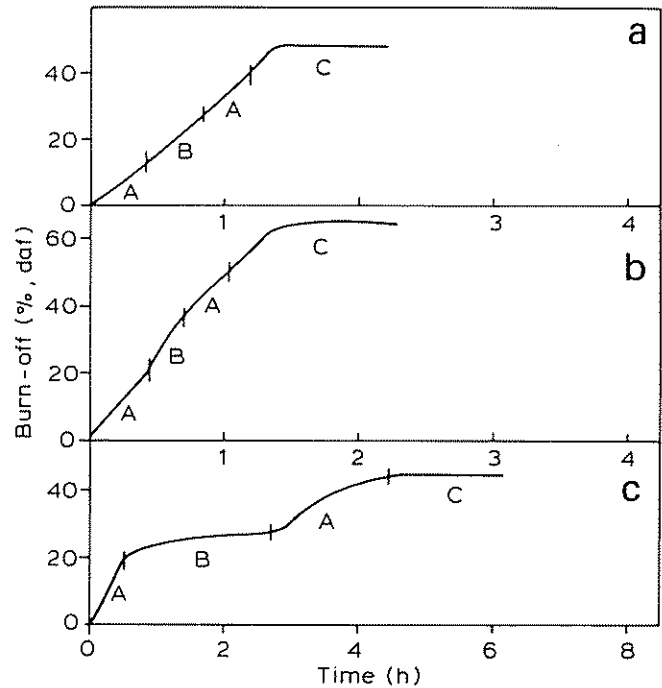


Figure 9 Reactivity plots at 1123 K in 2.3 kPa of steam for 1123 K chars prepared from raw, Na, and K-loaded lignites. Wet  $N_2$  (regions A), wet  $H_2$  (B), and wet CO (C). (a) Na; (b) K; (c) raw

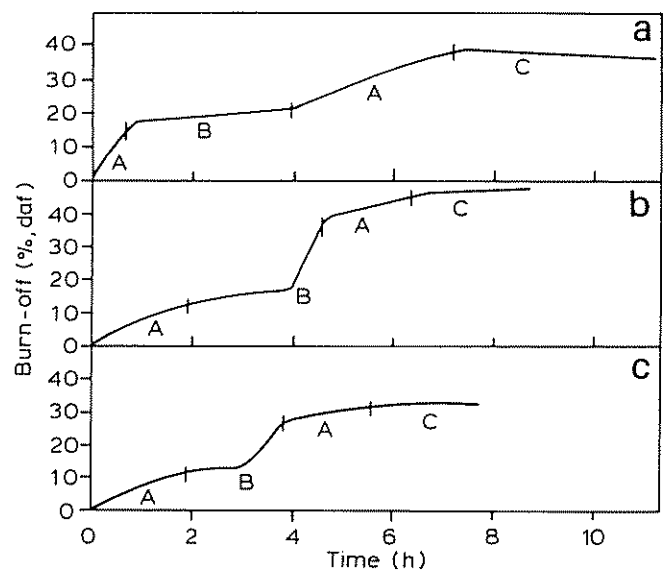


Figure 10 Reactivity plots at 1123 K in 2.3 kPa of steam for 1123 K chars prepared from demineralized, Ca, and Fe-loaded lignites. Wet  $N_2$  (regions A), wet  $H_2$  (B), and wet CO (C). (a) Ca; (b) Fe; (c) demineralized

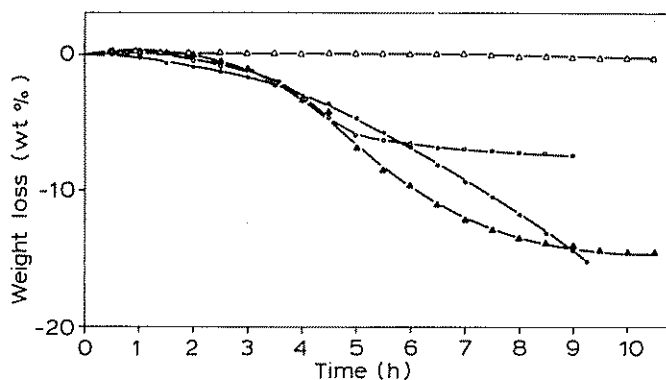


Figure 11 Carbon deposition over cation-loaded 1273 K lignite chars in 0.1 MPa of dry H<sub>2</sub>/CO at 1123 K.  $\Delta$ , Ca;  $\circ$ , K;  $\bullet$ , Fe;  $\blacktriangle$ , Na

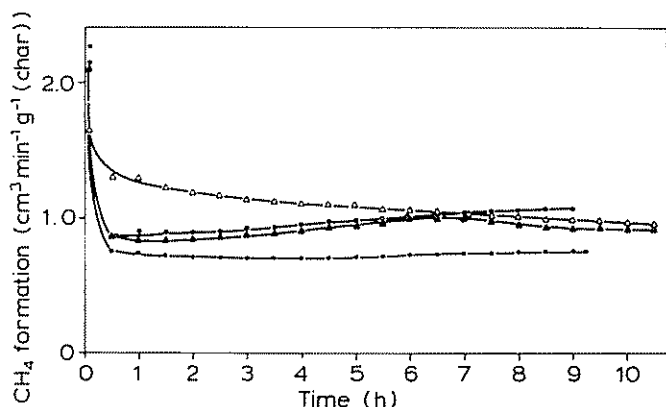


Figure 12 Methane formation over cation-loaded 1273 K lignite chars in 0.1 MPa of dry H<sub>2</sub>/CO at 1123 K.  $\bullet$ , Fe;  $\circ$ , K;  $\blacktriangle$ , Na;  $\Delta$ , Ca

other hand, the behaviour of the acid-treated (demineralized) lignite resembles that of the iron-loaded char. This again is to be expected since acid treatment will not remove all pyrite. Upon pyrolysis of the lignite in N<sub>2</sub>, pyrite will be converted to a pyrrhotite and, subsequently, to metallic iron in the presence of wet H<sub>2</sub>.

In an attempt to separate the effect of the H<sub>2</sub>/CO mixture from that of steam, loaded Texas lignite chars (1273 K) were reacted in dry H<sub>2</sub>/CO at 1123 K. The loadings of potassium, sodium and calcium onto the lignite were 1.0 ± 0.1 mmol g<sup>-1</sup> of coal; the iron loading was only 0.04 mmol g<sup>-1</sup> of coal. In the presence of lignite char, which has a positive free energy of formation relative to  $\beta$ -graphite, a 0.1 MPa dry H<sub>2</sub>/CO mixture is expected to result in net carbon gasification at equilibrium. As seen in Figure 11, CO disproportionation is the predominant reaction over the potassium, sodium and iron-loaded chars. But whereas carbon deposition essentially stops over potassium and sodium after weight gains of 7 and 12%, respectively, the carbon deposition rate over iron is still accelerating after a weight gain of 15% – this despite the fact that the iron loading on the lignite char is only about 2.5% that of the potassium and sodium loading. Iron is an excellent catalyst for CO disproportionation, as we will observe again in our studies on bituminous coal char. The fact that carbon deposition is initially found for the dry H<sub>2</sub>/CO mixture over potassium, sodium and iron, despite the fact that net carbon gasification is predicted at equilibrium, suggests that these elements are better CO

disproportionation catalysts than hydrogasification catalysts under conditions used.

Note that the introduction of only 2.7 kPa of H<sub>2</sub>O into the H<sub>2</sub>/CO mixture results in a net gasification of carbon. Either water is a strong inhibitor of CO disproportionation or the carbon formed from CO is highly reactive to H<sub>2</sub>O. As will be seen later in our studies on bituminous chars, at least, the latter explanation appears to be the case.

Methane formation was monitored when passing the dry H<sub>2</sub>/CO mixture over the loaded lignite char at 1123 K. As seen in Figure 12, after an initial higher rate of CH<sub>4</sub> production over each char, CH<sub>4</sub> concentration at the exit of the reactor levelled off at 400 to 500 ppm (a rate of CH<sub>4</sub> formation of 0.8–1.0 cc (STP) min<sup>-1</sup> g<sup>-1</sup> of starting char weight) for each sample. This is to be compared with a CH<sub>4</sub> concentration of 3700 ppm when the same bed volume of 3 wt% Co–10 wt% Mo on an alumina was used as the catalyst.

**Bituminous coal.** An Indiana HVC bituminous coal (50–100  $\mu$ m fraction) was used in this study. A coal of high ash (20.4 wt%), high pyrite (13.5 wt%) and high sulphur (8.3 wt%) contents was deliberately selected. Treatment of the coal with HCl and HF reduced the ash content to 4.7%, the majority of the ash in the demineralized sample being pyrite. Cations were added to both the raw and acid treated coals by soaking 1 g of material in 10 cc of varying concentrations of acetate solution at room temperature with stirring. The samples were then filtered and dried over night at 378 K in a vacuum oven.

Dependence of loading on the soak time is illustrated in Figure 13, when 0.6 M acetate solutions were used. For sodium and potassium, the soak time had little effect on loading. On the other hand, the amount of calcium

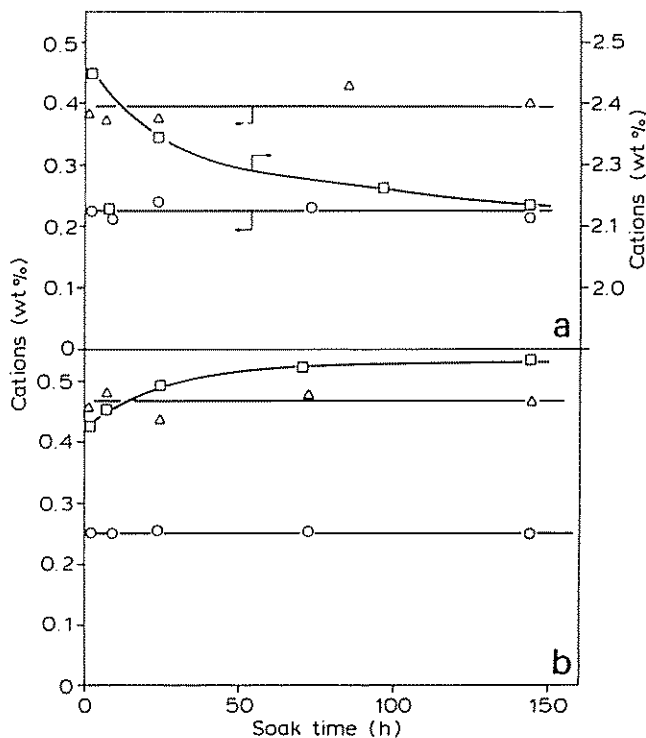


Figure 13 Effect of soak time on the amounts of cations loaded onto raw and demineralized bituminous coal (a) raw coal; (b) demineralized coal.  $\circ$ , Na;  $\Delta$ , K;  $\square$ , Ca



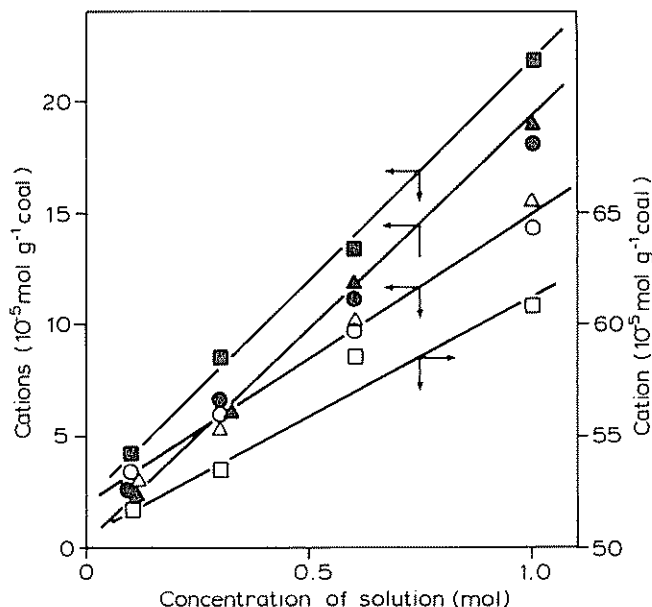


Figure 14 Effect of solution concentration on amounts of cations loaded onto bituminous coal. Open symbols, raw; closed symbols, demineralized coal. O, Na;  $\Delta$ , K;  $\square$ , Ca

present in the raw coal was much greater than amounts of potassium and sodium present and decreased as soak time increased due to the dissolution of calcium minerals, (16.0 wt% of the ash was CaO). Calcium content in the acid treated coal increased with increasing soak time up to about 70 h. The same findings were seen when other concentrations of solutions, ranging from 0.1 to 1.0 M, were used. It is known that bituminous coals have few carboxyl functional groups on their surface. Therefore, cations are loaded onto bituminous coal via sample impregnation. The effect of solution concentration on amount of cation loaded is shown in Figure 14. Values for calcium are for a loading time of 144 h. For all cations, loading increases linearly with increasing concentration of the solution.

Since this bituminous coal became fluid and caked during pyrolysis in  $N_2$ , it was first preoxidized in 0.1 MPa of air for 1 h at 473 K before heating at  $20\text{ K min}^{-1}$  in  $N_2$  to 1273 K. A weight gain of about 4% was observed during preoxidation. The yield of char was 70.7%, compared to 72.0% when no preoxidation was used. Unlike our previous studies on the effect of preoxidation on reactivity of highly caking coals where subsequent reactivity was markedly enhanced,<sup>12</sup> preoxidation of this weakly caking HVC coal did not significantly change its subsequent reactivity. From  $CO_2$  adsorption at 298 K, both the untreated and preoxidized coal chars had a surface area of  $11.4\text{ m}^2\text{ g}^{-1}$ .

Reactivity runs were conducted at 1123 K. Loaded chars, which were reacted, were derived from the acid treated bituminous coal loaded with  $0.183 \pm 0.007\text{ mmol}$  of cation  $\text{g}^{-1}$  coal.

Figure 15 presents a sequence of runs on the raw bituminous coal char. In dry  $H_2$ , initial weight loss is rapid as bulk pyrrhotite is converted to bulk iron. Carbon gasification rates are low in dry  $H_2$ , wet  $H_2$  and wet  $H_2/CO$ . When wet  $N_2$  is introduced, there is an initial weight gain as the iron is oxidized. This is followed by a rapid gasification rate in wet  $N_2$ . Obviously  $H_2$  and CO were inhibiting the  $C-H_2O$  reaction. Since the bituminous

char contained large amounts of pyrrhotite which was rapidly reduced to bulk iron in dry  $H_2$ , it is noteworthy that the gasification rate in wet  $H_2$  was low, since  $H_2$  is known to be a marked accelerator for the  $C-H_2O$  reaction in the presence of iron.<sup>19</sup> It is suggested that even though bulk iron is present after about 1 h exposure of the char to dry  $H_2$ , surface coverage by sulphur of the poorly dispersed iron particles is still significant. From studies of Grabke *et al.*, which give fractional coverage of iron by sulphur as a fraction of sulphur activity,<sup>20</sup> we estimate fractional coverage of sulphur of 0.95 and 0.50 at  $H_2S/H_2$  ratios of only  $0.2 \times 10^{-4}$  and  $1 \times 10^{-6}$ , respectively, at 1123 K.

Methane concentration in the product gas (Figure 15) slowly changes with time, in some cases, even though a deliberate injection of  $CH_4$  into the reactor shows up at the i.r. detector as a reasonably narrow pulse within 3 min. It suggests that  $CH_4$  production is very sensitive to the state of the surfaces of the inorganic impurities. Production of  $CH_4$  from dry  $H_2$  levels off at about 50% that produced from the wet  $H_2/CO$  mixture, suggesting that its production rate is roughly equal for the hydrogasification and methanation reactions under the conditions used.

Figure 16 presents results for the potassium-loaded bituminous char. Again, char gasification is slow in dry  $H_2$ , wet  $H_2$  and wet  $H_2/CO$  but very rapid in wet  $N_2$ .

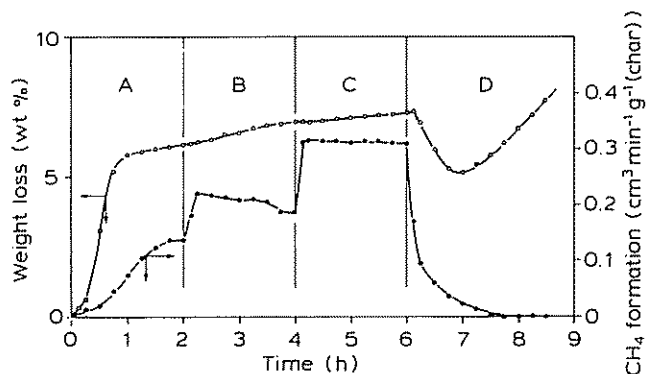


Figure 15 Reactivity plots and  $CH_4$  formation at 1123 K in different atmospheres for 1273 K char prepared from raw bituminous coal. A, Dry  $H_2$ ; B, wet  $H_2$ ; C, wet  $H_2/CO$ ; D, wet  $N_2$

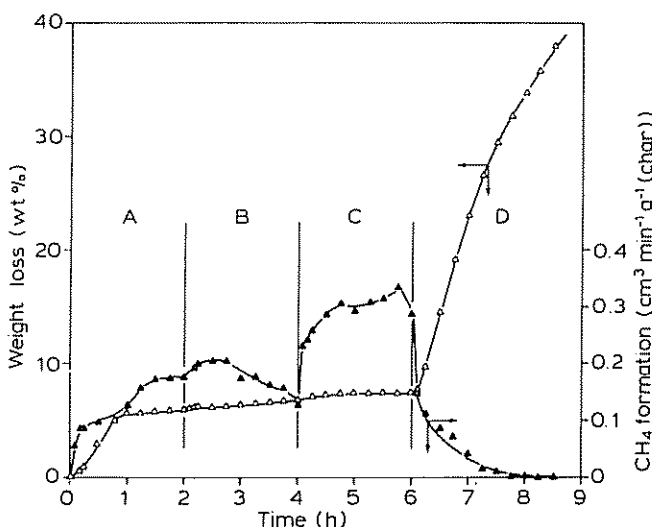


Figure 16 Reactivity plots and  $CH_4$  formation at 1123 K in different atmospheres for 1273 K char prepared from K-loaded bituminous coal. A, Dry  $H_2$ ; B, wet  $H_2$ ; C, wet  $H_2/CO$ ; D, wet  $N_2$

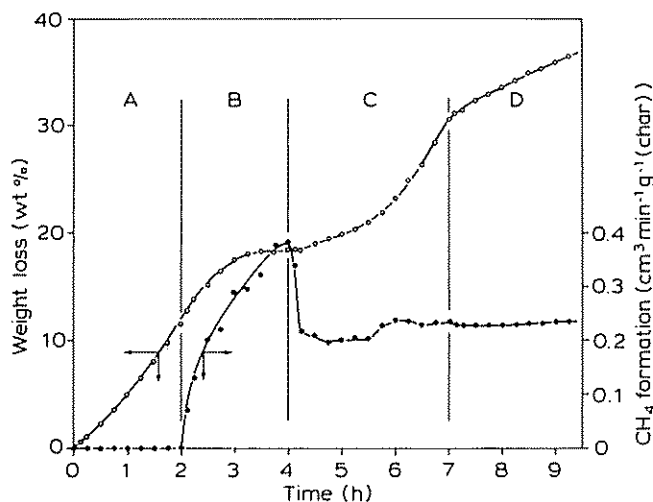


Figure 17 Reactivity plots and CH<sub>4</sub> formation at 1123 K in different atmospheres for 1273 K char prepared from K-loaded bituminous coal. Note reversal in the order of introduction of atmospheres from that used in Figure 16. A, Wet N<sub>2</sub>; B, wet H<sub>2</sub>/CO; C, wet H<sub>2</sub>; D, dry H<sub>2</sub>

Methane production is similar to that found over the raw bituminous char. Very similar results are found for the sodium and calcium-loaded chars.

The sensitivity of the gasification reactions to the sequence in which the potassium-loaded sample is exposed to the reactant gas is shown in Figure 17. The sequence of reactant gases is now reversed to give wet N<sub>2</sub>, wet H<sub>2</sub>/CO, wet H<sub>2</sub> and dry H<sub>2</sub>. Again, the C-H<sub>2</sub>O reaction is rapid in wet N<sub>2</sub>. Substituting the H<sub>2</sub>/CO mixture for N<sub>2</sub> leads to a progressive decrease in reaction rate in steam to a very low value. Substituting wet H<sub>2</sub> for the wet H<sub>2</sub>/CO mixture leads to a progressive increase in gasification rate to a value comparable to that in wet N<sub>2</sub>. This is consistent with the findings for the potassium-loaded lignite char; that is, CO inhibits the C-H<sub>2</sub>O reaction, as catalysed by potassium, whereas H<sub>2</sub> does not. Substituting dry H<sub>2</sub> for wet H<sub>2</sub> produces an immediate and continuing decrease in gasification rate, but it initially is much higher than when dry H<sub>2</sub> was introduced first (Figure 16). Methane production in wet N<sub>2</sub> is negligible, as expected. Introduction of wet H<sub>2</sub>/CO leads to a slow increase in the rate of CH<sub>4</sub> production to a value similar to that found previously (Figure 16). Introduction of wet H<sub>2</sub> leads to a relatively rapid decrease in the rate of CH<sub>4</sub> production to a value roughly half that found in wet H<sub>2</sub>/CO. Introduction of dry H<sub>2</sub> produces little change in the rate of CH<sub>4</sub> production.

#### Differences in reactivity of carbon deposited from CO and raw bituminous coal char

Studies were also conducted using the dry H<sub>2</sub>/CO mixture. Figure 18 shows results for the raw bituminous char at 1123 K. There is an initial weight loss as bulk pyrrhotite is converted to bulk iron. This is followed by carbon deposition, where the deposition rate slowly increases up to about 5 h. The substitution of dry CO for the dry H<sub>2</sub>/CO mixture after 6 h results in a progressive decrease in carbon deposition rate over the next 16 h. This is consistent with the previous finding from this laboratory that H<sub>2</sub> is an accelerator of CO disproportionation over iron.<sup>21</sup> As found in previous runs, the rate of CH<sub>4</sub> formation changes slowly with time,

requiring about 4 h to attain a constant rate after initial injection of the dry H<sub>2</sub>/CO mixture.

It has been previously shown in this laboratory that the carbon produced by CO disproportionation has a filamentous morphology, with fine particles of iron located at the tips of the filaments.<sup>22</sup> The fine particles of iron originate from massive iron particles which disintegrate in the CO atmosphere. It has also been shown that the deposited carbon has a high surface area and is highly reactive.<sup>21,22</sup> Therefore, it was of interest to explore the reactivity of the carbon deposited from CO within the pore structure of the bituminous coal char. Figure 19 summarizes some results.

Upon exposure of the raw bituminous char to dry H<sub>2</sub>/CO for 7.5 h, an increase in weight of 57% was obtained. After 5 h, the rate of carbon deposition was quite constant with time. Replacement of the dry H<sub>2</sub>/CO by wet H<sub>2</sub>/CO after 7.5 h resulted in an immediate cessation of carbon deposition and, instead, a rapid rate of carbon gasification. However, when the net weight loss returned close to zero, carbon gasification essentially stopped. The conclusion is that the deposited carbon was highly reactive in the wet H<sub>2</sub>/CO mixture, as catalysed by iron well dispersed through it; but, as found before, the base bituminous coal char is essentially unreactive. As found before, if wet N<sub>2</sub> is substituted for wet H<sub>2</sub>/CO the gasification rate increases sharply. Presumably gasification of the base coal char is being catalysed primarily by the calcium derived from the calcite present in the original coal.

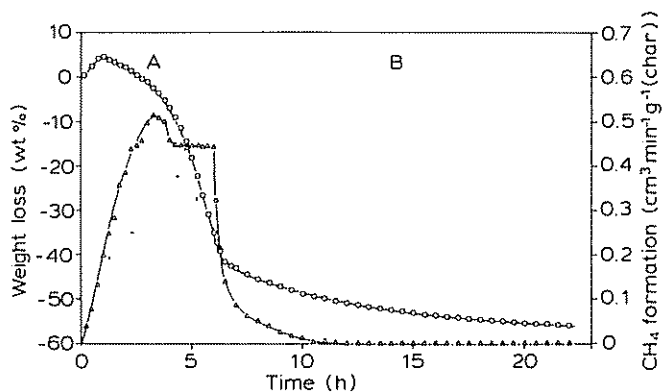


Figure 18 Carbon deposition and CH<sub>4</sub> formation over raw 1273 K bituminous coal char at 1123 K in dry H<sub>2</sub>/CO and dry CO. A, Dry H<sub>2</sub>/CO; B, dry CO

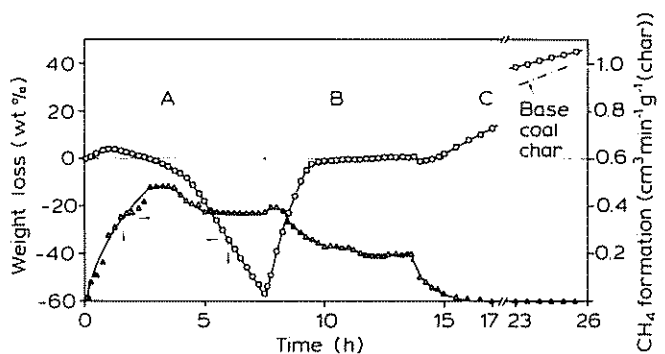


Figure 19 Carbon deposition and CH<sub>4</sub> formation over raw 1273 K bituminous coal char at 1123 K in dry H<sub>2</sub>/CO, followed by reaction of deposited carbon and coal char in various atmospheres. A, Dry H<sub>2</sub>/CO; B, wet H<sub>2</sub>/CO; C, wet N<sub>2</sub>

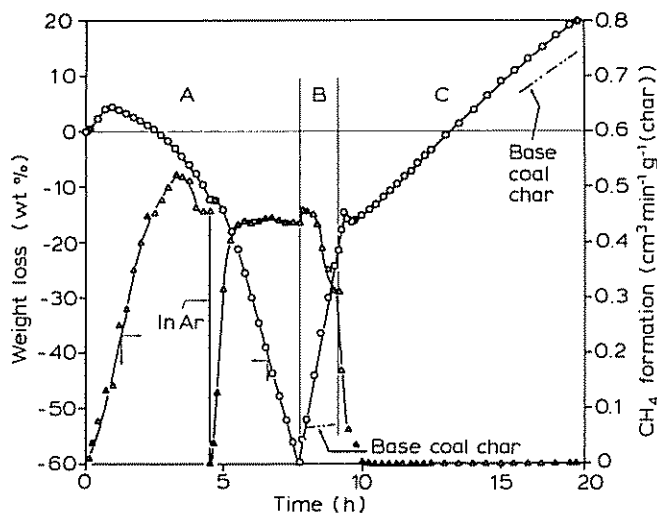


Figure 20 Carbon deposition and  $\text{CH}_4$  formation over raw 1273 K bituminous coal char at 1123 K in dry  $\text{H}_2/\text{CO}$ , followed by reaction of deposited carbon and coal char in various atmospheres. A, Dry  $\text{H}_2/\text{CO}$ ; B, wet  $\text{H}_2/\text{CO}$ ; C, wet  $\text{N}_2$

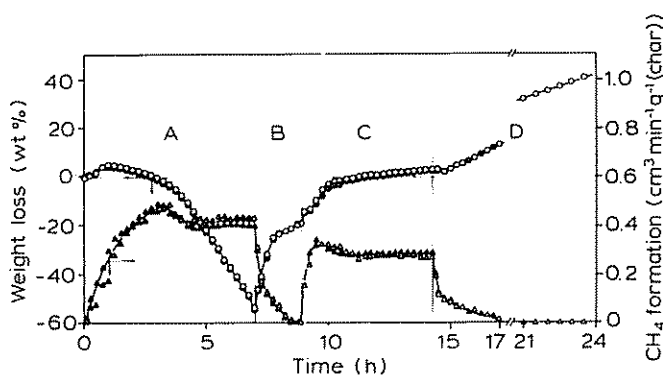


Figure 21 Carbon deposition and  $\text{CH}_4$  formation over raw 1273 K bituminous coal char at 1123 K in dry  $\text{H}_2/\text{CO}$ , followed by reaction of deposited carbon and coal char in various atmospheres. A, Dry  $\text{H}_2/\text{CO}$ ; B, wet  $\text{N}_2$ ; C, wet  $\text{H}_2/\text{CO}$ ; D, wet  $\text{N}_2$

Catalysis of the  $\text{C}-\text{H}_2\text{O}$  reaction by calcium is inhibited by the presence of  $\text{H}_2/\text{CO}$ , as we have already seen. Results summarized in Figure 19 reveal the complexities of carbon gasification – carbons of different reactivities, importance of association of the carbon with the catalyst, and different inorganic elements being active in different atmospheres.

Results for  $\text{CH}_4$  production, Figure 19, are interesting. In dry  $\text{H}_2/\text{CO}$ , the rate of  $\text{CH}_4$  production slowly increases, goes through a maximum, and only attains steady state at about the same time that the rate of carbon deposition attains steady state (about 5 h). The reason for the maximum is not understood. Substitution of wet  $\text{H}_2/\text{CO}$  for dry  $\text{H}_2/\text{CO}$  results in an initial small increase in rate of  $\text{CH}_4$  production, followed by a decrease in rate until steady state is attained at a rate  $\approx 50\%$  that in dry  $\text{H}_2/\text{CO}$ . It is concluded that steam inhibits the rate of the methanation reaction as catalysed by iron.

In another run, Figure 20, exposure of the raw bituminous coal char to dry  $\text{H}_2/\text{CO}$  was interrupted after 4.5 h, or just when steady state in the rate of carbon deposition and  $\text{CH}_4$  production had been attained, by the introduction of Ar for 15 h at 1123 K. When the dry  $\text{H}_2/\text{CO}$  mixture was again introduced, steady state was

attained in  $\approx 1$  h. Following a total weight gain of 60%, wet  $\text{H}_2/\text{CO}$  was introduced and a rapid gasification rate resulted. Introduction of wet  $\text{N}_2$ , before all of the deposited carbon was reacted away, resulted in a sharp decrease in gasification rate; but when a net weight loss of zero was reached, gasification continued at an uninterrupted rate. Therefore, the gasification rate of the deposited carbon is more rapid in wet  $\text{H}_2/\text{CO}$  than in wet  $\text{N}_2$ ; whereas, the gasification rate of the base coal char is more rapid in wet  $\text{N}_2$  than in wet  $\text{H}_2/\text{CO}$ . This again clearly shows the specificity of carbon gasification to particular morphologies of carbon, catalysts and reactive atmospheres.

Figure 21 shows duplicate runs. Following carbon deposition in dry  $\text{H}_2/\text{CO}$ , a rapid rate of carbon gasification in wet  $\text{N}_2$  is initially seen, as both deposited carbon and base char are gasified. However, as the iron catalyst becomes oxidized and deactivated, the gasification rate progressively decreases. Substitution of wet  $\text{H}_2/\text{CO}$  again reduces the iron and leads to an increase in gasification rate until the deposited carbon is completely reacted away, at which point base char gasification occurs at a low rate. Subsequent reinjection of wet  $\text{N}_2$  leads to an increase in gasification rate of the base char as expected. Results for  $\text{CH}_4$  production in this run follow previous results.

Figure 22 shows results where very high reactivity of deposited carbon in wet  $\text{H}_2$  is observed, compared to low reactivity of base char in either wet  $\text{H}_2$  or wet  $\text{H}_2/\text{CO}$ . Again high reactivity of base char in wet  $\text{N}_2$  is observed, but the rate is still only about 25% the gasification rate of the deposited carbon in wet  $\text{H}_2$ . The rapid and sharp increase in rate of  $\text{CH}_4$  production when wet  $\text{H}_2$  was substituted for dry  $\text{H}_2/\text{CO}$  is noteworthy. Obviously  $\text{CH}_4$  formation from the hydrogasification of the deposited carbon in wet  $\text{H}_2$  exceeded the rate of  $\text{CH}_4$  formation from the methanation reaction in dry  $\text{H}_2/\text{CO}$ .

To confirm the high reactivity of the deposited carbon to  $\text{H}_2$  for the production of  $\text{CH}_4$ , deposited carbon was reacted with dry  $\text{H}_2$  (Figure 23). Introduction of dry  $\text{H}_2$  resulted in an immediate and sharp increase in rate of  $\text{CH}_4$  production, reaching a maximum rate roughly three

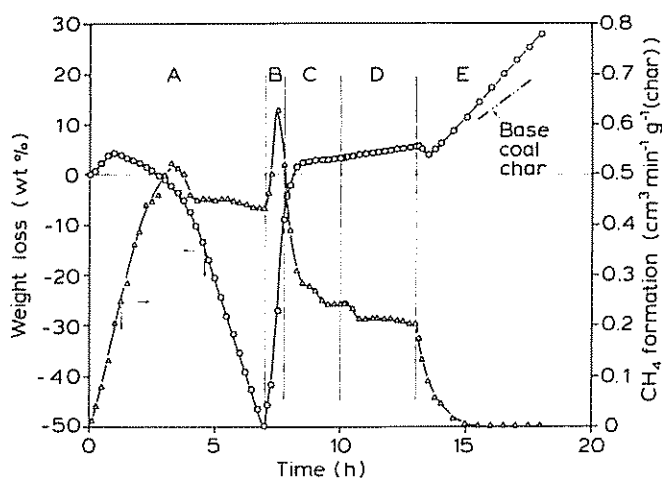


Figure 22 Carbon deposition and  $\text{CH}_4$  formation over raw 1273 K bituminous coal char at 1123 K in dry  $\text{H}_2/\text{CO}$ , followed by reaction of deposited carbon and coal char in various atmospheres. A, Dry  $\text{H}_2/\text{CO}$ ; B, wet  $\text{H}_2$ ; C, wet  $\text{H}_2/\text{CO}$ ; D, wet  $\text{H}_2$ ; E, wet  $\text{N}_2$

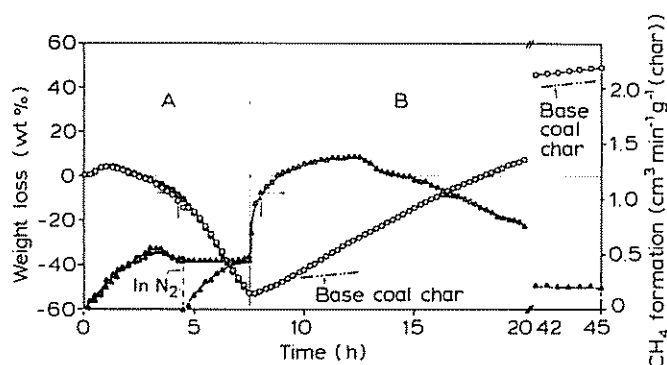


Figure 23 Carbon deposition and  $\text{CH}_4$  formation over raw 1273 K bituminous coal char at 1123 K in dry  $\text{H}_2/\text{CO}$ , followed by reaction of deposited carbon and coal char in dry  $\text{H}_2$ . Note that two deposition runs were made, one being interrupted by introduction of  $\text{N}_2$  for 15 h at 1123 K. A, Dry  $\text{H}_2/\text{CO}$ ; B, dry  $\text{H}_2$

times that found in the dry  $\text{H}_2/\text{CO}$  mixture. The rate of  $\text{CH}_4$  production then monotonically decreased as the deposited carbon was gasified away. Finally, the rate of  $\text{CH}_4$  production from hydrogasification of the base carbon fell to less than half the rate of  $\text{CH}_4$  production from the methanation reaction in the dry  $\text{H}_2/\text{CO}$  mixture.

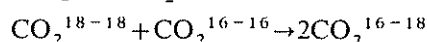
#### Mechanisms of catalysis of carbon gasification

**Potassium and sodium.** These alkali metals, added to low rank coal by ion exchange and to bituminous coals by impregnation using acetate solutions, are excellent catalysts for the  $\text{C}-\text{O}_2$ ,  $\text{C}-\text{CO}_2$  and  $\text{C}-\text{H}_2\text{O}$  reactions. McKee concluded that catalysis involves oxidation-reduction cycles, with carbon reducing the metal peroxide in the case of the  $\text{O}_2$  reaction and metal carbonate in the case of the  $\text{CO}_2$  and  $\text{H}_2\text{O}$  reactions.<sup>19,23-26</sup> Reduction of sodium and potassium carbonates by carbon at gasification temperatures involves a reaction of large positive free energy and, therefore, is strongly inhibited by  $\text{CO}$ , as found by McKee<sup>26</sup> and in this study.

**Calcium.** Calcium, an alkaline earth metal, is also an excellent catalyst for the  $\text{C}-\text{O}_2$ ,  $\text{C}-\text{CO}_2$  and  $\text{C}-\text{H}_2\text{O}$  reactions. Unlike potassium and sodium, a bulk peroxide has not been reported for calcium. However, it is thought that calcium has the ability to form a higher surface oxide. For example, Carberry *et al.*<sup>27</sup> suggested that the enhanced selectivity in silver-catalysed ethylene oxidation to ethylene oxide in the presence of a  $\text{CaO}$  promoter is due to superoxide formation on the surface calcium sites, as well as on the surface silver sites. Magnesium is a poor catalyst for the gasification reactions. A bulk peroxide has not been reported; and because of the relatively small size of the  $\text{Mg}^{2+}$  cation, it is doubtful if even a surface peroxide is formed.

McKee suggests that catalysis of the  $\text{C}-\text{CO}_2$  and  $\text{C}-\text{H}_2\text{O}$  reactions by calcium involves similar mechanisms to those proposed for potassium and sodium.

Recently it has been shown in this laboratory that  $\text{CaO}$  supported on carbon is a very active catalyst for oxygen exchange in  $\text{CO}_2$ , that is,



The reaction proceeds at a measurable rate at room temperature, but is not accompanied by carbon gasification. However, the fact that  $\text{CaO}$  is a very active

catalyst for the breakage of a carbon-oxygen bond in  $\text{CO}_2$  suggests a possible mechanism for catalysis of carbon gasification at higher temperatures where an oxygen atom can spill off the  $\text{CaO}$  surface.

Calcium is found to be a poor catalyst for the gasification of carbon by  $\text{H}_2$ , both in this study and when Saran char is mixed with calcite.<sup>28</sup> Therefore, it is understandable why differences in reactivity of US coal chars to  $\text{H}_2$  are not so great. Abundant, well dispersed calcium in lignite-derived chars is not significantly catalysing carbon gasification in  $\text{H}_2$  as it does in  $\text{O}_2$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

**Iron.** It has been shown, in this laboratory, that metallic iron is an excellent catalyst for the  $\text{C}-\text{O}_2$  and  $\text{C}-\text{CO}_2$  reactions but oxides of iron are poor catalysts.<sup>2,29</sup> McKee has reported a similar finding for the  $\text{C}-\text{H}_2\text{O}$  reaction.<sup>19,30</sup> Thus the finding that  $\text{CO}$  and  $\text{H}_2$  are accelerators for the  $\text{C}-\text{CO}_2$  and  $\text{C}-\text{H}_2\text{O}$  reactions, respectively,<sup>2,19</sup> if the  $\text{CO}/\text{CO}_2$  and  $\text{H}_2/\text{H}_2\text{O}$  ratios are sufficiently high for bulk metallic iron to be the stable phase is as expected.

The metallic iron surface is a good catalyst for dissociation of molecular oxygen-containing species. Once oxygen atoms are formed they are thought both to react with carbon at the iron-carbon interface, if an active carbon site is available, and to spill over from the iron surface to the carbon surface where they travel by surface diffusion until they find an active carbon site.

As discussed, catalysis by iron is also expected to be reduced by the presence of sulphur in the reacting atmosphere. For example, in the  $\text{C}-\text{H}_2\text{O}$  reaction, sulphur in the form of  $\text{H}_2\text{S}$  and  $\text{COS}$  will be formed by reaction of  $\text{H}_2$  and  $\text{CO}$  with both the organic and inorganic sulphur present in the coal. Very small amounts of  $\text{H}_2\text{S}$  and  $\text{COS}$  lead to significant coverages of surface iron sites by sulphur, even though bulk iron is the stable phase. Recently Huttinger and Krauss confirm that the elimination of sulphur from iron is a prerequisite for iron to be a catalyst of the  $\text{C}-\text{H}_2\text{O}$  reaction.<sup>31</sup>

Iron is an excellent catalyst for the dissociative chemisorption of  $\text{H}_2$  and thus the gasification of carbon by  $\text{H}_2$ . Again, catalysis by iron is inhibited strongly by sulphur. Cypres and co-workers recently studied the hydrogenation of graphite in the presence of pyrite.<sup>32</sup> They showed that neither pyrite nor pyrrhotite had catalytic activity but that it was necessary for metallic iron to be produced before catalysis began.

Iron is a good methanation catalyst, but again sulphur poisoning is frequently present. In a recent study in this laboratory, using iron supported on carbon black as a methanation catalyst, it was observed that at 500 K the catalyst was not active.<sup>33</sup> The carbon black contained 1.5 wt% sulphur. Pretreatment of the carbon black in 0.1 MPa of  $\text{H}_2$  at 1473 K for 12 h removed accessible sulphur. Iron supported on this carbon was a very active catalyst for the methanation reaction.

Iron has been shown to be a very active catalyst for the disproportionation of  $\text{CO}$  in a dry  $\text{H}_2/\text{CO}$  (3:1) mixture at 1123 K. If the iron is in an oxidized or a sulphided state, it is a poor catalyst. When the dry  $\text{H}_2/\text{CO}$  mixture was exposed to the bituminous coal char at 1123 K, a considerable period of time was required before the maximum carbon deposition rate was attained. As expected, if the char is pretreated in a reducing atmosphere of a  $\text{H}_2$ -containing gas for an extended period

of time, the maximum rate of carbon deposition is found to be attained immediately upon introduction of the H<sub>2</sub>/CO mixture. The deposited carbon is highly reactive to dry and wet H<sub>2</sub>, since the situation for catalysis by iron is optimal – that is, a high surface area carbon containing well dispersed metallic iron.

#### ACKNOWLEDGEMENTS

Research, reported on in this Paper, was supported by the US Department of Energy under Contracts EX-76-C-01-2030 and DE-AC01-79ET14882. S. Matsumoto was supported by the Government Industrial Research Institute of Kyushu. Discussions with L. Radović on catalysis of gasification by calcium are appreciated. Professor W. Spackman kindly supplied the coal samples which were used.

#### REFERENCES

- 1 Walker, P. L., Jr., Rusinko, F., Jr. and Austin, L. G. *Advances in Catalysis*, Vol. 11 (Eds. D. D. Eley, P. W. Selsood and P. B. Weisz), Academic Press, New York, 1959, p. 164
- 2 Walker, P. L., Jr., Shelef, M. and Anderson, R. A. *Chemistry and Physics of Carbon*, Vol. 4 (Ed. P. L. Walker, Jr.), Marcel Dekker, New York, 1966, p. 287
- 3 Jenkins, R. G., Nandi, S. P. and Walker, P. L., Jr. *Fuel* 1973, **52**, 288
- 4 Hippo, E. and Walker, P. L., Jr. *Fuel* 1975, **54**, 245
- 5 Tomita, A., Mahajan, O. P. and Walker, P. L., Jr. *Fuel* 1977, **56**, 137
- 6 Solano, A. L., Mahajan, O. P. and Walker, P. L., Jr. *Fuel* 1977, **56**, 451
- 7 Soledade, L. E. B., Mahajan, O. P. and Walker, P. L., Jr. *Fuel* 1978, **57**, 56
- 8 Ashu, J. T., Nsakala, N. Y. and Walker, P. L., Jr. *Fuel* 1978, **57**, 250
- 9 Mahajan, O. P., Yarzab, R. and Walker, P. L., Jr. *Fuel* 1978, **57**, 643
- 10 Linares-Solano, A., Mahajan, O. P. and Walker, P. L., Jr. *Fuel* 1979, **58**, 327
- 11 Hippo, E. J., Jenkins, R. G. and Walker, P. L., Jr. *Fuel* 1979, **58**, 338
- 12 Mahajan, O. P., Komatsu, M. and Walker, P. L., Jr. *Fuel* 1980, **59**, 3
- 13 Walker, P. L., Jr. *Fuel* 1980, **59**, 809
- 14 Walker, P. L., Jr. *Fuel* 1981, **60**, 801
- 15 Mahajan, O. P. and Walker, P. L., Jr. *Analytical Methods for Coal and Coal Products*, Vol. II (Ed. C. Karr, Jr.), Academic Press, New York, 1978, p. 465
- 16 Gan, H., Nandi, S. P. and Walker, P. L., Jr. *Fuel* 1972, **51**, 272
- 17 Morgan, M. E., Jenkins, R. G. and Walker, P. L., Jr. *Fuel* 1980, **60**, 189
- 18 Hirsch, R. L., Gallagher, J. E., Jr., Lessard, R. R. and Wesselhoft, R. D. *Science* 1982, **215**, 121
- 19 McKee, D. W. *Chemistry and Physics of Carbon*, Vol. 16 (Ed. P. L. Walker, Jr. and P. A. Thrower), Marcel Dekker, New York, 1981, p. 1
- 20 Grabke, H. J., Petersen, E. M. and Srinivasan, S. R. *Surface Sci.* 1977, **67**, 501
- 21 Walker, P. L., Jr., Rakszawski, J. F. and Imperial, G. R. *J. Phys. Chem.* 1959, **63**, 140
- 22 Walker, P. L., Jr., Rakszawski, J. F. and Imperial, G. R. *J. Phys. Chem.* 1959, **63**, 133
- 23 McKee, D. W. and Chatterji, D. *Carbon* 1975, **13**, 381
- 24 McKee, D. W. and Chatterji, D. *Carbon* 1978, **16**, 53
- 25 McKee, D. W. *Carbon* 1979, **17**, 419
- 26 McKee, D. W. *Carbon* 1982, **20**, 59
- 27 Carberry, J. J., Kuczyuski, G. C. and Martinez, E. J. *Catal.* 1972, **26**, 247
- 28 Tomita, A., Mahajan, O. P. and Walker, P. L., Jr. *Preprints 173rd Meeting Am. Chem. Soc., Div. Fuel Chem.* 1977, Vol. 22, No. 1, p. 4
- 29 Walker, P. L., Jr. and Thomas, J. M. *Chem. Eng. Prog. Symp. Series* 1967, **63**, No. 73, 139
- 30 McKee, D. W. *Carbon* 1974, **12**, 453
- 31 Huttlinger, K. J. and Krauss, W. *Fuel* 1982, **61**, 291
- 32 Cypress, R., Ghodsi, M. and Stocq, R. *Fuel* 1981, **60**, 247
- 33 Vannice, M. A., Walker, P. L., Jr., Jung, H.-J., Moreno-Castilla, C. and Mahajan, O. P. *Proceedings Seventh International Congress on Catalysis, Tokyo, 1980*, p. 460

# Low temperature gasification of brown coals catalysed by nickel\*

Akira Tomita, Yasuo Ohtsuka and Yasukatsu Tamai

Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Katahira, Sendai 980, Japan

Nickel catalyst exhibited an extremely high activity in the gasification of some low rank coals at a temperature as low as 750 K. Approximately 85% of Yallourn coal was converted within 30 min in steam at 773 K. A high nickel loading, > 4 wt% was necessary. It seems essential for coal high in oxygen and low in sulphur to be gasified in this manner. Oxygen-containing functional groups on the coal surface seemed to play an important role in keeping the nickel catalyst in a finely dispersed state. Hydrogen sulphide was strongly adsorbed on the nickel catalyst and retarded this reaction. Hydrogen and carbon dioxide were the main products of low-temperature steam gasification. Similar low-temperature gasification reactions were also observed in hydrogen and in carbon dioxide.

(Keywords: brown coal; nickel; catalyst; gasification)

The use of catalysts in coal gasification has attracted increasing attention, because of the many advantages of a lower gasification temperature.<sup>1</sup> For example, methane may be produced directly from coal and steam with high thermal efficiency. Since it was found that a significant proportion of an activated carbon can be gasified at low temperatures ( $\approx 800$  K) in the presence of nickel catalyst,<sup>2</sup> the application of nickel to coal gasification has been investigated with the aim of carrying out similar low-temperature gasification for coal.

Some low rank coals can be rapidly gasified with nickel catalyst in this low-temperature region.<sup>3</sup> Potassium carbonate, which has been commonly recognized as the best catalyst for the steam gasification of coal, and other alkali or alkaline earth salts were not active at this low-temperature region. *Figure 1* schematically illustrates the steam gasification profile for Yallourn coal with 10 wt% of nickel. After devolatilization the fixed carbon is catalytically gasified in two stages. Since the reaction velocity at the first gasification stage is very high, even at 773 K the gasification proceeds at a significant rate, which was similar to the non-catalytic reaction velocity at 1073 K. Thus a lowering of gasification temperature by 300 K was achieved for this reaction stage. The amount of coal converted in this stage reached about 85 wt% (daf). This stage is referred in this Paper as the 'rapid gasification stage'. At a higher temperature, a shorter time was enough to complete this stage. The reaction for the remaining 15 wt% proceeded very slowly. Therefore, at 773 K the reaction actually stopped at a conversion of 85 wt%. The rate of this slow stage at 1023 K was relatively large and all fixed carbon was gasified within 30 min (*Figure 1*).

Other aspects that have recently received attention include the oxygen content of coals in relation to the catalytic activity of metals,<sup>4,5</sup> catalyst loading,<sup>6</sup> and catalyst inhibition by sulphur.<sup>7</sup>

The aim of the present study was first to identify the

factors that influence this rapid gasification at  $\approx 800$  K and to elucidate the reaction mechanism, secondly to determine the composition of product gas, and finally to investigate the effects of other gasifying agents.

## EXPERIMENTAL

### Coal and catalyst

Ten coals from various countries were used; the analyses are summarized in *Table 1*. Yallourn coal from Victoria, Australia, was investigated in detail. It was received in a briquette form and then crushed into particles 1–2 mm in diameter. The proximate analysis was: moisture, 14.3 wt%; volatile matter, 47.3 wt%; fixed carbon, 37.6 wt%; ash, 0.8 wt%.

As a starting material for nickel catalyst, hexamine nickel(II) carbonate was selected from a view point of facile catalyst recovery from the gasification residue.

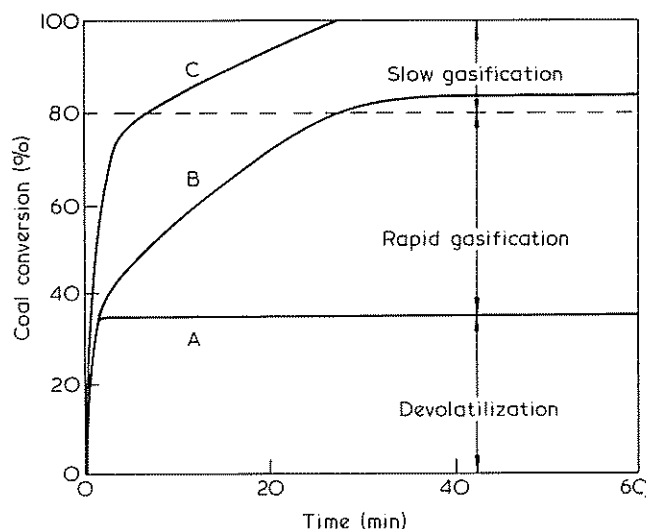


Figure 1 Gasification profile of Yallourn coal with 10 wt% Ni. A, in  $N_2$  at 773 K; B, in  $H_2O$  at 773 K; C, in  $H_2$  at 1023 K

\* Presented at International Symposium, 'Fundamentals of Catalytic Coal and Carbon Gasification', held at Amsterdam, The Netherlands, 27–29 September 1982