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Enhancement of lignite char reactivity to steam by cation addition

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Chars produced from lignites typically have much higher reactivities to gasification than those produced from bituminous coals. This has been attributed previously to the presence of carboxylate salts of inorganic constituents on the lignites. Upon charring of the lignites, the carboxylate salts decompose leaving behind well dispersed inorganic constituents which act as catalysts for gasification. In this study, a raw lignite has been treated with HCl and HF to demineralize it and to increase its carboxyl content prior to exchanging selected cations with the hydrogen on the carboxyl groups. Up to 2.14 mmol of calcium per g of coal could be added using this procedure. Addition of varying amounts of calcium to the lignite resulted in the production of chars containing calcium contents ranging from 1.1 to 12.9 wt %. Such addition resulted in a rectilinear increase in reactivity of the char to steam with increasing amount of calcium added. Maximum reactivity attained was over ten times the reactivity found for the char produced from the raw lignite. At comparable molar loadings of metal cations onto the acid-treated lignite, the chars subsequently produced had reactivities in steam in the order: $K > Na \approx Ca > Fe > Mg$. Char reactivity could also be enhanced by the addition of cations to nitric acid-treated char which had been produced, in turn, from demineralized lignite.

Walker and co-workers have shown that the reactivity of coal chars to air, CO₂, and steam is strongly dependent upon the rank of coal from which the char is produced¹⁻⁴. That is, chars produced from high-rank coals (anthracite and low-volatile bituminous) have reactivities which are, in some cases, as much as 200 times as small as reactivities of lignite chars produced under identical heating cycles. These differences in reactivity are attributed to three factors. The low-rank-coal chars have: (1) a higher concentration of active carbon sites, (2) better site utilization because of a greater concentration of feeder pores, and (3) impurities of higher specific catalytic activity than the high-rank-coal chars. Factor (3) will be of particular interest in this paper.

The amount and nature of oxygen functional groups on coals vary considerably with coal rank⁵. Unlike coals of other rank, lignites contain a high concentration of carboxyl groups⁵. With time, significant exchange of the hydrogen on the carboxyl groups with metal cations has occurred as water carrying these cations has migrated through the micro-pore structure of the lignites. Exchange between hydrogen and calcium has been particularly prevalent, but exchange of many other cations such as potassium, sodium, and magnesium has occurred. Amounts of different cations exchanged have varied with the particular geographical location of the lignite deposit.

Upon heating of lignites to gasification temperatures, the carboxylate salts of the inorganic constituents dissociate releasing CO₂ and leaving behind highly dispersed inorganic species. As expected, at least some of these inorganic species, like calcium^{2,4}, have high activity for the catalysis of carbon gasification.

In this study, attempts have been made to further enhance the reactivity of a lignite char to steam by the addition of metal cations onto carboxyl groups of the lignite which were not cation-exchanged in nature. Cations added were calcium, sodium, potassium, magnesium, and iron.

EXPERIMENTAL

Lignite

A bench sample of a Gulf Province lignite from the Darco Mine near Darco City, Texas was used in this study. Table 1 presents proximate and ultimate analyses for the sample, using ASTM procedures. From reflectance measurements on a polished section, the sample was estimated to contain (by volume) 70% vitrinite, 13.2% micrinite, 8.8% fusinite, 3.8% exinite, and smaller amounts of other macerals⁶. Major elements in the ash were 38.4% SiO₂, 21.0% Al₂O₃, 11.8% Fe₂O₃, 10.0% CaO, and 1.7% MgO. From ion-exchange of calcium on the raw lignite, it was estimated

Table 1 Analyses on lignite

Proximate analysis	(wt %, dry basis)	Ultimate analysis	(wt %, daf) ^a
Ash	9.4	C	71.7
VM	44.8	H	5.2
Fixed C	45.8	N	1.3
		S	0.72
		Cl	0.02
		O ^b	21.1

^a Dry, ash free

^b Oxygen was determined by difference

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that it contained 2.36 mmol of carboxyl groups per g of dry mineral-matter-free coal.

About 30 kg of lignite, much of which was in large lumps, were first broken to -4 Tyler mesh, air dried for two days, and then ground to -28 Tyler mesh. The 28 × 48 mesh fraction, which was used primarily in this study, was stored in sealed plastic containers under N₂ until used.

Procedures and apparatus

Demineralization of lignite. Demineralization of the lignite served two purposes. It converted essentially all of the carboxyl groups which had metal cations associated with them back to the hydrogen form by ion exchange and it removed essentially all the discrete minerals like kaolinite, illite, quartz, and calcite from the coal. Demineralization was effected by first passing boiling 10% (by wt) HCl over the coal continuously for 2 h. At the end of this period no calcium ions were detected in the liquid leaving the column. The acid-washed lignite was then immersed in a 50–50 mixture of 50% HF and 10% HCl and heated to boiling water temperature for 48 h. The solution was then decanted off and the lignite continuously washed with boiling water in a column for 2 h. At the end of this time, no chlorine ions were detected in the exit steam.

Ion exchange on the demineralized lignite. Schafer's method was used to effect ion exchange⁷. Complete details of exchange are given elsewhere⁸. Ten levels of calcium, ranging from 0.10 to 2.14 mmol of cation/g of coal (daf), were added by exposing the demineralized lignite to calcium acetate solutions ranging in concentration from 0.04 to 2.0 molar for 24 h. To increase both the rate and amount of exchange required to attain some of the higher loadings, the pH of the solution was increased by the addition of sodium hydroxide and exchange was carried out at 60°C instead of room temperature. As exchange progressed, the decrease in pH of the solution was followed. Assuming that two hydrogen ions were produced for each calcium ion (that is Ca⁺⁺) exchanged on the coal, the amount of exchange could be calculated. This calculation was found to be in good agreement with the amount of calcium added to the coal as determined by atomic absorption measurements.

Demineralized lignite was also exchanged in 0.10 molar solutions of ferric nitrate, magnesium nitrate, magnesium acetate, potassium acetate, and sodium acetate. Approximately 0.3 mmol of cation/g of coal was exchanged from the various solutions in 24 h.

Charring of the lignite. Conversion of raw, demineralized, and ion-exchanged lignites to chars was carried out in a fluid bed. As described in detail elsewhere⁸, appropriate fluidization conditions in N₂ were determined in a glass column at room temperature. Fluidization was conducted at conditions between minimum aggregative and slugging⁹. By setting the flow rate at the beginning of a run so as to just be above minimum aggregative fluidization, decreases in particle density during charring (or gasification) did not remove fluidization from this regime.

Charring was accomplished in a fluidized-bed reactor 760 mm in length and 50 mm in diameter. The lignite charge was held in N₂ for 30 min at room temperature under fluidization conditions before heating up in N₂ at a rate of 10°C/min to maximum temperature. A soak time of 2 h at maximum temperature was used in all cases.

Ion exchange on selected chars. In addition to adding metal cations to the demineralized lignite, they were also

introduced into the char produced at 800°C from raw lignite. The char was first demineralized using the same approach as discussed previously. Demineralization of the char produced from the raw lignite reduced its ash yield to 3.0%, while the char produced from the demineralized lignite yielded just 1.0% ash. Charring would be expected to alter the chemical and physical form of the inorganic constituents¹⁰, as well as their accessibility to acid leaching.

As a result of heating the lignite to 800°C, all carboxyl groups would have been decomposed¹¹. Therefore, following demineralization, the char was treated with boiling concentrated nitric acid for 6 h to add carboxyl groups onto the char¹². After treatment, the char was washed thoroughly with boiling distilled water. Selected cation exchanges using 0.4 molar solutions were then conducted, as described previously.

Reacting lignite chars in steam. The reactor system consisted essentially of three parts: a steam generator, a 50 cm long by 35 mm diameter fluid-bed vertical reactor, and a gas analysis section. The system is described in more detail elsewhere⁸. A weighed amount of char (about 20 g) was placed in the reactor and brought to reaction temperature in N₂. After thermal equilibrium had been achieved, N₂ flow was stopped and steam introduced at a controlled and predetermined flow rate to produce aggregative fluidization. Gasification was conducted at 1 atm* total pressure. At the exit of the reactor, unreacted steam was condensed and the product gas was passed through a wet test meter to measure cumulative product gas volume as a function of time. Samples of gas leaving the wet test meter were taken at intervals to analyse for CO, CO₂, and H₂, using gas chromatography.

After the desired carbon burn-off was reached, the run was stopped and the sample allowed to cool in N₂ before being removed from the reactor and weighed. All chars were reacted at 650°C. Selected samples were also reacted at 700, 735, and 750°C.

Characterization of lignite and chars. Surface areas were determined using the Dubinin–Polanyi equation with CO₂ adsorption at 298 K. Lignites and lignite chars are molecular-sieve materials. Therefore, as discussed previously¹³, the surface area determined by CO₂, using the D–P equation, is representative of the accessible micropore surface area. Mercury and helium densities were also measured; differences in the reciprocals of these densities gave total open pore volumes¹⁴.

RESULTS

All chars were reacted in steam, at least, at 650°C. Variables studied were char heat-treatment temperature, cation type, calcium loading, and conditions of exchange. All samples were characterized by CO₂ adsorption at 298 K, mercury and helium displacement at room temperature, and ash yields for mass balance calculations. A complete compilation of results is given elsewhere⁸.

Properties of lignite and chars

Table 2 summarizes important properties on the 28 × 48 mesh lignite fraction. Demineralization produced some increase in surface area and pore volume, as expected. Subsequent ion exchange of the demineralized samples did not substantially alter these values.

*101.3 kPa

Table 3 summarizes surface area and density data on the chars produced from the raw and demineralized lignites. Charring of the lignite produced large increases in surface area and pore volume, as volatile matter was evolved. Increasing calcium exchange on the lignite from 0.10 to 2.14 mmol/g resulted in a monotonic increase in surface area of the 800°C char produced, that is from 720 to 850 m²/g. It resulted in little change in char pore volume. Ion exchange of 0.3 mmol/g of potassium, sodium, and iron onto the lignite resulted in mixed results for surface areas of chars produced by heating to 800°C. Surface areas of chars produced from potassium- and sodium-exchanged lignites were sharply reduced from that for the char produced from the demineralized lignite, that is 400 and 450 m²/g, respectively, compared with 680 m²/g. Conversely, surface area of the char produced from the iron-exchanged lignite was higher, that is 800 m²/g. Again, pore volumes of the chars were changed little by starting with lignites containing various cations. Modifying the micro-pore surface area of chars by the prior introduction of metal cations into precursor lignites has interesting implications for the production of activated carbons of variable properties, but this area will not be considered further in this study.

Demineralization of the 800 and 900°C chars produced from the raw lignite reduced their surface areas (to 740 m²/g) but had a negligible effect on pore volume. Subsequent introduction of cations into the 800°C demineralized char resulted in insignificant changes in surface area and pore volume.

Reactivity results

Mass balances. By weighing the amount of solid before and after reaction, measuring ash yield, and calculating the amount of carbon gasified from gas analysis for CO and CO₂ (an insignificant amount of CH₄ and higher hydrocarbons are produced at 1 atm pressure), overall carbon and ash balances were determined. An overall mass balance on carbon and ash showed small losses, apparently due to fine

particulate elutriation from the fluid bed and production of some H₂S during gasification. Typical balances indicated a range of up to 1.0% solid loss; but for some runs where carbon burn-off exceeded 50%, 2–3% of the total carbon and ash were lost.

Equilibrium considerations. Approach to equilibrium for two reactions were of interest, that is the C–H₂O reaction and the water-gas-shift reaction. Approach to equilibrium for the C–H₂O reaction was small at all reaction temperatures. For example, at 650°C even for the most highly exchanged calcium-containing char the quotient $(p_{CO})(p_{H_2})/(p_{H_2O})$ at the exit of the reactor was less than 0.2% of the value at equilibrium. In contrast, the approach towards equilibrium was much greater for the water-gas-shift reaction. For the calcium-containing chars, the approach to equilibrium increased monotonically from 14% to 98% as cation loading on the demineralized lignite increased from 0.10 to 2.14 mmol/g. These results are summarized in Table 4. Also shown in the Table are approaches to equilibrium for the water-gas-shift reaction for chars produced from lignite containing 0.30 mmol/g of other cations. At this loading, a compound of potassium was the most active catalyst and magnesium the least active. As will be seen, this activity parallels that for catalysis of char gasification. Approaches to equilibrium did not vary much with extent of carbon gasification.

Burn-off curves and reactivity. The amount of carbon burn-off could be closely monitored by measuring continuously the cumulative volume of product gas and its composition. Reactivity was expressed as previously^{1,2} by

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

Table 4 Approach to equilibrium for the water-gas-shift reaction at 650°C for chars produced from various ion-exchanged lignites

Cation exchanged	Amount of exchange (mmol/g of daf coal)	Approach to equilibrium (%)
Ca	2.14	98
Ca	1.20	48
Ca	0.95	45
Ca	0.66	44
Ca	0.56	41
Ca	0.45	32
Ca	0.37	31
Ca	0.32	28
Ca	0.25	25
Ca	0.10	14
K	0.30	42
Na	0.30	27
Mg	0.30	5
Fe	0.30	10

Table 2 Properties of raw and demineralized lignite (28 × 48 mesh)

Property	Raw	Demineralized
Ash (wt %, dry basis)	10.8	0.5
VM (wt %, daf)	47.1	47.1
CO ₂ surface area (m ² /g, daf)	120	200
He density (g/cm ³ , mmcb) ^a	1.44	1.38
Hg density (g/cm ³ , mmcb)	1.33	1.20
Pore volume (cm ³ /g, mmcb)	0.06	0.11
Porosity (% , mmcb)	8	12

^aMineral matter containing basis

Table 3 Properties of chars produced from raw and demineralized lignites

Property	Raw			Demineralized		
	700	800	900°C	700	800	900°C
CO ₂ surface area (m ² /g, daf)	730	800	860	680	680	680
He density (g/cm ³ , mmcb) ^a	1.92	1.97	2.00	1.74	1.88	1.89
Hg density (g/cm ³ , mmcb)	1.33	1.33	1.37	1.20	1.18	1.20
Pore volume (cm ³ /g, mmcb)	0.23	0.24	0.23	0.27	0.31	0.30
Porosity (% , mmcb)	31	32	31	32	37	37

^aMineral matter containing basis

Table 5 Reactivities in steam of chars prepared from raw, demineralized and calcium-exchanged lignites

Heat-treatment temperature (°C)	Reaction temperature (°C)	Reactivity (g/g h daf)		
		Raw	Dem.	Ca i.e.
700	650	0.057	0.0062	0.68
800	650	0.050	0.0050	0.43
900	650	0.020	0.0046	n.d. ^a
800	700	0.352	0.032	0.85
900	700	0.132	0.020	0.68
800	750	0.956	0.078	1.03
900	750	0.352	0.038	n.d.

^a Not determined

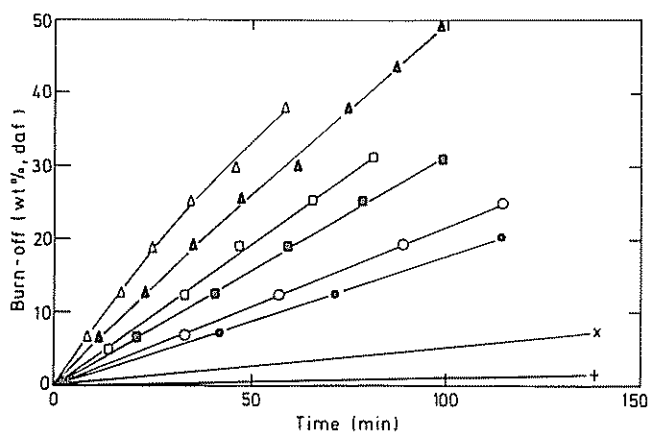


Figure 1 650°C reactivity plots for 800°C chars produced from raw, demineralized, and various calcium-exchanged lignites. x raw, + demineralized, ● 1.1% Ca, ○ 2.1% Ca, ■ 5.7% Ca, □ 7.0% Ca, ▲ 9.1% Ca, △ 12.9% Ca

where w is the initial char weight (daf) and dw/dt the rate of char gasification. Since all chars were reacted to at least 10% burn-off, reactivities are given at this level. However, for most samples reactivity remained essentially constant to much higher burn-off levels. The iron-containing chars were an exception, as will be seen shortly.

Table 5 summarizes reactivity results (R) for the chars produced from raw, demineralized, and calcium-exchanged (1.20 mmol/g) lignites. As previously shown^{1,2}, char reactivity decreased as its heat-treatment temperature (HTT) was increased. This has been attributed to a decrease in number of active carbon sites, and catalyst sintering. At each reaction temperature, reactivity of the chars produced from the demineralized lignite was lower by a factor of about ten compared to chars produced from the raw lignite. This reduction in reactivity is attributed to removal of discrete mineral matter and metal cations associated with carboxyl groups on the raw coal. By contrast, reactivities of the chars produced from the calcium-exchanged lignite were in all cases higher than those for the chars produced from the raw lignite. The higher reactivity of the calcium-exchanged lignite char is attributed to its containing a higher calcium loading than that on the char produced from the raw lignite, as will be seen shortly. It is interesting that differences in reactivity between the calcium-exchanged and raw lignite chars become less as reaction temperature is increased. This can be attributed to increasing mass-transport control of the reaction and possibly enhanced

catalyst deactivation due to particle agglomeration and sintering.

Reactivity plots for selected 800°C chars prepared from various calcium loaded lignites are presented in Figure 1. Reaction temperature was 650°C. Reactivity plots are rectilinear to high carbon burn-offs, except for the plot at the greatest calcium loading. Again catalyst deactivation due to particle agglomeration would be expected to be most marked for this sample. R values are summarized in Table 6. A rectilinear increase in reactivity (R) with increasing calcium loading was found, as shown in Figure 2. Clearly reactivities for the chars derived from the raw and demineralized lignites fall below the line. This suggests that some of the calcium in these samples had a lower specific catalytic activity owing to differences in its degree of agglomeration, crystallinity, and/or chemical form. Reactivity of the char produced from the lignite sample having maximum calcium loading was over ten times as great as that for the char produced from the raw lignite.

Portions of the demineralized coal were exchanged with approximately 1.2 mmol calcium/g at varying pH levels to see if varying the pH used during exchange would have an effect on subsequent reactivity of the char produced. For the limited results obtained, there was no effect found, as seen in Figure 3.

Reactivity plots for 800°C chars prepared from cation-exchanged lignites loaded to 0.3 mmol/g with various metal ions are presented in Figure 4. Reaction temperature is 650°C. Again, reactivity plots for chars produced from

Table 6 Reactivities in steam at 650°C of 800°C chars prepared from calcium-exchanged lignites

Amount of exchange (mmol/g of daf coal)	Ca in char (wt %)	Reactivity (g/g h daf)
2.14	12.9	0.63
1.29	9.1	0.45
1.20	8.5	0.43
1.15	8.4	0.40
0.95	7.0	0.33
0.66	5.3	0.30
0.56	4.5	0.23
0.45	3.1	0.20
0.37	2.6	0.17
0.32	2.1	0.14
0.25	1.9	0.13
0.10	1.1	0.11

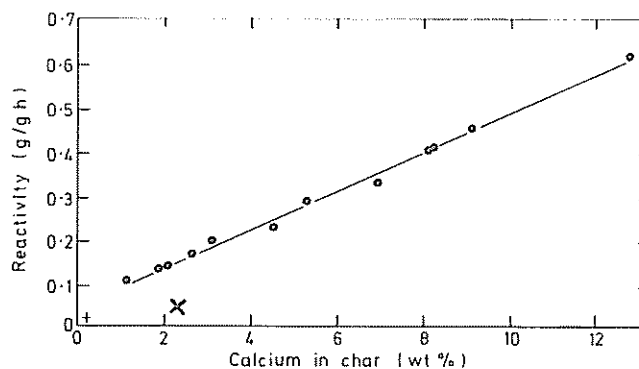


Figure 2 Reactivities in steam at 650°C of 800°C chars prepared from x raw, + demineralized, and ● various calcium-exchanged lignites

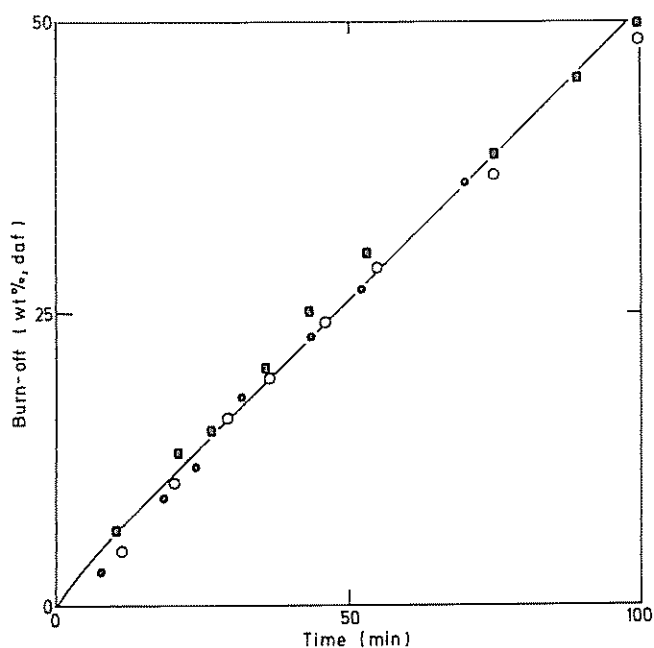


Figure 3 650°C reactivity plots for chars produced from calcium-exchanged lignites having a loading of 1.2 mmol/g. Exchange conducted to the following end-point pHs: ● 7.5, ○ 9.5, ■ 11.5

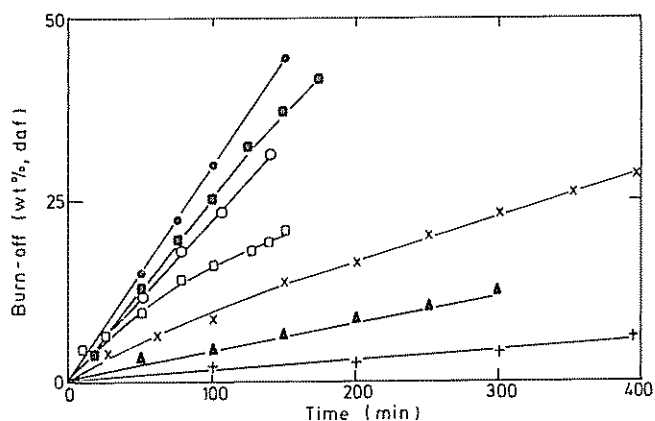


Figure 4 650°C reactivity plots for 800°C chars produced from raw, demineralized, and various metal-exchanged lignites. Metal loading on lignites was 0.3 mmol/g. x raw, + demineralized, ● K, ○ Na, ■ Ca, □ Fe, ▲ Mg

the raw and demineralized lignites are given for reference. For similar cation loadings on the demineralized lignite, potassium was the most active catalyst followed by calcium, sodium, iron, and magnesium. In fact, the presence of magnesium produced little enhancement in reactivity, the magnesium-containing char having a lower reactivity than that for the char produced from the raw lignite. The sharp decrease in reactivity of the iron-containing char as burn-off progressed was in marked contrast to the behaviour of the other exchanged samples. This was presumably due to continuous catalyst deactivation as will be discussed later.

Reactivity of samples produced from ion-exchanged 800°C demineralized, nitric acid-treated chars was studied. The amount of ion exchange on the chars was about 0.2 mmol/g for each cation. Following ion exchange at room temperature, the chars were reheated to 800°C before measuring their reactivity at 650°C. Results are presented in Figure 5. As found for the chars produced from various

ion-exchanged lignites, the iron-containing char initially had the highest reactivity; but again its reactivity decreased rapidly with burn-off. Some decrease in reactivity for the calcium-loaded char was also seen — a greater decrease than was found for the char produced from the calcium-exchanged lignite at a similar loading. Again, there was no fall-off in reactivity of the sodium-loaded char as burn-off proceeded. The reactivity of the magnesium-loaded char was only about one-quarter of that for the sodium-loaded char.

Reactivity (*R*) at 10% burn-off for equivalent calcium-loading of the char was essentially independent of whether the loading was accomplished on the lignite or the char. That is, when loading was accomplished on the lignite, the char containing 1.1% calcium had a reactivity of 0.11 g/g h at 650°C. When loading was accomplished on the char, the char containing 0.8% calcium (Figure 5) had a reactivity of 0.09 g/g h.

DISCUSSION

It turns out that raw lignites are almost ideal supports for gasification catalysts. They have high surface areas and contain large amounts of carboxyl groups on their surface. Carboxyl-group content can be further increased by exposure of raw lignites to HCl and HF at about 100°C. In this study, following such treatment, it was possible to exchange up to 2.14 mmol Ca/g of coal back onto the lignite. If exchange involves the hydrogen on two carboxyl groups for each calcium ion, the demineralized lignite is taken to have about 4.3 mmol of carboxyl groups/g of coal. Assuming that the carboxyl groups are located at the periphery of aromatic and hydroaromatic regions in the coal, an area of about 0.083 nm² (8.3 Å²) can be assigned to each carboxyl group¹⁵. Calculations then show that essentially all of the surface area in the demineralized lignite is covered by these groups.

Upon conversion of the cation-exchanged lignite to char, the carboxylate salts of the inorganic constituents will dissociate releasing CO₂ and depositing the inorganic constituent on the char surface. The extent of dispersion of the inorganic constituents has not been measured in this study; hence it has not been possible to estimate turn-over numbers. It is interesting, however, that specific catalytic activity to gasification, as measured by reactivity per unit weight of calcium in the char, was constant over a wide

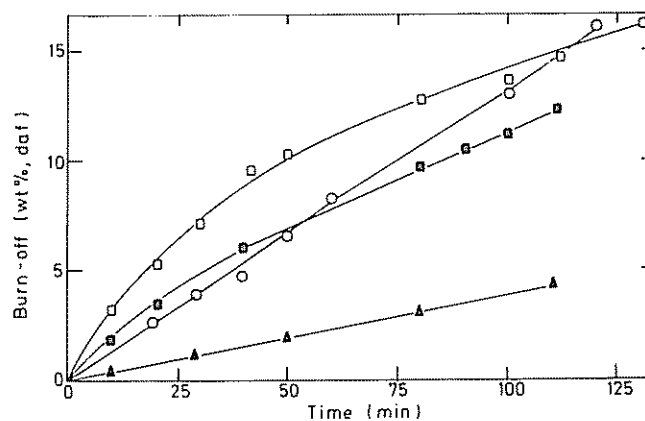


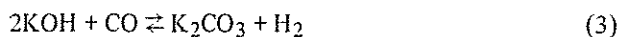
Figure 5 650°C reactivity plots for samples produced from ion-exchanged 800°C chars. Metal loading on chars was 0.2 mmol/g. ○ Na, ■ Ca, □ Fe, and ▲ Mg

range of calcium loading, i.e. from 1.1 to 12.9 wt %, as seen in *Figure 2*. If the catalyst is in the form of a solid, this is generally taken to mean that degree of dispersion is independent of loading. Similar results have been reported by Johnson¹⁶ who studied the effect of sodium and calcium loading (by cation exchange) to a lignite on char reactivity to hydrogen and Epperly and Siegel¹⁷ who studied the effect of potassium loading (by salt impregnation) to a high-volatile bituminous coal on char reactivity to steam.

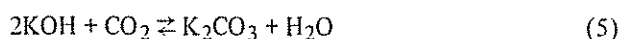
Of paramount interest in studies on catalysis of carbon gasification is what is the mechanism of catalysis and what is the active chemical form of the catalyst¹⁸. Following extensive gasification at 650°C, the samples were examined by X-ray diffraction. For iron, the presence of a high concentration of Fe₃O₄ and γ -Fe₂O₃ was confirmed; for calcium, CaCO₃; and for magnesium, MgO. For sodium and potassium, diffraction peaks were very broad and weak; no major component could be identified. Free-energy calculations, taking into account the known amount of CO₂ produced during gasification, indicate that carbonates of potassium, sodium, and calcium would be expected to be present during gasification. Similar calculations indicate that the oxides of iron and magnesium should be the equilibrium phases.

It is thought that the catalytic behaviour of iron in this study is understood. McKee has shown that iron is a very active catalyst for the carbon–steam reaction as long as it is in the reduced state¹⁹. Once oxidized to Fe₃O₄ or Fe₂O₃, its catalytic activity is markedly reduced. As seen in *Figures 4* and *5*, the catalytic activity of the iron phase was the highest of any inorganic constituent added at very low char burn-offs (reaction times); but its catalytic activity steadily decreased, with increasing reaction time, to a low level. Such a decrease is thought to coincide with the conversion of iron from the metallic to the oxidized state. Previous results show that catalytic activity can be regenerated by the conversion of the oxide(s) back to metal in the presence of a high H₂/H₂O ratio¹⁹.

An understanding of the catalytic activity in the case of potassium, sodium, and calcium is not as clear to the present authors. Other workers find that potassium is a particularly active catalyst for the carbon–steam reaction^{17,20–24}, whether it is added by ion exchange or as a salt. McKee and Chatterji suggested the following sequence of reaction steps for both potassium and sodium²³:



Veraa and Bell²⁴ studied the effect of impregnation of a coal char with both KOH and K₂CO₃ solutions on subsequent catalysis of char gasification by steam. They find strong and identical catalytic activity at comparable potassium loadings from the two solutions. By contrast, catalyst activity when potassium is added as a chloride solution is much reduced. They conclude that K₂CO₃ is the active catalyst and propose a series of reactions similar to those proposed by McKee and Chatterji²³. Reactions (1) and (2) are identical. In place of reaction (3) they propose



Both sets of authors recognize that the standard-state free energy for reaction (1) is highly positive at reaction temperatures but conclude that it should proceed at the low pressures of metal vapour present in a flow-reactor system. McKee and Chatterji^{23,25} confirmed that forward reaction (1) proceeds rapidly in flowing dry helium above the melting points of potassium and sodium carbonate phases, that is 891°C and 851°C, respectively. Below 700°C the rate of reaction is negligible. They used one-to-one mixtures, by weight, of carbonate and spectroscopic natural graphite. Other workers have shown clearly, from microscopy studies, that molten phases on the carbon surface can be very active catalysts for carbon gasification^{26,27}. These liquid phases such as V₂O₅ and MoO₃ also exhibit high mobility on the carbon surface during its gasification in oxygen.

McKee and Chatterji²³ conclude that reaction (1) is the rate-determining step in the cycle and that the overall gasification rate will depend on the salt–carbon interfacial contact area, which will be rapidly increased as the carbonate phase melts and wets the carbon surface. This should mean that gasification rates show a discontinuous increase as reaction temperature passes from below to above the carbonate melting point. Contrary to this conclusion, however, McKee and Chatterji²³ report a smooth Arrhenius plot for the graphite–steam reaction in the presence of added potassium carbonate over the temperature range 850 to 1035°C. Veraa and Bell²⁴ also report a smooth Arrhenius plot for a coal char–steam reaction in the presence of added potassium carbonate over the temperature range 700 to 900°C.

In the present study, most gasification runs were carried out well below the melting points of K₂CO₃ and Na₂CO₃, that is at 650°C. Further, CaCO₃ does not melt but decomposes at about 825°C. The possibility that the hydroxide was the active phase by way of its rapid rate of reduction by carbon was examined, since the melting points of KOH (360°C) and NaOH (319°C) are lower than those of the corresponding carbonates. One-to-one mixtures of hydroxides and spectroscopic natural graphite were heated at 10°C/min in ultrapure N₂ up to a maximum temperature of 700°C. During the heating cycle, the mixture was held isothermally at the melting point of the hydroxide until a constant weight (indicating removal of water) was obtained. In neither case was there detectable gasification of carbon; that is, weight loss was negligible above the melting point of the hydroxide and corresponded closely to that when the hydroxide was heated up in the absence of carbon.

Of significance in understanding the mechanism of catalysis of gasification could be the fact that the inorganic additives showed the same order of activity for both the carbon-gasification and water-gas-shift reactions. It is accepted that the dissociation of water into adsorbed oxygen and hydrogen atoms is an integral step in both the overall water-gas-shift reaction²⁸ and the uncatalysed carbon–steam reaction²⁹. Probably it is an important step also in the catalysed carbon–steam reaction scheme. It suggests that the inorganic phase active as the gasification catalyst does so by dissociating steam. The oxygen atom produced then spills over from the catalyst onto the lignite char surface, where its interaction with an active carbon site leads to gasification. Such a mechanism has been found to be responsible for the enhanced reaction of hydrogen with carbon to which platinum has been added³⁰. It is thought to be the mechanism by which iron catalyses carbon gasification¹⁸.

Clearly more studies need to be conducted on the mechanisms of carbon gasification by alkali and alkaline metals in the presence of steam and carbon dioxide. In particular, kinetics of oxygen transfer between the gas-phase reactants and the metal carbonates and metal hydroxides would be informative. The use of isotopes would make such studies possible. Quantitative studies should also be conducted on the rate of forward reaction (1), using different metal carbonates.

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REFERENCES

- Jenkins, R. G., Nandi, S. P. and Walker, P. L. Jr *Fuel* 1973, 52, 288
- Hippo, E. and Walker, P. L. Jr *Fuel* 1975, 54, 245
- Linares-Solano, A., Mahajan, O. P. and Walker, P. L. Jr *Fuel* 1979, 58, 327
- Walker, P. L. Jr *Industrial Heating* 1977 (Nov.), 44, 16
- Dryden, J. G. C., in *Chemistry of Coal Utilization*, Suppl. Vol. (Ed. H. H. Lowry), John Wiley, New York, 1963, p 232
- Van Krevelen, D. W. and Schuyer, J., *Coal Science*, Elsevier, Amsterdam, 1957
- Schafer, H. N. S. *Fuel* 1970, 49, 197
- Hippo, Edwin, J., *PhD Thesis*, The Pennsylvania State University, 1977
- Morse, R. D. *Ind. Eng. Chem.* 1947, 41, 1117
- O'Gorman, J. V. and Walker, P. L. Jr *Fuel* 1973, 52, 71
- Puri, B. R., in *Chemistry and Physics of Carbon*, Vol. 6 (Ed. P. L. Walker Jr), Dekker, New York, 1970, p 191
- Puri, B. R., Singh, S. and Mahajan, O. P. *J. Indian Chem. Soc.* 1965, 42, 427
- Walker, P. L. Jr and Patel, R. L. *Fuel* 1970, 49, 91
- Gan, H., Nandi, S. P. and Walker, P. L. Jr *Fuel* 1972, 51, 272
- Laine, N. R., Vastola, F. J. and Walker, P. L. Jr *J. Phys. Chem.* 1963, 67, 2030
- Johnson, J. L., *Preprints Div. Fuel Chem., 170th Meeting ACS*, 1975, 20, (No. 4), pp 85-102
- Epperly, W. R. and Siegel, H. M., *Proc. 11th Intersociety Energy Conversion Engr. Conf.*, 1976, pp 249-253
- Walker, P. L. Jr, Shelef, M. and Anderson, R. A., *Chemistry and Physics of Carbon*, Vol. 4 (Ed. P. L. Walker Jr), Dekker, New York, 1968, pp 287-383
- McKee, D. W. *Carbon* 1974, 12, 453
- Wilks, K. A., Gardner, N. C. and Angus, J. C., *Preprints Div. Fuel Chem., 170th Meeting ACS*, 1975, 20, (No. 3), pp 52-60
- Haynes, W. P., Gasior, S. J. and Forney, A. J., *Preprints Div. Fuel Chem., 165th Meeting ACS*, 1973, 18, (No. 2), pp 1-28
- Willson, W. G., Sealock, L. J., Hoodmaker, F. C., Hoffman, R. W., Cox, J. L. and Stinson, D. L., *ibid.*, pp 29-41
- McKee, D. W. and Chatterji, D. *Carbon* 1978, 16, 53
- Veraa, M. J. and Bell, A. T. *Fuel* 1978, 57, 194
- McKee, D. W. and Chatterji, D. *Carbon* 1975, 13, 381
- Walker, P. L. Jr and Thomas, J. M. *Chem. Eng. Prog. Symp. Series*, 1976, 63, (No. 73), 139
- Hennig, G. R., *Chemistry and Physics of Carbon*, Vol. 2 (Ed. P. L. Walker Jr), Dekker, New York, 1966, pp 1-49
- Mezaki, R. and Oki, S. *J. Catalysis* 1973, 30, 488
- Walker, P. L. Jr, Rusinko, F. Jr and Austin, L. G., *Advances in Catalysis*, Vol. 11 (Ed. D. D. Eley, P. W. Selwood and P. B. Weisz), Academic Press, New York, 1959, pp 133-221
- Robell, A. J., Ballou, E. V. and Boudart, M. *J. Phys. Chem.* 1964, 68, 2748