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**EFFECT OF CATION EXCHANGE ON THE SUBSEQUENT
REACTIVITY OF LIGNITE CHARS TO STEAM**

Technical Report No. 4

By
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MASTER

U. S. DEPARTMENT OF ENERGY

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ABSTRACT

Introduction

Generally, chars produced from low rank coals (i.e. lignites) are more reactive than chars produced from higher rank coals. The presence of exchangeable cations, which are associated with carboxylic acid groups found most abundantly in lignites, are believed to be responsible for the enhanced reactivity of chars produced from lignites. The purpose of this investigation is to determine the role which cations in coal play in the subsequent reactivity of chars. It is hoped that this investigation will aid in an understanding of the catalytic nature of inorganic constituents in coal during its gasification.

Experimental

Since many gasification schemes utilize the steam-char reaction, steam was employed as the reactant gas. The coal selected was a bench seam sample of a lignite from the Darco mine near Darco City, Texas. Prior to the deliberate addition of metallic cations [K(+), Na(+), Ca(++), Mg(++), and Fe(+++)], a 28 x 48 mesh size fraction of the raw coal was demineralized by treatment with HCl and HF. Chars were prepared at various heat treated temperatures (700°C, 800°C, and 900°C) from the raw, demineralized, and cation exchanged coals. A series of samples was also prepared by demineralization of char prepared from the raw coal. The demineralized, raw coal char was treated with nitric acid to add carboxyl groups, was exchanged with the cations listed above, and was reheated to temperatures in the

range of 650°C to 850°C. All chars were reacted in a fluidized bed at 650°C. The pore structure of the solid samples were characterized and ash yields of all samples were determined. Variables included in this study were level of calcium exchange, type of cation exchanged, conditions of exchange, and char heat treatment temperature.

Results and Conclusions

It was found that increased heat treatment temperature decreased reactivity. The decrease in reactivity was shown to be due, at least in part, to the changes in the nature of the cation with increased heat treatment temperature.

Reactivity was found to be a linear function of the amount of Ca(++) exchange on the demineralized coal. The constant utilization factor over the wide range of loadings employed indicated that below 800°C the calcium did not markedly sinter.

Potassium, sodium, and calcium-containing chars were found to be much more reactive than the iron and magnesium-containing chars. However, the iron and magnesium containing chars were more reactive than chars produced from the demineralized coal. The iron char was highly active at first but the iron phase was quickly oxidized to a comparatively unreactive $\gamma\text{Fe}_2\text{O}_3 - \text{Fe}_3\text{O}_4$ phase. The state of magnesium was found to be MgO. Sodium and calcium were equally active as catalysts but not as active as potassium.

The pH of exchange (7.5, 9.5, and 11.5) did not affect subsequent char reactivity or the properties of the chars produced. The acetate or nitrate anion present during magnesium exchange did not affect the subsequent reactivity of the char or other char properties.

In general, it was found that the impurities present did not affect the total pore volume of the char produced but did affect the total surface area as measured by carbon dioxide adsorption at 25°C.

1. INTRODUCTION

In 1960 the United States consumed 30 quadrillion Btus of energy, 34% of the world's consumption (1). By 1990, the United States is expected to consume 109 quadrillion Btus of energy per year, 26% of the expected world consumption (1). Since the rest of the world is starting to consume a larger share of the total energy supply and The Organization of Petroleum Exporting Countries, OPEC, has been formed, the price of energy imports to this country has risen and will continue to rise. The formation of OPEC has made energy flow dependent on political policies. Dwindling domestic reserves (2) of oil and natural gas emphasize the shortage of domestic energy supply. Increased prices, political dependence and dwindling supplies of other fossil fuels have made domestic production of energy from coal more desirable in this country (2,3,4).

Increased domestic production will not mean total energy independence. Imports are expected to level off at about 16 quadrillion Btus by 1980 (1). The percentage of total energy consumption being imported will rise to about 20% in 1977 and decrease after that time (1). However, by the year 2000 10% of the energy being consumed will be imported energy (1).

Synthetic fuels are expected to play a major role in decreasing the percentage of energy being imported. By the year 2000 the synthetic fuel industry is expected to account for 7.5% of total energy consumption. Most of the synthetic fuel will be derived from coal. The United States' coal deposits account for 17% of the world's recoverable energy supplies, and lignite deposits in the United

States account for 5% of the total world fossil fuel supply (1). Thus, it can be shown that lignites constitute one third of the recoverable United States' supply of fossil fuels. As such they will become an increasingly more important source of energy.

Hendrickson (5) has reviewed most of the gasification processes now being studied, in addition to schemes which have been used previously. He states that a wide range of conditions has been proposed for gasification schemes. Most processes consist of primary and secondary gasification steps. Primary gasification reactant gases include H_2O , CO_2 , air, O_2 , and H_2 as well as recycle gases. Various conditions exist in the primary gasification reactor. Pressures range from 14.7 to 1000 psi and gas products can consist of different mixtures of CO_2 , CO , CH_4 , H_2 , H_2O , H_2S , and N_2 .

A solid char product also results from primary gasification (5). The residue char is usually reacted with steam in a secondary gasification step. The secondary gasification is aimed at the production of carbon monoxide and hydrogen. The amount of char residue formed during primary gasification is somewhat dependent on char reactivity and process conditions. An understanding of reactivity is needed to develop economical gasification processes. It is known that chars produced from lignites are generally more reactive than chars made from other ranks of coal (5-11). It has been suggested that this reactivity may, in part, be due to highly dispersed metallic species in the char (6-9). These highly dispersed metallic species are thought to be derived from ion exchanged cations present in low rank coals. Since lignites are highly active and

there are large domestic energy reserves, lignites are likely to be a prime energy source. Thus, great interest exists in their properties.

2. LITERATURE SURVEY

2.1 Gas-Carbon Reactions

Because of the complexity of the phenomena, gasification of carbonaceous materials is not well understood. Constantly changing heterogeneous surfaces, effects of various inorganic constituents, effects of mass transfer, and inhibition due to presence of product and impurity gases, make theoretical treatment difficult. Although complex, great strides in understanding gas-carbon reactions have been made in the recent past.

2.1.1 The Carbon-Steam Reaction

The carbon-steam reaction:

results in the formation of combustible gases. Unfortunately, studies of this reaction are complicated because many secondary reactions (carbon-carbon dioxide, water gas shift, and methanation) can result. Walker, Rusinko, and Austin (12) reported that the exothermic carbon-steam reaction i) ranges from zero to first order with respect to reactant gas concentration, ii) has an activation energy of about 80 Kcal/mole, and iii) follows the rate equation:

$$R = \frac{K_1 P_{\text{H}_2\text{O}}}{1 + K_2 P_{\text{H}_2} + K_3 P_{\text{H}_2\text{O}}} \quad (2.2)$$

where K_1 , K_2 , and K_3 are reaction rate constants.

They also reported that although workers agreed on the rate of the reaction, some dispute existed over the mechanism of the reaction. Walker, Shelef, and Anderson (13) subsequently reported that the mechanism of the carbon-steam reaction was:

where i_1 , j_1 , and j_3 are rate constants for the reactions. C_f is the number of free sites; $C(O)$ is the number of free sites covered by O atoms; and $H_2O(g)$, $H_2(g)$, and $CO(g)$ are the molecules in the gas phase. The carbon-steam reaction is of significant industrial importance because it is endothermic (easily controlled), it produces highly combustible gases, and it is a source of hydrogen.

2.1.2 Water Gas Shift Reaction

The following reaction is a result of interaction between a primary reactant gas and a primary product gas.

The slightly exothermic reaction (9.65 Kcal/mole) is reported to be catalyzed by solid carbon, to attain equilibrium rapidly under steam-carbon reaction conditions, and to be uninhibited by carbon monoxide production (12). It is important industrially as a source of pure hydrogen for ammonia synthesis and reactions involving hydrogenation of organic molecules.

2.1.3 Other Carbon-Gas Reactions

Walker et al (12) also discussed the other carbon-gas reactions. They included the carbon-carbon dioxide reaction in the discussion:

They state that the carbon-carbon dioxide reaction is 40.79 Kcal/mole endothermic, equilibrium is favored by low pressure, equilibrium is less favorable than that of the carbon-carbon dioxide reaction at the same temperature, equilibrium is not favorable at temperatures under 1000°K, the reaction is inhibited by carbon monoxide and hydrogen, the reaction follows a similar mechanism to the carbon-steam reaction, the order of the reaction ranges from zero to first, the activation energy of the reaction is 86 Kcal/mole, and the rate of reaction is given by:

$$R = \frac{K_1' P_{\text{CO}_2}}{1 + K_2' P_{\text{CO}} + K_3' P_{\text{CO}_2}} \quad (2.7)$$

where K_1' , K_2' , and K_3' are rate constants.

This discussion (12) also included the methanation reaction:

Equilibrium of the slightly exothermic methanation reaction (17 Kcal/mole) is favored at high pressure. At one atmosphere of pressure, and a temperature of 900°K or above, equilibrium conversion of methane is highly unfavorable.

Walker et al (12) also discussed reactions involving oxygen with solid carbon or product gas of the gas-carbon reactions:

They state that the above reactions are strongly exothermic (-93.03 Kcal/mole, -26.62 Kcal/mole, and -67.41 Kcal/mole, respectively) and are not limited by equilibrium at temperatures below 4000°K. Thus, in any system involving carbon oxides below a temperature of 4000°K, formation of oxygen from the carbon oxide is not favorable.

When an excess of steam is used in a reaction system containing solid carbon at 900°K to 1000°K and one atmosphere of pressure, the majority of product is hydrogen and carbon monoxide with some carbon dioxide present. Since the reaction rate of the carbon-carbon dioxide reaction is slightly lower than that of the carbon-steam reaction and also since the carbon-carbon dioxide reaction is inhibited by carbon monoxide (12), only two reactions are likely to be important under the above conditions. The two reactions are carbon-steam and water gas shift reactions.

2.1.4 Mass Transfer Effects

At one time much confusion existed over the activation energies of the catalyzed reactions. Walker et al (12) suggested that mass transfer had to be taken into account when considering activation energies. When diffusion of reactant gases into porous materials is considered, three distinct reaction zones can be differentiated. One zone, Zone I, is termed the chemical control zone. In this

zone, diffusion is not important because the rate of the reaction is chemically controlled, and, thus, the true activation energy is measured. Concentration of the reactant gas is constant throughout the particle and bulk gas phase and all of the internal surface is used.

In the second zone, Zone II, reactions can be considered as being jointly controlled by chemical reactivity and diffusion of reactant gases to the internal surface. Not all of the surface is used for the reaction and the activation energy measured in Zone II is about one-half the true activation energy of the reaction.

The third zone, Zone III, is limited by diffusion of reactant gas from the bulk phase to the external solid surface. In Zone III internal surface is not used and the activation energy approaches zero. Two transitional zones may be defined where conditions are intermediate to the conditions listed for the three distinct zones.

Following along these lines, Wen (14) has developed a shrinking core model. This theoretical model is limited in application since it depends on uniform particle size and requires detailed knowledge of particle parameters and reactions conditions.

2.1.5 Catalysis of Gas-Carbon Reactions

Two theories (electronic and oxidation-reduction) of catalysis of gas-carbon reactions have been advanced (13). The electronic theory centers around the hypothesis that impurities interact with the carbon lattice to raise the Fermi level of carbon by donating electrons. Addition of electrons to the carbon lattice changes the electronegativity of the edge sites, making them more reactive. Little experimental evidence can be cited to support this theory. Walker

and Allardice (15) did report that this may be occurring in the case of gasification of boronated graphite with oxygen.

The oxidation reduction theory has been found more applicable to experimental results. In order for gasification to take place, reactant gas must first dissociate. The probability of dissociation of gaseous reactant to occur upon collision at an impurity site may be much greater than at a carbon site. The dissociated species then seeks out a carbon site and gasifies it. McKee and Chatterji (16), using simultaneously thermogravimetric analysis - differential thermal analysis (TGA-DTA) and hot stage microscopy, noted the effect of catalyzed carbon gasification in an inert and oxidizing atmospheres of helium and carbon dioxide. They cite evidence that the alkali metals go through the following cycle during gasification with oxygen.

Another cycle is postulated for gasification with CO_2

The authors state that these cycles are thermodynamically feasible.

No cycle has been proposed for the carbon-steam reaction.

Many workers have investigated relative activities of various catalysts (13). The elements present can have an effect on activity (13). However, other factors must be considered. For example, simple mixing of a catalyst is far less efficient than impregnation (8). Thus, the method of catalyst addition is important. The method of addition determines the amount of carbon-catalyst contact and the dispersion of catalysts. In general, the more dispersed a catalyst the greater its specific catalytic activity (12). Rewick, Wentreck, and Wise (17) report that the order of relative activity may be a function of temperature. During burn-off, sintering, that is the combining of many small individual particles of catalysts to a fewer number of large particles of catalysts, can occur (12). In addition to sintering, the catalysts can change physical and chemical form. For example, it has been reported that deactivation of catalysts occurs as metallic iron is converted to Fe_3O_4 at 850°C in CO_2 . McKee (18) reported the same phenomenon in a steam atmosphere. Changing chemical form may also lead to changes in physical properties. Molybdenum is a solid at gasification temperature; however, MoO_3 is a highly mobile liquid at reaction temperature. The mobility of the liquid provides more carbon catalyst contact and enables the catalysts to diffuse into porous materials (19). A change in phase may also mean loss of catalyst. For example, Watt (20) reported that some workers found that NaCl will vaporize at a rapid rate at 800°C .

The amount of catalyst is important. Walker et al (13) reported that even small amounts of catalysts can cause major differences in the rates of carbon gasification. They also report that increasing

amounts of catalysts usually results in an increased rate of reaction but that the rate of increase in gasification decreases with each additional incremental amount of catalyst added.

In addition to amounts of catalysts, the rate may be affected by an addition of a small amount of another catalyst (13). If the rate is greater than the sum of rates expected by the catalysts acting separately, a synergistic effect is said to be occurring.

Anionic impurities can catalyze reactions. Walker et al (13) gave two possible reasons, cleaning of active sites by removal of hydrogen and enhanced surface area development. They report that the acetate anion has been found to be more active than most. The halides are found to be more stable than other anions.

Impurities affect Arrhenius parameters. In general the addition of impurities lower the activation energy of a reaction (13). Walker et al (13) reported that a compensation factor, a change in the preexponential factor which accompanies the change in activation energy, has been found for the carbon-oxygen and carbon-carbon dioxide reactions. Pulsifer (21) recently reported a compensation factor for the steam reaction.

For the carbon-steam reaction, workers (22) have reported alkali impregnated salts to be effective catalysts. Another worker (23) reports that the carbon dioxide - carbon monoxide ratio of products is affected by the catalysts present. Relative catalyst activities at 800°C and 1300 torr of pressure were reported as follows:

2.2 Characterization

Coal is a complex mixture of inorganic and organic phases. The organic phases consist of different types of macerals. The different organic types consist of various aromatic and hydroaromatic compounds in addition to various peripheral functional groups (methoxyl, carboxyl, and phenolic). Mineral matter and trace elements may or may not be associated with specific groups. The poor packing of the organic structural groups and interfaces between different phases, organic and inorganic, give rise to porosity. Thus, due to its complexity many techniques can and must be used to characterize coal in order to understand the material.

2.2.1 Surface Area Measurements

Several good reviews on the characterization of surface area of porous materials exist (24-26). Initially surface area measurements were reliant on use of the Langmuir equation (24). However, for many materials this theory was unsatisfactory, because adsorption did not follow the four basic assumptions used to derive the Langmuir equation (24). Langmuir assumed that all the surface was uniform, no interactions occurred between adsorbed molecules, all adsorption occurred by the same mechanism, and adsorption was limited to a monolayer. Brunauer, Emmett, and Teller (BET) (27) proposed the use of their equation to measure surface area of porous material through physical adsorption. They assumed uniformity of the surface but considered that adsorption was not limited to a monolayer. They then assumed that the heat adsorption of the first layer was dependent on interaction between the surface and the first layer of molecules. Heat of

adsorption above the first layer is assumed equal to the heat of vaporization of the adsorbate. Thus, two adsorption mechanisms were defined; and interaction between adsorbed gas molecules was implied.

The BET equation is now well known and widely used. A derived form of the equation can be found in almost any standard text on porous solid characterization or heterogeneous catalysis (25,28). A common form of the equation may be written as follows (28):

$$\frac{1}{V(P_o - P)} = \frac{1}{V_m C} + \frac{P}{P_o} \frac{(C-1)}{V_m C} \quad (2.18)$$

where P is the equilibrium pressure, P_o is the saturation pressure, C is a constant that incorporates kinetic and energy terms for the interaction between sorbent and sorbate, and V_m is a monolayer volume. The equation holds generally for the range of relative pressure (P/P_o) of 0.05 to 0.3. A plot of (P/P_o) versus $1/V (P_o - P)$ usually yields a straight line. Monolayer volume, V_m , can be calculated from the slope (S) and intercept (I) of the plot.

$$V_m = \frac{1}{S + I} \quad (2.19)$$

The monolayer capacity, V_m , is proportional to the surface area of the coal.

Dubin (29) incorporated the Polanyi theory (25) in an equation that can be applied to the adsorption of gases to determine surface areas. The equation can be expressed as follows:

$$\text{Log } V = \text{Log } V_o - BT^2 [\text{Log } (P/P_o)^2] \quad (2.20)$$

where V is the calculated volume absorbed, V_o represents the volume of

adsorbed gas at a relative pressure of one, P_0 is the equilibrium saturation pressure, T is the absolute temperature of adsorption, and B is a constant (30). The equation holds over a wide range of reduced pressures. Marsh and Siemieniewsak (31) reported the use of the Dubinin-Polanyi, D-P, equation to measure surface area. Walker and Patel (32) reported excellent agreement between areas measured by CO_2 adsorption in different pressure ranges at 298°K. They used the BET equation for high pressure adsorption, ($P/P_0 = 0.05-0.3$) and the D-P equation to calculate areas from low pressure adsorption, ($P/P_0 = 6 \times 10^{-5} - 5 \times 10^{-2}$).

Walker and Geller (33) have applied the BET equation to adsorption of nitrogen on coal at 77°K. They felt that the nitrogen area gives an estimate of the transitional and macropore area of a coal. Anderson and co-workers (34) concluded that coal ranges in porosity from 5 to 18%, that most pore openings are of the order of 4.6 to 5.6 Å, and that nitrogen will not penetrate pores with openings of less than 4 to 5 Å. Walker and co-workers (6,32,35-38) have used the BET equation to measure surface areas. Walker et al (32,37) used CO_2 adsorption on coal chars at high pressures and the BET equation to measure area of coals. They felt that the areas represented the closest approach at measuring the total surface area of the coals.

Thus, coals and chars can be considered as solid porous carbons containing a distribution of pores. Being of different sizes and temperatures, carbon dioxide (298°K) and nitrogen (77°K) diffuse at varying rates. Pores can be divided into macropores, transitional pores, and micropores. From carbon dioxide adsorption at 298°K and at equilibrium pressures below 760 Torr one can estimate the total surface area in the micropores of coal using the D-P equation. On the

other hand, using nitrogen adsorption at 77°K, gives an estimate of transitional and macropore surface area.

2.2.2 Density and Porosity Measurements

Porosity, open pore volume, and pore size distribution may affect behavior of coal and chars in conversion processes. Thus, it is important to measure these properties. It has been shown that by measuring a true density and an envelope density, porosity and pore volume can be obtained. Pore volume can be calculated by:

$$P.V. = \frac{1}{\rho_E} - \frac{1}{\rho_R} \quad (2.21)$$

where P.V. = pore volume

ρ_E = envelope density

ρ_R = real density.

The percentage of porosity can be calculated by:

$$\%P = P.V. \times \rho_E \quad (2.22)$$

where %P = percentage porosity.

Franklin (39) suggested that helium displacement could be used to measure real density, since it is not appreciably adsorbed on the carbon surface and penetrates into almost all pores. It is believed that helium will penetrate all pores with openings greater than 4.2 Å (40). However, some pores in coal are closed to helium (41).

Helium's dispersion potential is very small, yet workers (42,43) have reported some adsorption of helium on carbon. This adsorption was more pronounced at low temperature (42). However, Kini and Stacy (43) have reported that adsorption of helium on vitrinite at room temperature is negligible.

Spencer (25) and Winslow (44) discuss the use of mercury to determine envelope densities. Scholten (45) and Winslow (44) also reported that pore size distributions could be measured by mercury penetration under pressure by use of the Washburn equation (46). However, the application of the equation is to some extent limited by the strength of the materials. At high pressures pores may collapse leading to meaningless data. Gan (36) limited penetration to 10,000 psig of pressure, corresponding to 150 Å pore openings. He termed these macropores. Nitrogen adsorption at 77°K to a relative pressure of 0.93 was used to determine pore distributions for pores with 12 to 300 Å openings using the Cranston-Inkley method (47). These pores were termed transitional pores. He also assigned pores with openings smaller than 12 Å as micropores. Rootare and Prenzlow (48) reported that surface area could be estimated by mercury penetration. However, they assumed cylindrical pores and no ink bottle pores. These assumptions do not hold for coals. Many workers (49-51) have reported problems with determining inter- and intra-particle voids. Recently Kamishita (51) has studied the problem using anthracite samples. He found that at 200 psig all the inter-particle voids were filled for a sample size above 200 mesh. That pressure was then applied as a standard for measurements on lignite coals and chars.

Various methods used to characterize porous solids can be used to characterize coal and coal char. Walker and Stacy (35) have used these methods to characterize coal chars. They report that the char's properties are dependent on the coal and the temperature reached during heat treatment. Gan (36) used nitrogen and carbon dioxide adsorption, helium and mercury densities, mercury porosimetry, and the

Cranston-Inkley method (47) to describe the pore structure of coals.

2.2.3 Particle Size

Coal ranges in hardness due to the variety of its constituent materials. Thus, coals will physically break in varying sizes and distributions of particles. The size of particles can be of importance in determining physical and chemical properties during coal conversion. Thus, when considering coal behavior in such processes, particle size and size distribution are important.

A set of particles can be described by a size distribution.

Three distribution functions commonly used for this purpose are the Gaudin-Schuhmann, Rosin-Rammler, and log-normal (52). These three distributions have been discussed in detail by Allan (53) and Orr (54).

It has been suggested that the Rosin-Rammler equation gives a better fit for systems involving coal (52). The Rosin-Rammler distribution was developed in Germany for use in the coal industry (55). The Rosin-Rammler size distribution can be described by the following equation:

$$Y_v(X) = 1 - \exp \left[- \left(\frac{X}{K_r} \right)^m \right] \quad (2.23)$$

$Y_v(X)$ = fraction of the total volume or mass finer than size X

X = diameter of the particle (opening of the screen in this case)

K_r = size of X when $Y_v(X)$ equals 63.21%

m = slope of the $\log \log \left(\frac{1}{1 - Y_v} \right)$ versus $\log X$ plot.

At $X = K_r$, $Y_v(X)$ becomes 63.21. $Y_v(X)$ may either represent volume or mass distribution functions. They are identical if the density of the particles is not a function of particle size. If the density is a function of the particle size, the distribution must be differentiated to obtain the density function. Then each incremental size X must be

transformed. For example:

$$Y_v(X) = \int_0^{\infty} y_v(X) dx \quad (2.24)$$

where $Y_v(X)$ = volume distribution function

$y_v(X)$ = volume density function

and

$$Y_m(X) = \int_0^{\infty} y_v(X) dx \rho(X) \quad (2.25)$$

where $Y_m(X)$ = mass distribution function

$\rho(X)$ = particle density as a function of X .

Equation 6 can be rearranged to the following form:

$$1 - Y_v(X) = \exp \left[- \left(\frac{X}{K_r} \right)^m \right] \quad (2.26)$$

By taking the log of the inverse of each side, the equation becomes:

$$\log \frac{1}{1 - Y_v(X)} = (X/K_r)^m \quad (2.27)$$

Thus a log log - log plot of the above equation should yield a straight line with slope m . A high value for m , greater than 3 would indicate a very narrow size distribution. A value of $m \approx 1$ is required for the density function to pass through a maximum and, thus, the distribution to be valid.

2.2.4 Mineral Matter and Ash Determinations

An excellent review of mineral matter analysis and ash composition analysis has been written by Watt (20). Various methods have been used to characterize mineral matter. They include optical microscopy, x-ray diffraction, scanning electron microscopy, and infrared

spectroscopy among others. Also, O'Gorman (56) has described various methods used to characterize the mineral matter and ash of American coals. In addition to x-ray diffraction and infrared spectroscopy listed by Watt (20), O'Gorman used thermal analysis. Both reviews agree that atomic absorption is the best way to measure major constituents of ashes. Procedures used for atomic absorption analysis were discussed by Medlin et al (57).

2.3 Properties of Coals

2.3.1 Physical Properties of Coals

In the previous section, methods used to determine the pore structure, ash, and size distribution of coals and chars were discussed. Walker, Nandi, and Gan (58) reported the physical properties of American coals of various ranks. They reported that nitrogen areas of most coals ranged between 1 and 2 m²/g. However, some bituminous coals (in the range of 74 to 83% fixed carbon content) had nitrogen areas as high as 100 m²/g. Carbon dioxide areas ranged from 30 to 400 m²/g. The carbon dioxide areas go through a shallow minimum in the same range that the nitrogen go through a maximum. Carbon dioxide areas of lignites ranged from 200 to 300 m²/g. Helium densities were reported to decrease with increasing rank to a fixed carbon content of 81%. Helium densities increase sharply with increasing rank for coals containing greater than 87% fixed carbon content. Helium densities reported by Walker et al (58) ranged from 1.35 to 1.45 g/cc on a mineral matter free basis for lignites. Mercury densities were found to vary widely with rank. Mercury densities for the lignites range from 1.24 to 1.41 g/cc on a mineral matter

containing basis. Pore volumes and pore size distributions were also reported. Although lignites and anthracite were found to have similar pore volume, the pore volume in lignites were reported to be evenly distributed in micro- and macro-pores, but most of the pore volume in anthracites was contained in micropores. Caking coals were found to have higher porosities than lignites or anthracites. This porosity is destroyed by heat treatment, whereas the porosity in lignites is not destroyed by heat treatment.

Hirsch (59) using x-ray diffraction suggested that coals could be treated as three distinct phases: 1) an open pore structure as found in low rank coals, 2) a nonporous liquid structure of caking coals, and 3) a highly crystalline, highly porous anthracite like material. The pore structure in coals is believed to be caused by the poor packing of structural groups which exist in the coal (38).

Spackman (60) has suggested that coal can be characterized on several levels. These levels include the elemental level (ultimate analysis), molecular or submolecular level (functional groups), and the maceral-mineral level.

Both organic and inorganic elements are found in coal. The major organic elements according to ASTM analysis (61) are C, H, N, S, and O. Inorganic elements will be discussed later.

Given (62) has briefly reviewed the functional groups found in coal. He states that coals are predominantly aromatic (60-90%). Other workers (63-65) have shown the existence of aliphatic H by I.R. and NMR methods. Methoxyl ($-\text{OCH}_3$) and phenolic groups exist in lignites in addition to carboxyl groups (62). Schafer (66) has measured carboxylic groups by ion-exchange methods. In addition, carbonyl groups

and hetrocyclic O, N, and S rings are likely to exist in coals (66). According to Ouchi et al (67-69) aromatic groups in coals are connected by $(-\text{CH}_2-)$, $(-\text{CH}_2-\text{CH}_2-)$, and $(-\text{CH}_2-\text{CO}-)$ groups. Most peripheral groups $(-\text{OCH}_3, -\text{OH}, \text{ and } -\text{COOH})$ decrease markedly with increasing rank (62). Thus, lignites contain more functional groups than other coals.

Spackman (60,70) has reviewed the macerals which occur in coals. The humic fraction, vitrinite, is the highly reflecting material derived from the woody tissues of plants. Its properties varies with rank. According to Hendrickson (5), the vitrinite variety found in lignites can be termed xylinoïd. It is important to keep in mind that these different types of organic materials can behave differently in coal conversion processes (60).

2.3.2 Mineral Matter in Coals

There are some excellent reviews (20,56,71,72) of mineral matter in coals. O'Gorman (56) classified minerals in specific groups. The groups included shales, kaolins, sulfides, carbonates, chlorides, and accessory groups. Gluskoter (72) and Spackman (60) used similar classifications. There is general agreement (20,56,71,72) that the major and minor inorganic elements found in coal are Si, Al, Ti, Ca, Mg, Fe, P, S, Na, and K. Trace elements found in coal include (56) Ag, B, Ba, Be, Co, Cr, Cu, Ga, Ge, La, Mn, Ni, Pb, Sc, Sn, Sr, V, Y, Yb, Zn, and Zr. Gluskoter (72) studied the composition of ashes of coals derived from specially prepared sink-float functions. He concluded that some trace elements (Ge, B, and Be) had an affinity for the organic phase. Other elements were reported to have a greater

affinity for the inorganic phase. Those elements include Hg, Zr, Zn, As, Cd, Pb, Mn, and Mo. The remainder of the elements occurred in both the sink and float fractions. P, Ga, Sb, Ti and V appeared to be associated more with the organic phase and Co, Cr, Cu, Ni and Se appeared to be associated more with the inorganic phase. Some of the inorganic elements occur as cation exchangeable organic salts (20). Both major and trace elements may affect behavior of coal in conversion processes.

2.3.3 Properties of Lignites

Lignites are highly porous. The porosity is evenly distributed in macro, transitional, and micropores, and it is not destroyed by heat treatment. Most of the surface area in lignites exists in the micropores and transitional pores (58). While containing many pores, the low helium density of lignites suggests great structural disorder and that some porosity is closed. The lignites also contain functional groups not found in abundance in other ranks of coal. These functional groups include carboxylic acids which can be found in the form of organic salts. In addition to salts, mineral matter commonly found in American lignites include quartz (SiO_2), kaolinite, illite, calcite (CaCO_3), gypsum (CaSO_4), ankerite, siderite (FeCO_3), and pyrite (FeS_2). Lignites from the Darco seam in Texas also contain some rutile (TiO_2) and montmorillonite (56). O'Gorman also reported the content of trace elements in lignites. He found B, Ba, Sr, to be in higher concentrations in lignites than in other coals.

2.4 Heat Treatment

2.4.1 Theory of Pyrolysis

Coals may be considered as either thermoplastic which soften upon heat treatment, or thermosetting which do not soften on heat treatment (38). Lignites behave as thermosetting materials on heat treatment. When coals are heated they first lose water (71). Then they begin to undergo structural change (38,71,72). In the range of 350–550°C, phenolic, methoxyl and aliphatic groups decompose and some lower molecular weight aromatics are liberated. Between 500 and 600°C the coal layers begin to rearrange (71) and between 600 and 700°C crosslinks begin to become unstable and hydrogen is liberated (71–73). Above 700°C (72) packing of layers continues to be enhanced by gradual rearrangement. As growth develops porosity increases, but accessibility to the porosity decreases (73).

2.4.2 Changes in Properties With Heat Treatment

Heat treatment first opens porosity as volatile matter is released, but the gradual rearrangement begins to close the porosity. The net result, as reported by many workers (75–80), is that the surface area goes through a maximum and decreases rapidly. The exact temperature at which the area will become a maximum depends on the nature of coal rank (77), heating rate (80), and soak time. To some extent the maximum is determined by the method of measurement. Gauger (81) as early as 1928 reported that mineral matter affected development of physical properties of cokes and chars. Helium densities increased with heat treatment temperature while volatile matter was being released (75–77). As a result of volatile matter being released,

pores are opened; and helium penetrates into previously closed pores (38). When the coal char begins to realign it begins to shrink and density goes through a maximum (38, 75-78). Densities measured by methanol, n-hexane, and water (78,79) also show similar behavior. Maxima were attained at different temperatures depending on pore size distribution of the char and the ability of various molecules to penetrate certain size pore openings (75,76). Density measured in water corresponds closely with helium density (usually < 0.01 g/cc difference) for chars heated to less than 900°C . Chars heated to 900°C or above contain porosity closed to water penetration (77). These properties are important to reactivity of chars for the gasification reactions which are partially diffusion controlled. They determine diffusion parameters and the availability of active sites.

2.4.3 Changes in Mineral Matter

O'Gorman (56, 82) has studied the effect of heat treatment on behavior of individual minerals, synthetic mixtures of minerals, whole coals, and mineral fractions removed from coal by low temperature ashing. His studies were conducted by DTA and DTG using various atmospheres. He concluded that minerals in coal go through many changes and that these changes are dependent on atmosphere used and the type of mineral matter present. Although O'Gorman investigated effects of a 10% hydrogen - 90% nitrogen atmosphere on minerals, no work was done on the effect of steam-hydrogen mixtures.

Mitchell and Gluskoter (83) investigated the effect of heat treatment on minerals in an air atmosphere. Their work centered on x-ray diffraction methods. They concluded that a lignite ash behaved

as follows. From 400 to 500°C, its kaolinite phase disappeared and a meta-kaolinite phase appeared. Other clay and silicate minerals underwent dehydration to form anhydrites. Between 500 and 600°C pyrite, FeS_2 , decomposes to form hematite, the CaCO_3 disappears, and only traces of meta-kaolinite were left. In the 600 to 700°C range little change occurred, but by 800°C an anorthite phase appeared and meta-kaolinite disappeared completely. By 900°C no hematite was found and most other phases had disappeared. By 1000°C even the quartz begins to show signs of instability and by 1200°C the ash had completely fused.

Watt (20) reviews thermal decomposition and volatilization of inorganic matter in coal. This is a fairly comprehensive review of thermal decomposition of minerals in an oxygenating atmosphere, but little work has been reported in hydrogen-water systems. Watt also discusses volatilization of sulfur and alkali salts. He states, that below 650°C in the presence of an inert or oxidizing atmosphere, that calcium and sulfur will combine to form CaSO_3 . Above 650°C, it decomposes to CaSO_4 and CaS ; both of these phases are stable to 850°C. Sodium salts tend to vaporize below 800°C, when studied separately; but, in the presence of coal the salts do not vaporize even at 850°C. Potassium salts were found to be less stable than sodium salts when heated separately but more stable when mixed with coal.

2.5 Reactivity and Activation of Coal Chars

2.5.1 Reactivity of Chars in General

A great deal of work has been done on reactivity measurements of coal char and on production of activated carbons from coal char.

Reactivity of any porous carbon including coal chars is dependent on three factors; concentration of active sites; accessibility of reactant gas into internal area of the char and hence to the active sites; and catalytic material present (12,84). The ability to measure active site concentrations and correlate them with surface area eluded investigators until Walker and co-workers (84) were able to show that for the $C-O_2$ reaction the appropriate term was given by dissociative oxygen chemisorption. Walker et al (84), Henning (85), and Thomas and Roscoe (86) showed that active sites of a trigonally bonded carbon, graphite, or polyaromatic structure were located at the periphery of the layer planes and at vacancies and non-basal dislocations within layer planes. Thus, one would prefer to keep crystallite size to a minimum and defect concentration in the layer planes at a maximum to maximize reactivity.

The concept of diffusion control and, hence, the availability of reactant gases to active sites has been discussed in a previous section (2.1). Since low rank coals are thermosetting (Sec. 2.4) and have a very high percentage of their pore volume in macropores, chars derived from the lower rank coals would be expected to have less transport limitation than chars derived from low volatile bituminous coals. Nandi, Jenkins, and Walker (6) although not performing an exhaustive study, have reported data that confirms this explanation. Pregermain, Chiche, and Durif (77) also reported that lignite chars tend to give higher total surface area and pore volume in addition to a larger macropore area as measured by nitrogen adsorption. Patrick and Shaw (9) reported that sodium carbonate alters the coking mechanism of bituminous coals, makes crosslinks more stable and provides a better pore structure.

The third factor affecting reactivity is inorganic material present. Walker and co-workers (13) have reported that almost any metal in a reduced state or oxidized state increases gasification of carbonaceous solids. As mentioned in Section 2.1, catalyst activity is dependent on the type of impurity, its concentration, its dispersion, and its chemical state. Much activity concerned with reactivity is centered around these points.

Reactivity measurements have centered around three techniques; first, the measurement of ignition temperatures (11); second, the measurement of weight loss with thermal balances (6,7,87,88); and, third, the measurement of off-gas concentration and flow rates to determine weight loss (89,90). Nandi, Jenkins and Walker (6) cite many parameters that have been used in describing reactivity. They suggest a convenient and reproducible parameter:

$$R = \frac{1}{W_o} \frac{dW}{dt} \quad (2.28)$$

R = reactivity (g/(g hr))

W_o = original weight of sample on a dry ash free basis (g)

dW/dt = rate of reaction (g/hr).

This parameter has subsequently been used by other authors (7,87,88). They (6) measured reaction in air at 500°C of chars prepared from 21 American coals. An increase in reactivity with decreasing heat treatment temperature was reported. It was not determined if the effect was caused by differences in the chemical nature of the char, differences in pore structure, differences in the chemical and physical nature of the impurities, or differences in a combination of these

variables. Low rank coals were found to produce the most reactive chars. Reactivities of chars prepared from acid washed and demineralized coals indicated that the type and amount of impurities present profoundly affect the reactivity of chars and reduce the spread in reactivities of the low rank coals. A strong correlation between reactivity and the content of CaO and MgO in the ash was also reported.

Other workers (8,9,11,91) have reported high reactivity of low rank coal chars. Daly and co-workers (11) reported that the sub-bituminous coals of New Zealand produced very reactive chars even though the ash content of the coals was low (1-3%). Allardice et al (91) suggest that brown coals may be auto-catalytic at room temperature if dried in an inert atmosphere prior to exposure. Siemieniowska and co-workers (10) reported that reactivities of lignite chars were dependent on the impurities present. They suggest that the active species are associated with coal as highly dispersed cations attached to carboxyl groups in the coals. Johnson and co-workers (8) have confirmed that the ion-exchanged cations account for high reactivity of lignites. They also report an empirical correlation of reactivity with carbon content.

Walker and Hippo (7) measured reactivity in carbon dioxide at 900°C of the same chars used by Jenkins et al (6) and confirmed their basic conclusions. In addition, reactivity was reported to increase with decrease in particle size of the char. Demineralization of a high rank coal apparently increased the reactivity of the resulting char. The increase was attributed to opening of pores that were blocked by the presence of mineral matter.

Soledade (87) measured reactivities of American coal chars in air at 405°C. He concluded that reactivity is proportional to oxygen partial pressure. He confirmed basic principles stated by Walker and co-workers (6,7). Soledade reported that the shape of the burn-off curves is similar of all chars and if the time scale of the burn-off curve is normalized by dividing by τ , the time for 50% burn-off to occur, reaction curves could be reasonably represented by one very narrow band of points. This has subsequently led Walker and co-workers (92) to adopt the following empirical equation to describe the curves:

$$R = aT + bT^2 + cT^3 \quad (2.29)$$

where a , b , and c , are constants, R is reactivity, and T is absolute temperature. Values of a and b are positive and values of c are negative.

Kamishita (51) has reported that carbon deposited on the surface of a lignite char decreases open pore volume, active surface area, accessibility of reactant gases to char, and subsequently reactivity of the char. The carbon was assumed to be deposited following chemisorption and cracking of methane on the surface. It was also suggested that the impurity sites might be covered by deposited carbon, thus lessening their effectiveness. The carbon deposited was reported to affect the burn-off rate throughout the burn-off range. Kamishita concluded that carbon deposited during heat treatment should be kept at a minimum, if one wishes to maximize reactivity.

Mukherjee and Chowdhury (93) reported that hydrogasification of coal char was increased by increase in mineral matter. However,

It was (94) found that some minerals are inhibitors while others are accelerators of the carbon-hydrogen reaction. He found siderite (FeCO_3) and pyrite (FeS_2) to be catalysts; ankerite and dolomite to be slight inhibitors; and illite, quartz, gypsum, rutile, kaolinite, and especially calcite to inhibit hydrogasification significantly. It was also found that char reactivity was essentially independent of parent coal rank in the constant rate region. However, during initial burn-off the reaction rate was dependent on parent coal rank. He also showed that particle size had little effect on reactivity. One would assume from this that the reaction rate was primarily chemically controlled.

2.5.2 Reactivities of Chars to Steam

Nandi and co-workers (95) studied the carbon-oxygen and carbon-steam reactions. They found that the relative rates of the carbon-oxygen and carbon-steam reactions calculated by Walker et al (12) were much less for chars than expected from results obtained from pure carbon reactions. Activation energies of the reacted chars and coke in steam ranged from 23 to 82 kcal/mole and were found to be highly dependent on coal rank and ash content.

Pulsifer et al (22) have studied the kinetics of the coal char-steam reaction in a small fixed bed reactor. Various catalysts and in varying amounts were added by mixing and impregnation. Alkali salts and, in particular, impregnated potassium carbonate were found to be the most effective catalysts. Calcium oxide (CaO) and iron oxide (Fe_3O_4) were found to be ineffective, carbonate forms of the alkali metals were more effective than the chloride forms. The addition of catalysts

lowered the activation energy and frequency factor for the reaction. In another paper these authors (21) also reported a compensation effect for the carbon-steam reaction. Under conditions reported, the water gas shift reaction approaches equilibrium when catalyzed but does not when uncatalyzed.

Wilks et al (96) have studied the effect of dual catalyst systems on gasification rates of the char-steam reaction. They found that potassium salts are more active catalysts used alone than when used in combination with cracking or methanation catalysts [$K_2CO_3-Al_2O_3$] (SiO_2)₃ and ($K_2CO_3-CoO_3-MoO_3$)}. Rates were increased by annealing, indicating that diffusion of catalysts may be limiting rates.

2.5.3 Pore Development During Gasification

Although this thesis is concerned with reactivity of chars, activated carbon production from residue chars should not be overlooked as a possible by-product of coal gasification. Kawahata (89), Rovesti (90), Bessant (97), and Almagro (98) have all studied gas-carbon reactions while producing active carbon from variously treated anthracites. They all report that active carbon can be produced from coals in the laboratory which compare favorably with commercial carbons. They report increased surface areas with increased burn-off. Optimum burn-off conditions are dependent on activating gas and type of char used. Total pore volume and helium density were increased with burn-off. Activation in steam of chlorinated anthracite resulted in rapid removal of chlorine from the char surface (98). Prechlorination increased the rate of the steam reaction. Bessant (97) suggested that steam activation produced a far superior active carbon. Torikai (99) studied activation of bituminous lithotypes in carbon dioxide. He

found the rate to be zero order with respect to the amount of carbon present between 900 and 1000°C. As reported by others (90,97,98) he reported a linear increase of nitrogen surface area with burn-off. However, the carbon dioxide surface area was maximized at 10 to 15% burn-off and decreased slowly after that point. Mercury densities decreased and helium densities increased with increasing burn-off.

3. STATEMENT OF PROBLEM

Establishing an understanding of the catalytic nature of the inorganic constituents of coals is of fundamental importance in the development of gasification processes. It is well known that the most reactive coal chars are those produced from low rank coals, i.e. sub-bituminous and lignite coals. It has been suggested that the presence of exchangeable cations, which are associated with carboxylic acid groups in the coals, are to some extent responsible for this enhanced reactivity (Section 2.5). This investigation is aimed at determining the role of cations in catalyzing the gasification reactions and in the development of physical properties of the chars.

The following objectives were set to help determine the role which cations play during reaction of lignite chars:

- a) to explore the effect of heat treatment temperature on pore development during heat treatment
- b) to explore the effect of burn-off, heat treatment temperature, and reaction temperature on reactivity
- c) to explore the effect of metallic cation addition on the variables mentioned in objectives a and b.

To accomplish these objectives, steam was selected as the reactant gas since many gasification schemes utilize the steam-carbon reaction. The coal used was a Darco, Texas lignite. Prior to cation exchange, the coal was demineralized by treatment with HCl and HF. Thus, the carboxyl groups were in the acid form. Cations exchanged onto the coal included K(+), Na(+), Ca(++), Mg(++), and Fe(+++). Chars

were prepared at various heat treatment temperatures (650°C to 900°C) in an inert atmosphere. For comparison chars were prepared from the raw and demineralized coal. Another series of samples were prepared by demineralization of chars prepared from raw coals. The demineralized chars were oxidized with nitric acid to add carboxylic acid groups in the structure. These were exchanged with the cations listed above and reheated to the same maximum heat treatment temperatures (650°C to 850°C). All chars were reacted in a fluidized bed at 650°C. Variables studied were char heat treatment temperature, cation type, cation loading, and conditions of exchange. All samples were characterized by measurement of carbon dioxide surface area to follow micropore area, mercury and helium density to follow porosity, and sieve analysis to determine a characteristic size by a Rosin-Rammler distribution function. Ash yields were determined for all samples.

4. EXPERIMENTAL MATERIALS, APPARATUS, AND PROCEDURES

4.1 Selection of Sample

The following list of abbreviations will be used throughout this thesis:

daf = dry ash free

mmfb = mineral matter free basis

mmcb = mineral matter containing basis

V.M. = volatile matter

Dem. = demineralized

A.W. = acid washed

I.E. = ion exchange

N.A. = nitric acid treated

n.d. = not determined

Several criteria were used in selecting a coal. First, a large amount of sample was needed (greater than 30 Kg). Second, since vitrinite is the maceral whose properties vary most systematically with rank (5) and most American coals contain a large amount of vitrinite (62), a high vitrinite content was desired. In addition, unusual ash yields and composition were undesirable. Finally, the reactivity of the char produced from the coal needed to be typical for a lignite.

A bench sample of a Darco, Texas lignite, PSOC 140, from the Darco mine near Darco City, Texas satisfied the above demands. About 30 kilograms of lignite were obtained in two five gallon metallic drums. Table 1 contains some of the information received from The Pennsylvania State University Office of Coal Research for PSOC 140. The major maceral constituent of PSOC 140 is vitrinite.

TABLE 1
ANALYSES DETERMINED FOR PSOC 140, A GULF
PROVINCE LIGNITE FROM DARCO, TEXAS

PROXIMATE ANALYSIS:	Dry Basis	ULTIMATE ANALYSIS:		
% Ash	9.37	% C		71.73
% V.M.	44.81	% H		5.20
% Fixed C	45.82	% N		1.26
Calorific Value	11,324	% S		0.72
(BTU/lb)		% O ^a		21.10 ^b
		% Cl		0.02
SULFUR DATA:	Pyritic	Sulfatic	Organic	Total
(daf)	0.32%	0.02%	0.72%	1.06%
MACERAL ANALYSIS:	Vitrinite	Pseudo-Vitrinite	Semi-Fusinite	
(% by volume, mmfb)	69.8	0.0	3.1	
	Extinite	Granular Micrinite	Massive Micronite	
	3.8	8.7	4.5	
	Resinite		Fusinite	
	1.3		8.8	
COOH Acidity: 2.36 meqv/g of coal (dmmf)				

- a) Oxygen is determined by difference
b) The percentage of oxygen as COOH is 33.26.

PSOC 140 yields about 9.4% ash, which is a typical value for ash content as reported by O'Gorman for American coals (56). According to the sulfur data, PSOC 140 contains about 1% total sulfur. Table 1 also lists the proximate and ultimate analyses of PSOC 140.

Table 2 lists the major constituents and trace elements of the ash of PSOC 140 as determined by O'Gorman (56). He reported a high calcium concentration. The high concentration of Ba and Sr trace elements found are probably due to association of these elements with calcium. Boron, is most abundant in the ash of PSOC 140. On the other hand, the amount of Sr found in the ash is much less than the amounts found in other lignites.

Reactivities of 1000°C chars produced from a 40 x 10 mesh size fraction of PSOC 140 were previously measured in air at 500°C (6) and in carbon dioxide at 900°C (7). Results indicated that chars made from raw PSOC 140 have a reactivity of 1.4 (g/g hr) in air at 500°C. Reactivities in air at 500°C of other lignite chars ranged from 1.3 to 4.0 (g/g hr). Similar results were reported for the reaction of carbon dioxide at with the 1000°C chars at 900°C.

After the coal was obtained it was spread on a table and dried in air for 2 days. Chunks of coal ranged in size from fines to 6 inch diameter lumps. Large pieces were broken to -1/8 inch (4 mesh) diameter. After air drying, the lignite was crushed in a Staub Company (model 4-E) mill. After grinding, the coal was placed on a nest of screens and sieved for 30 minutes on a Ro-tap sieve. Coal which did not pass the Tyler 28 mesh screen was reground and sieved again. Three size fractions, 28 x 48 mesh, 48 x 60 mesh, and 60 x 100 mesh Tyler were collected.

TABLE 2

CHEMICAL ANALYSIS OF ASH DERIVED FROM A 40 x 100 MESH
 SIZE FRACTION OF PSOC 140, A DARCO, TEXAS LIGNITE (56)

Major Constituents of Ash		Trace Elements of Coal			
Oxide	% by Weight	Element	ppm by Weight	Element	ppm by Weight
SiO ₂	38.4	Ag	1	Ni	215
Al ₂ O ₃	21.0	B	1900	Pb	70
Fe ₂ O ₃	11.8	Ba	3000	Sc	58
TiO ₂	1.12	Be	7	Sn	78
CaO	9.95	Co	15	Sr	1800
MgO	1.70	Cr	140	V	360
Na ₂ O	0.65	Cu	350	Y	105
K ₂ O	0.53	Ga	22	Yb	7
SO ₃	14.5	Ge	20	Zn	50
		La	20	Zr	470
		Mn	1000		

After sieving, the samples were stored in one gallon plastic containers which had previously been flushed with nitrogen. The caps were sealed with plastic tape to retard diffusion of oxygen to the coal. Chars and partially reacted chars were stored in nitrogen flushed sample bottles of various sizes.

4.2 Gases

Research grade nitrogen, carbon dioxide, argon, and helium, manufactured by The Matheson Company, were obtained from Philip Wolf Company. Argon and nitrogen were used as carrier gases for chromatography. Ultrapure helium used for helium density measurements was obtained from The Matheson Company in one liter flasks.

4.3 Procedures and Apparatus

4.3.1 Demineralization

A large portion of the 28 x 48 mesh size fraction was demineralized. First, the coal was acid washed in a Pyrex column by passing boiling 10% by weight HCl over the coal continuously for about 2 hours. Samples of spent acid leaving the column were neutralized with ammonium hydroxide solution and tested for calcium by adding ammonium oxalate. At the end of the 2 hour period no calcium ions were detectable. The acid washed lignite was then placed in a plastic beaker. A 50-50 mixture of 50% HF solution and a 10% HCl solution was added to the contents of the beaker. The beaker was then partially immersed in boiling water. Any evaporative losses were replaced with concentrated HF solution. After 48 hours the solution was decanted and the lignite washed with distilled water. After washing by a batch method, the

coal was transferred back to a washing column and washed with boiling water continuously for 2 hours. At the end of 2 hours, no chlorine ions were detected (by silver nitrate solution) in the exit stream.

4.3.2 Ion Exchange

Metallic cations were added to demineralized coals by ion exchange. Theoretical treatments of ion exchange have been discussed by Kelly (100) and Breck (101). Although there have been extensive studies of ion exchange on many materials, studies on coals have been rather limited.

Following Schafer's method (66) ion exchange was accomplished by mixing about seventy grams of 28 x 48 mesh demineralized coal with 500 ml of distilled water and a desired amount of a salt at room temperature. For exchange of 5% by weight calcium or less, the coal was allowed to exchange for 24 hours. The coals were thoroughly washed in a Pyrex washing column with one liter of distilled water. The amount of exchange was controlled by varying the concentration of solution. A 0.10 molar solution of salt led to 0.3 mmole of cation exchanged/g of coal (daf). A 0.6 molar solution of calcium ions led to an exchange of 0.95 mmole of calcium/g of coal (daf). About 50 ml of standardized 3.56 molar sodium hydroxide was added to one and two molar solutions of calcium acetate to increase pH [increased pH increases amount of exchange (102)]. Coals in the 1 and 2 molar solutions were also heated to 60°C [a rise in temperature increases both rate and amount of exchange (66,102)]. The above treatment led to 1.20 and 2.14 mmoles of Ca(++) exchanged/g of coal (daf) from the 1 and 2 molar solution respectively.

Refluxing, as suggested by Shafer (66), was found unnecessary since exchange occurred rapidly under conditions listed.

Altekar, Shshani, and Saha (102) reported that 95% of the total amount of exchange which takes place for an Indian lignite at a given temperature occurs within 5 minutes. This author's results indicate that exchange is not that rapid (approximately one hour is required for 95% exchange). Since both coals were exchanged from similar molar solutions and both coals contained similar exchange capacities, differences in pore structure probably cause the difference in rate of exchange. Little information on the pore structure of the Indian lignite was available. Thus, no valid comparisons could be made.

A Corning (model 12) pH meter was used to follow the effect of pH on exchange over the range 6.0 to 13.0. Amount of cation added could be calculated by following the pH of the exchange solution. (Exchange of the calcium may be monovalent.)

The amount of $\text{Ca}(++)$ exchanged should be one-half the amount of the hydrogen ions produced. (For monovalent exchange the amount exchanged would be equal to the amount of hydrogen ions produced.) Assuming two hydrogen ions produced for each calcium ion exchanged on the coal, the amount of calcium exchanged can be calculated from the measured pH change in 500 ml of solution in which exchange takes place. By measuring composition of ash of exchanged coal by atomic absorption the amount of exchanged materials can be measured. The amount of

calcium estimated by the two methods described above agreed. Therefore, all the materials found in the coal were considered to be ion-exchanged. No evidence of divalent or trivalent ions exchanging as monovalent was found at higher levels of exchange.

The possibility of extracting humic acid from coal at high pH levels was checked. Ten grams of demineralized coal were added to a 500 ml solution of NaOH at a 13.5 pH for 24 hours. The coal was filtered and acid washed in 10% by weight hot HCl. After acid washing, the coal was washed with hot water in a Pyrex column. Spent wash water was analyzed for Cl(-) by using silver nitrate solution. When no Cl(-) was detected the coal was allowed to dry in an oven at 105°C. The dried coal was then weighed. Less than 0.1 gram of coal was lost. Apparently very little humic acid was extracted from coals under the exchange conditions employed. Mixing of raw coal and NaOH solution resulted in discoloration at solution from humic acid extraction. Apparently the severe conditions of demineralization resulted in changes in the organic structure.

Ten levels of Ca(++) were exchanged on demineralized coal ranging from 0.10 to 2.14 mmoles of cations/g of coal (daf). The coals were exchanged from calcium acetate solutions ranging in concentration from 0.04 to 2.0 molar as mentioned above. Coals were also exchanged in 0.10 molar solutions of ferric nitrate, magnesium nitrate, magnesium acetate, potassium acetate, and sodium acetate. The exchanged led to 0.3 mmole/g of coal (daf) exchanged from the various solutions.

Coal was prepared to similar loadings at three different end point pH levels (11.5, 9.4, 7.5). About 70 grams of coal was prepared at an end point pH of 11.5. It was made from a one molar solution of calcium acetate at a starting pH of 12.5. The coal was exchanged for

10 minutes until a pH of 11.5 was reached. The contents of the beaker were emptied into a 100 mesh screen and washed with one liter of water. An equal amount of coal was prepared from a one molar calcium acetate solution at a starting pH of 12.25. That coal was heated to 60°C and allowed to stand overnight. After cooling, the pH of the solution was 7.5. Similarly about 70 grams of coal in a one molar calcium acetate solution with a starting pH of 12.4 was allowed to stand overnight at room temperature. The coal was treated to an end point pH of 9.5 with one liter of water.

4.3.3 Acid Treatment and Ion Exchange of Chars

In order to obtain a thermally stable pore structure for ion exchange some chars were specially treated. About 300 grams of 800°C and 900°C char produced from the 28 x 48 mesh raw coal were demineralized by the procedures outlined above. Demineralization of the chars was not as efficient as demineralization of raw coal. The demineralized char contained about 3 percent ash, whilst the demineralized portion of the raw coal contained less than 0.5 percent ash. During heat treatment, minerals in the coal could change phase or agglomerate. Both processes might make demineralization less efficient.

After demineralization, chars were treated with concentrated nitric acid to add carboxyl groups to the char. Nitric acid treatment of the chars demineralized after heat treatment consisted of spreading the char in a flat, glass pan, adding the concentrated nitric acid to the char in the pan, and boiling nitric acid under a hood for six hours. After treatment, the char was washed with boiling distilled water in the Pyrex glass columns described in the demineralization procedures.

Carboxyl groups added, served as sites for exchange. Portions of the 800°C char treated in the above manner was exchanged from 0.04 molar solutions of calcium acetate, sodium acetate, magnesium acetate and ferric nitrate to a level of 0.2 mmoles of cation/g of demineralized char. The 900°C char was exchanged to a level of 0.4 mmoles of calcium per gram of demineralized char from a 0.04 molar solution of calcium acetate.

4.3.4 Determination of Critical Fluidization Velocities

It was decided that a fluidized bed should be employed for heat treatment and reaction. Fluidized beds give superior gas-solid contact and a uniform temperature distribution in the reaction bed. The bed provides uniform mixing and therefore uniform reaction of particles. Ideally the bed provides for constant concentration of reactant and product gases throughout the bed. At the very least, each particle sees the same average environment during charring or reaction. However the correct gas flow velocity is required to provide for proper mixing and heat transfer. In order to determine proper conditions, behavior of coal and char particles in the fluidized bed at room temperature was studied.

Determination of proper conditions requires an understanding of the behavior of fluidized beds. Behavior of fluidized beds is classified as quiescent, aggregative or slugging (89). Gas flow rate in a fixed bed of particles determines pressure drop as is specified in the Carman-Kozeny equation (103). As gas flow rate increases, pressure drop increases. When the pressure drop equals the weight of the bed, the particles separate, local circulation of

particles occurs and no stable arrangement of particles exists. The gas velocity under these conditions is defined as the minimum fluidization velocity. The condition of the bed is termed quiescent. Increasing the gas flow rate above the minimum fluidization velocity causes the bed to expand. When bubbles begin to form, the velocity gradient in the radial direction becomes greater, some particles travel to the wall and fall, causing the overall mixing of the bed to increase. This behavior is termed aggregative fluidization. At large enough gas flow rates bubbles fill the diameter of the bed and slugging occurs. Solid circulation decreases when slugging occurs. From the above discussion, conditions between minimum aggregative and slugging are desired to obtain proper mixing and equal temperature distribution.

Kawahata (89) reviewed methods of characterizing behavior of particles in fluidized beds. He reported that critical gas flow rates at which a bed enters quiescent, aggregative, or slugging regimes, could be correlated by a plot of $(D_p G \mu / \rho_f)$ versus $\ln(D_p^3 \rho_s)$ (104) where:

D_p = the mean particle diameter

G = gas flow rate $[\text{g}/\text{cm}^2(\text{hr})]$

μ = viscosity (centipoise)

ρ_f = density of fluid (g/cc)

ρ_s = density of solid (g/cc).

Using this approach and assuming ρ_s in a fluidized bed to be similar to the particle's mercury density (105), critical flow rate values were determined. A Pyrex fluidization column with a diameter similar to the reactor diameter was constructed to determine critical flow rates.

A porous fritted disk served as bed support and gas disperser. Two pressure taps, above and below the bed, were connected to a water manometer. Nitrogen was used as the fluidizing medium. Its flow rate was monitored by a rotameter. Pressure drop was monitored as a function of gas flow rate at 50 cc/min NTP increments at 25°C.

A plot of pressure drop versus gas flow rate was made for each sample. The pressure drop over the fixed bed was a linear function of gas velocity as predicted by the Carman-Kozeny equation (103). After minimum fluidization was reached, the pressure drop remained constant over a 300 to 400 cc/min interval. The velocity flow rate at which constant pressure was achieved was considered the minimum fluidization velocity. As the flow rate was increased bubbles began to form. The point at which the bubbles were first detected was termed the critical flow rate for aggregative fluidization. The velocity was increased until the bubbles just filled the diameter of the bed. That flow rate was termed the critical slugging flow rate.

Critical flow rates for quiescent, aggregative, and slugging conditions were determined for various sizes (28 x 48, 48 x 60, and 60 x 100 mesh Tyler) of raw coal and chars (700°C, 800°C, and 900°C) and are listed in Table 3. Particle density, particle diameter, and critical flow velocities were also listed. All values are given in cgs units. These values were plotted in Figure 1. The plot yielded three straight lines marking boundaries of each fluidization condition. By use of particle diameter, particle density, viscosity of the gas at reaction temperature, and gas density at that temperature it is possible to estimate the correct gas flow

TABLE 3

CRITICAL FLOW RATES UNDER QUIESCENT, AGGREGATIVE, AND SLUGGING CONDITIONS
FOR VARIOUS PARTICLE SIZES OF COALS AND CHARs

Heat Treatment Temperature (°C)	Particle ^a Diameter (D_p) (cm)	Particle Density (ρ_s) (g/cc)	$(D_p^3 \times \rho_s)^b$ $\times 10^5$	Quiescent Fluidization	Aggregative Fluidization	Slugging Conditions
				u_{mf}^c	u_{ma}^d	u_{ms}^e
None	0.045	1.33	12.1	1800	2000	--
None	0.028	1.33	2.9	550	780	1650
None	0.021	1.33	0.9	280	480	930
700	0.051	1.33	17.0	1150	1300	2000
800	0.049	1.33	15.6	1200	1400	2100
900	0.047	1.37	14.2	1300	1500	2200
700	0.023	1.32	1.6	600	840	1750
800	0.024	1.34	1.9	720	1000	1840
900	0.020	1.32	1.1	960	1400	1900
700	0.017	1.33	0.65	160	540	1600
800	0.016	1.28	0.51	390	700	1400
900	0.015	1.32	0.43	400	740	1550

a) Average size.

b) $(D_p^3 \times \rho_s)$; cc x g/cc, D_f = diameter of particles, ρ_s = mercury density of particles.

c) u_{mf} = volume flow rate of gas at minimum fluidization conditions

d) u_{ma} = volume flow rate of gas for aggregative fluidization.

e) u_{ms} = volume flow rate of gas for slugging condition.

Figure 1 CRITICAL FLOW RATES FOR QUIESCENT, AGGREGATIVE, AND SLUGGING CONDITIONS IN A FLUID BED OF LIGNITE COALS AND CHARs (FLUID: NITROGEN)

rate at reaction conditions to ensure proper fluidization. The size of the particles measured by sieving did not change significantly during reaction or charring and, therefore, posed no problems in the calculations. Density of the fluid could be calculated using the ideal gas law, and the viscosity could be obtained from tables (106). Density of particles did change during charring and reaction. Fluctuation in densities during charring and reaction were accounted for by setting initial gas velocities equal to velocities needed for minimum aggregative fluidization. By maintaining the initial flow rate, small changes in densities did not cause improper mixing. The flow rate chosen for the reaction of char with steam was 1100 cc/min NTP.

4.3.5 Charring

Charring was accomplished in a fluidized bed reactor 760 mm in length and 50 mm in diameter. Figure 2 is a schematic diagram of the reactor used for char production. The body of the reactor was made of Vycor. A Vycor fritted disk at the bottom of the main body of the reactor served as a bed support and gas dispersion device. A 10 mm i.d. Vycor inlet tube wrapped around the body of the reactor allowed preheated gas to enter the reactor through an opening at the bottom. A 35 mm graded seal connected the main body of the reactor to the top of the reactor. The top of the reactor consisted of a ground glass joint which fitted inside the reactor cap. A 7 mm i.d. Vycor thermocouple well was connected to the reactor cap through a Pyrex-Vycor graded seal. Gas passed out of the top of the reactor to an exhaust line. Exhaust gases were bubbled through a quinoline bath to remove tars.

The reactor tube was heated by a Burrell furnace with glowbar element, Model BT-1-23. Temperatures were measured by a chromel-alumel

Figure 2 SCHEMATIC OF CARBONIZATION AND REACTION UNIT

thermocouple connected to a West temperature controller. A charge of 200-250 grams of lignite was heat treated in each run. The lignite was placed in the reactor at room temperature and purged for 30 minutes in nitrogen. The reactor temperature was increased at a rate of 10°C per minute to maximum temperature and held for two hours. Approximately 700 grams of char produced from the 28 x 48 mesh size fraction of the raw coal were prepared for each heat treatment temperature.

About 50 grams of 800°C char were produced from all exchanged coals. In addition, 50 grams of 700°C and 900°C char were produced from the coal exchanged with 1.20 mmoles Ca(++)/g of coal (daf).

The demineralized, nitric acid treated, variously cation exchanged, chars were reheated to 800°C, that is, using the same heat treatment temperature as was used for original charring. These chars were reheated to check if volatile release affects relative reactivities of chars. The 900°C, demineralized nitric acid treated, Ca(++) exchanged char was reheated to temperatures of 650°C, 700°C, 800°C, and 850°C. Reheating of a thermally stable pore structure provided samples to study the effect of heat treatment on the catalytic contribution of calcium to the steam-char reaction.

4.3.6 Steam Reaction System

A flow diagram of the reactor system appears in Figure 3. The apparatus can be considered in 3 parts: a gas inlet, a reactor, and a gas outlet. The gas inlet section consists of a water feed system and a preheater. Compressed nitrogen was introduced from the tank through rotameter, A, and a trap, which is a safety precaution to prevent steam from entering the rotameter.

A Rotameters
 B Feed Water Storage Tank
 C Feed Pump
 D Steam Generator
 E Preheater

F Temperature Controller
 G Temperature Controller
 H Furnace
 I Water Trap
 J Condenser

K Sampling Port
 L Wet Test Meter
 M Reactor
 N Thermocouple

Figure 3 FLOW DIAGRAM OF STEAM REACTION SYSTEM

Water flowed from the water line in the laboratory to water feed tank B. The water feed tank was made from a 25 in length of 6 in O.D. steel pipe. Water enters at the top of the tank and leaves through its bottom. Helium can be introduced through a copper tube. Helium is vented through a needle valve at the top of the tank. Bubbling helium was used to remove dissolved oxygen from the water.

The water enters steam generator D, a "hot Shot" boiler (model MB-4) complete with automatic feed pump C. Steam pressure of the boiler was regulated by use of a 15 amp variac which controls electrical power input. Steam leaves the generator through 1/4 in copper tubing. The excess steam can be conducted to a drain.

The gas inlet line from the generator to preheater E is wrapped with heating tape. The preheater, filled with copper turnings, is maintained at a set temperature of 600°C. Traces of oxygen left in the inlet gas were removed at this stage. The preheater is a 35 mm Vycor tube. Gases were conducted from the preheater through Pyrex tubing (wrapped in heating tape) to the reactor.

The main body of the reactor is a 50 cm length of 35 mm Vycor tubing with a Vycor fritted disk at the bottom (similar to that shown in Figure 1). The fritted disk supported the bed of particles and dispersed the gaseous medium. The 7 mm Vycor inlet tube wrapped around the main body of the reactor serves as an additional preheater. The cap of the reactor serves as a gas outlet. The reactor is set inside furnace H. The furnace was the same as that used for charring. Chromel-alumel thermocouples, N, were used to measure temperature in the center of the bed. The leads of the thermocouples were attached to a controller and mercury relay, F and G.

The gas outlet system consisted of Tygon hose connected to a condenser J. Condensed water left through the bottom of the condenser. A sampling port, K, appeared after the condenser. A trap collected water and allowed gas to leave through the top. After leaving the trap, gases passed through a wet test meter, L, and out through an exhaust fan.

4.3.7 Procedures for Steam Reaction

A weighed amount (20 g) of char was placed in the reactor. The system was purged for five minutes with nitrogen before the furnace preheater and steam generator were turned on. During purging, water was admitted to the steam generator and condenser. The reactor was brought to reaction temperature. After thermal equilibrium was achieved, nitrogen flow was stopped and steam introduced. The volumes of gas passing the wet test meter with time were recorded. Samples of gas were taken and analyzed for carbon monoxide, carbon dioxide, and hydrogen. A Fisher gas partitioner, calibrated with five different carbon monoxide and carbon dioxide concentrations, was used to analyze product gases. A Hewlett-Packard chromatograph with a Carbosieve B column was used to measure hydrogen concentration. Helium was used as a carrier gas for the Fisher gas partitioner and argon was used as a carrier gas for the other chromatograph. After the desired burn-off was reached, the run was stopped. The sample was allowed to cool in a nitrogen atmosphere, before it was removed and weighed.

All samples were reacted at 650°C. Selected samples were also reacted at 700°C, 735°C, and 750°C. These samples will be listed later (Section 5.1). A steam flow rate of 1100 cc per minute, corrected to STP, was employed.

4.3.8 Characterization of Solids

Both nitrogen and carbon dioxide surface areas of samples were determined from adsorption isotherms of nitrogen at 77°K and carbon dioxide at 298°K. A conventional volumetric apparatus described by Kamishita (43) was used for sorption of gases. Prior to sorption, samples were dried in an oven for one hour at 105°C. Samples of known weight were outgassed in the sorption apparatus at 110°C under 10^{-4} to 10^{-5} torr of pressure for over 12 hours. After outgassing, samples were immersed in a constant temperature bath of either liquid nitrogen at 77°K for nitrogen adsorption or water at 298°K for carbon dioxide sorption measurement. The dead space in the holders was determined by an expansion method. After the dead space was determined, the apparatus and sample holder were evacuated for 30 minutes at room temperature. The 30 minutes of evacuation allowed the apparatus to be evacuated to 10^{-5} torr. Then, sorption of nitrogen and carbon dioxide were determined by taking a series of known volumes of gas and exposing them to the sample. For each dose, sorption was allowed to continue for 30 minutes or until pressure equilibrium was obtained. Nitrogen surface areas were calculated from the BET equation and carbon dioxide areas were calculated using the D-P equation (both equations were discussed in Section 2.2).

An Aminco porosimeter, which has been described by Gan (36) and Kamishita (43), was used to obtain apparent densities in mercury. About one gram of sample was dried in an oven for one hour at 105°C, placed in a preweighed penetrometer, and placed in turn into a glass filling device. The glass filling device, penetrometer, and sample

were outgassed for a 60 minute period. At the end of the 60 minute period, the glass filling device was tilted so that the bottom of the penetrometer stem sat in a pool of mercury. The chamber was slowly pressurized, allowing mercury to enter the penetrometer stem. The mercury filled penetrometer was weighed and the temperature of the room recorded. After weighing, the filled penetrometer was placed in the high pressure portion of the porosimeter. The vessel was then pressurized to 200 psig. The volume of mercury used to fill the interparticle voids was read by noting the level of mercury on the calibrated stem. The sample volume was calculated using the following equation:

$$V_s = V_f - \frac{(W_p + W_s + W_{Hg} + W_G) - (W_p + W_s + W_G)}{\rho_{Hg}} - V_{st} \quad (4.2)$$

V_s = sample volume (cc)

V_f = free space volume of penetrometer (cc)

W_p = weight of penetrometer (g)

W_s = weight of sample (g)

W_{Hg} = weight of mercury (g)

W_G = weight of grease (g)

V_{st} = volume of stem (cc)

Hg = density of mercury (g/cc)

The density was calculated by dividing the weight of the sample by the volume of the sample (V_s).

Helium densities were determined by helium displacement in an apparatus described by Kamishita (43). Briefly, the apparatus sits

in a heated insulated box. Helium is supplied by a pair of one liter flasks. Volumes of gas can be measured by raising and lowering mercury levels in a calibrated burette and in precision bore tubing.

Pressure was detected by a Datrometrics Borrocel Pressure Sensor, Model S-23-AH-12, connected to the density apparatus and a Datrometrics Electric Manometer, Model 108-26-57.

Prior to helium density determinations, known weights of sample were dried in an oven at 105°C for one hour. The dried samples were placed in preweighed sample holders. The filled holders were weighed and glass wool placed in the neck of the holders. The holders were weighed and mounted on the apparatus. The sample was heated in an oil bath for over 12 hours under a pressure of 10^{-4} to 10^{-5} torr. After outgassing, helium was introduced to the apparatus with the sample holder stopcocks closed. Fifty minutes were allowed for the apparatus to come to thermal equilibrium. After fifty minutes, a pressure reading was taken; and the helium was introduced to the sample. The mercury level in the burette was adjusted to bring the helium pressure to near the initial pressure. After another fifty minutes the height of mercury in the precision tubing was adjusted so that the pressure reading on the sensor returned to the original reading. The volume of the filled sample holder was calculated from the mercury levels in the burette and tubing. The volume of glass wool was determined from the weight of glass wool and its density (2.23 g/cc). The empty volume of the sample holders were predetermined. The volume of a sample was calculated from the following equation:

$$V_s = V_H - V_B - V_W - 0.281 (H) \quad (4.3)$$

V_s = sample volume (cc)

V_H = volume of empty holder (cc)

V_B = volume of burette bulbs filled by mercury (cc)

V_W = volume of the glass wool (cc)

0.28 = cross sectional area of the precision tubing (cm^2)

H = rise or fall in mercury height in tubing during the procedure (cm).

The density was determined by dividing the weight of the sample by its volume as determined above.

Both helium and mercury densities were measured for all samples to determine the porosity and pore volume of samples. Proximate analyses were performed on raw, demineralized, and $\text{Ca}(++)$ exchanged coals according to ASTM specifications (61). Ash yields were determined for all samples by oxidizing the samples in a muffle furnace at 650°C . The ash of all coals and the 700°C char prepared from the 28 x 48 mesh size fraction of the raw coal were analyzed by atomic absorption and the use of a Leco sulfur analyzer in The Mineral Constitution Laboratory of The Pennsylvania State University.

4.3.9 X-Ray Diffraction

X-ray diffraction patterns of -200 mesh partially reacted chars produced from the various cation exchanged coals were taken by use of a Philips Norclco x ray diffractometer. Copper $\text{K}\alpha$ radiation produced at 40 Kv and 16 mamp was used. Scanning rates were 1° (2 θ) per minute and $(1/4)^\circ$ per minute. The faster scan was used to detect major peaks; the slower scan was used to help distinguish minor peaks from background noise and to resolve some major peaks appearing as doublets. X-ray diffraction was used to identify major crystal phases which had been present during reaction.

5. RESULTS AND DISCUSSION

5.1 Research Plan

Since coal is a complex material, many variables influence its behavior in a conversion process. This investigation studied the effects of several parameters on the conversion of chars (derived from PSOC 140, a Darco, Texas lignite) to gaseous products by reaction with steam. A diagram of the sample plan is shown in Figure 4. Prior to cation exchange, coal was demineralized by treatment with HCL and HF, thus ensuring that the carboxyl groups were in the acid form. Cations exchanged on the coal included K(+), Na(+), Ca(++), Mg(++), and Fe(+++). Chars were prepared at various heat treatment temperatures (650°C to 900°C) in an inert atmosphere. Chars were also prepared from the raw and demineralized coal.

Another series of samples was prepared by demineralization of chars derived from the raw coal. The demineralized chars were oxidized with nitric acid to add carboxylic acid groups on the char surface. These chars were exchanged with the cations listed above and reheated to the same maximum heat treatment temperatures (650°C to 900°C) at which the original charring occurred. All chars were reacted with steam in a fluidized bed at 650°C. Variables studied were char heat treatment temperature, cation type, cation loading, and conditions of exchange. All samples were characterized by measurement of carbon dioxide adsorption to follow micropore area, mercury and helium density to follow porosity, and sieve analysis to determine a characteristic size by a Rosin-Rammler distribution function. Ash yields were determined on all samples for mass balance purposes. Porosity and

Figure 4 RESEARCH PLAN

pore volumes are used in the sense of the volume of pores accessible to helium.

The smaller size fractions (48 x 60 and 60 x 100 mesh Tyler) were treated in a similar manner. However, at the constant flow rate employed in the fluid bed apparatus for the gasification reaction (approximately 1100 cc/min), heavy loss of particulates from the reactor was experienced. A constant flow rate was desired to ensure that similar reaction conditions existed for all samples. A change in flow rate might have altered the concentration of gas in the bed and resulted in changes in reaction zone. The heavy loss of particles resulted in unreliable data. Thus, the effect of particle size was not pursued in this study.

The research plan outlined above was set up to accomplish the objectives listed in Chapter 3. Again these objectives were:

- a) to explore the effect of heat treatment temperature of chars on their pore development.
- b) to explore the effect of burn-off, heat treatment temperature, and reaction temperature on char reactivity.
- c) to explore the effect of metal cation addition on the variables mentioned in objectives a and b.

5.2 Properties of Coals

5.2.1 Properties of Exchanged Coals

Carbon dioxide surface areas, helium densities, mercury densities, ash contents, and size distribution were determined for all coal samples. Table 4 lists the values of these parameters for the 28 x 48

TABLE 4

PROPERTIES OF 28 x 48 MESH COAL EXCHANGED WITH VARIOUS CATIONS

Treatment of Coal	Raw	Dem.	Ion Exchanged [0.3 mmole/g of coal (daf)]					
			K(+)	Na(+)	Fe(+++)	Ca(++)	Mg(++) ^a	Mg(++) ^b
% Ash (dry)	10.8	0.5	3.2	2.2	5.7	3.0	2.0	2.0
% V.M. (daf)	47.1	47.1	n.d.	n.d.	n.d.	48.4	n.d.	n.d.
CO ₂ Surface Area (daf) (m ² /g)	120.	200.	200.	200.	200.	195.	205.	200.
He Density (mmcb) (g/cc)	1.44	1.38	1.43	1.42	1.58	1.47	1.44	1.45
Hg Density (mmcb) (g/cc)	1.33	1.20	1.25	1.24	1.28	1.24	1.20	1.21
Pore Volume (mmcb) (cc/g)	0.06	0.10	0.10	0.10	0.15	0.13	0.14	0.14
% Porosity (mmcb)	8.	12.	12.	12.	19.	16.	17.	17.
Rosin-Rammler Parameter K(cm)	0.045	0.042	0.047	0.048	0.045	0.048	0.048	0.045

a) Coal prepared from a magnesium acetate solution.

b) Coal prepared from a magnesium nitrate solution.

mesh size fraction of the raw, demineralized, and various cation [Ca(++), Fe(+++), Mg(++), K(+), and Na(+)] exchanged coals. All exchanged coals were loaded to the same level of ion exchange [0.3 mmole/g of coal (daf)]. The 0.3 mmole loading is similar to the concentration of exchangeable calcium in the raw coal. The ash content of the demineralized coal was less than 0.5%. Determinations below 0.5% were considered inaccurate since the errors in measuring such a small amount of ash are considerable. For ash contents of other coal materials the accuracy was of the order of $\pm 0.5\%$. Volatile matter (according to ASTM specifications) was determined only for the raw, demineralized, and Ca(++) exchanged coal. Since the accuracy of measuring volatile matter is $\pm 2\%$, differences in the values listed are considered insignificant.

It is significant that surface area shows a marked increase when the raw coal is demineralized due to opening of closed porosity by removal of mineral matter. Subsequent ion exchange by the various cations has little effect on surface areas. (Carbon dioxide surface areas were reproducible to $\pm 10 \text{ m}^2/\text{g}$.) Areas were calculated on a daf basis assuming the area of the ash to be insignificant.

Mercury and helium densities decreased significantly as a result of demineralization due to loss of mineral matter which is denser than the carbonaceous phase. The pore volume and porosity for the demineralized coal were larger than those of the raw coal. In general, the mercury densities of the exchanged coal were slightly higher than those for the demineralized coal. The changes in mercury and helium densities resulted in larger pore volumes and porosity for the cation exchanged coals. However, it should be pointed out that small errors

in density measurement can result in comparatively large errors in pore volumes and porosities. Mercury density reproducibility was of the order ± 0.01 g/cc and that for helium density was of the order of ± 0.02 g/cc. These errors can lead to $\pm 2\%$ error in percentage porosities (that is a porosity of 8% can range from 6 to 10%) and ± 0.03 cc/g errors in pore volumes.

Values of the Rosin-Rammler distribution parameter indicated that the characteristic size of the distribution does not change appreciably on demineralization or ion exchange. Some fluctuation was seen but this could be attributed to inaccuracies in data plotting. The slope of the Rosin-Rammler plots was very steep and was identical within experimental error (5 ± 0.5) for all samples. The problems associated with plotting data, together with inaccuracies in weighing, loss of fines, etc., led to these errors.

As revealed in Table 4, data on demineralized coal exchanged in magnesium acetate and magnesium nitrate solutions suggest that nitrate and acetate have similar effects on the parameters studied.

5.2.2 Effect of Amount of Exchange on Ash, Volatile Matter, and Porosities

Properties of the 28 x 48 mesh coal ion exchanged to various levels of calcium contents are listed in Table 5. The Ca(++) exchange levels are reported within ± 0.025 mmole/g of coal (daf). Inaccuracies in determining ash contents account for most of these errors. Estimates of Ca(++) exchanged were calculated from atomic absorption data. The highest loaded calcium coal [2.14 mmole/g of coal (daf)] has a higher calcium content than would be predicted from the concentration of carboxyl groups in this coal (Table 1). However, the amount of

TABLE 5

PROPERTIES OF 28 x 48 MESH Ca(++) EXCHANGED COALS

Amount of Exchange [mmoles/g of coal (daf)]	2.14	1.20	0.95	0.66	0.56	0.45	0.37	0.32	0.25	0.10
% Ash (dry)	16.1	9.2	7.2	5.1	4.7	4.2	3.5	3.0	2.5	1.3
% V.M. (daf)	52.8	50.7	50.0	49.7	49.3	48.7	48.6	48.4	48.3	48.1
CO ₂ Surface Area (daf) (m ² /g)	210.	210.	210.	210.	225.	205.	185.	195.	200.	200.
He Density (mmcb) (g/cc)	1.62	1.55	1.54	1.52	1.50	1.50	1.48	1.47	1.46	1.44
Hg Density (mmcb) (g/cc)	1.36	1.30	1.29	1.26	1.27	1.26	1.25	1.24	1.23	1.22
Pore Volume (mmcb) (cc/g)	0.12	0.12	0.12	0.12	0.12	0.13	0.12	0.13	0.13	0.13
% Porosity (mmcb)	16.	16.	16.	16.	15.	16.	16.	16.	16.	15.

exchange is dependent on the conditions of exchange. The concentration of the exchange solution (2 molar) and pH of the exchange solution (11.5) were much greater than those used to obtain the data in Table 1 (1 molar and pH 8.2). As discussed earlier, increased pH leads to increased exchange (102).

The size distribution, within experimental limits, does not change with the loading of the coal, suggesting that the Ca^{++} was distributed within the coal structure. Increased loading results in a tendency toward increasing densities with loading, as expected since calcium is denser than the coal. Pore volume and porosity remains independent of loading. One would expect pore volume and porosity to decrease with increased loading, because the added Ca^{++} would occupy pore space. However, the volume occupied by the exchanged Ca^{++} is insignificant (< 0.001 cc/g). Carbon dioxide surface areas are essentially independent of loading, within experimental error, indicating that the exchange is not causing a significant reduction of pore diameter or blockage of pores. Volatile matter increases with loading. The most plausible explanation may be that the increase is the result of adding acetate anions to the surface during exchange. Since the Ca^{++} concentration in the wash water is less than that in the solution from which the coal was exchanged, a thorough washing of the lignite could also result in a loss of calcium in the coal. A small amount (0.15 mmole) of acetate adsorbed on the surface could account for a 1% increase in volatile matter.

5.2.3 Effect of Exchange Conditions

Table 6 lists the properties of the 28 x 48 mesh coal exchanged to similar Ca^{++} levels but at different end point pH. Exchange

TABLE 6
 PROPERTIES OF 28 x 48 MESH COAL Ca(++) EXCHANGED AT
 DIFFERENT END POINT pH

End pH of Exchange	7.5	9.5	11.5
Amount of Exchange [mmole/g of coal (daf)]	1.15	1.20	1.29
% Ash (dry)	8.7	9.2	9.4
% V.M. (daf)	50.7	50.7	50.9
CO ₂ Surface Area (daf) (m ² /g)	210.	210.	210.
He Density (mmcb) (g/cc)	1.49	1.55	1.50
Hg Density (mmcb) (g/cc)	1.28	1.30	1.30
Pore Volume (mmcb) (cc/g)	0.11	0.12	0.10
% Porosity (mmcb)	14.	16.	13.

at different pH had negligible effects on the surface area and porosity of the coal.

5.2.4 Analyses of Ashes of Coals

Raw, demineralized, and various ion exchanged 28 x 48 mesh coals were ashed in air at 650°C. At least 0.2 gram of ash sample was collected and sent to The Mineral Constitution Laboratory of The Pennsylvania State University for analysis of major constituents using atomic absorption and the Leco sulfur analyzer. Results are listed in Table 7.

Acid washing (treatment with hot 10% by weight HCl) removed some of each of the major constituents but preferentially removed calcium, sodium, potassium, and magnesium. Demineralization removed over 95% of all ash forming materials. Rutile (TiO_2) and trace elements were not analyzed for. Not all constituents were determined for all the coals. In addition, the amount of each element was determined and then calculated by assuming only oxides exists in the ash. For example, calcium was reported on a CaO basis. But, the actual phase might have been different. The percentage of CaO in the ash increased with Ca(++) loading. As can be seen from the data, the percentage of SO_3 in the ash varied with loading and type of cation loaded.

From the amount of ash and the percentage of sulfate in the ash, the amount of sulfate which remained in the ash of the oxidized coal can be calculated. If the amount of sulfur in the coal is known, the percentage of sulfur in the coal which remains in the solid phase can be calculated, by assuming the amount of sulfur in the coals was the same as that reported in Table 1 and that not much pyritic sulfur is

TABLE 7

ASH ANALYSES OF RAW, DEMINERALIZED, AND VARIOUS CATION EXCHANGED 28 x 48 MESH COAL

Treatment	Amount of Exchange [mmole/g of coal (daf)]	% Ash (dry)	Oxides (% by weight of ash)								
			CaO	SO ₃	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	Na ₂ O	K ₂ O	Balance
None		10.8	10.4	17.6	36.7	21.6	9.4	1.9	0.53	0.47	1.4
Acid Washed (HCl)		4.5	1.4	2.4	57.8	28.0	3.5	1.0	0.16	0.44	5.4
Demineralized (HCl and HF)		0.5	22.0	n.d.	21.9	10.2	9.6	1.2	0.29	0.21	34.6
Ca I.E.	2.14	16.1	74.4	6.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	19.3
Ca I.E.	1.29	9.4	76.8	12.0	1.7	n.d.	n.d.	n.d.	n.d.	n.d.	9.5
Ca I.E.	1.20	9.2	73.0	n.d.	n.d.	n.d.	n.d.	n.d.	0.71	n.d.	26.4
Ca I.E.	1.15	8.7	74.2	15.2	2.9	0.12	0.55	1.47	0.98	0.19	4.4
Ca I.E.	0.95	7.2	74.6	15.2	3.4	n.d.	n.d.	n.d.	0.67	0.19	5.9
Ca I.E.	0.66	5.1	73.0	22.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	4.3
Ca I.E.	0.56	4.7	67.0	23.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	9.5
Ca I.E.	0.45	4.2	61.1	25.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	13.6
Ca I.E.	0.37	3.5	59.3	27.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	13.7
Ca I.E.	0.32	3.0	54.1	30.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	15.9
Ca I.E.	0.25	2.5	56.4	36.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	7.6
Ca I.E.	0.10	1.3	45.5	36.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	17.7
K I.E.	0.30	3.2	1.0	31.5	n.d.	n.d.	n.d.	n.d.	n.d.	45.0	21.5
Na I.E.	0.30	2.2	4.0	32.5	n.d.	n.d.	n.d.	n.d.	41.4	n.d.	22.1
Fe I.E.	0.30	5.7	3.3	4.5	n.d.	n.d.	44.0	n.d.	n.d.	n.d.	48.2
Mg I.E. ^a	0.30	2.0	4.6	18.8	n.d.	n.d.	n.d.	61.4	n.d.	n.d.	15.2
Mg I.E. ^b	0.30	2.0	3.5	20.7	n.d.	n.d.	n.d.	62.0	0.34	n.d.	13.5

a) Coal was prepared from a magnesium nitrate solution.

b) Coal was prepared from a magnesium acetate solution.

present in the coal. Since almost all iron is removed (about 96%), and pyrite is not dissolved by HCl and HF; probably the amount of pyritic sulfur in the 28 x 48 sample was not significant. As is seen in Table 8, above 0.45 mmole of Ca(++)/g of coal (daf), the amount of sulfur fixed in the solid phase is independent of calcium loading. At the same level of exchange [0.3 mmole/g of coal (daf)], different cations fixed different amounts of sulfur. The order of sulfur fixation was: raw > K > Ca > Na > Mg > Fe > acid washed. The ability of the ash from the raw coal to fix sulfur suggests that the dispersed cations in the raw coal contribute to sulfur fixation. However, this effect may be due, in part, to the presence of iron which catalyzes the following reaction:

Thus, the presence of iron compounds might aid the transfer of sulfur to a state which might be more readily fixed. It should be noted that these data were taken under limited conditions (oxidation in air at 650°C in a shallow bed). However, the data indicate that highly dispersed cations do fix sulfur.

5.3 Char Properties

5.3.1 Nitrogen Surface Areas

Adsorption of nitrogen and, hence, surface areas calculated from nitrogen adsorption were found to decrease with time of exposure of char to air. If surface area is plotted against the number of days exposed to moist air, as in Figure 5, it is seen that areas decrease markedly with time. In 29 days the area dropped one order of magnitude,

TABLE 8
SULFUR FIXATION IN THE ASH OF VARIOUS EXCHANGED COALS

Cation Exchanged	Amount of Exchange [mmoles/g of coal (daf)]	% Ash In Char	% Ash As SO ₃	Amount of Sulfur In Ash [g/g of coal (daf)]	% Total Sulfur From Coal In Ash
Ca(++)	2.14	16.1	6.3	0.0040	55.
Ca(++)	1.29	9.4	12.0	0.0040	55.
Ca(++)	0.45	4.2	25.3	0.0040	55.
Ca(++)	0.37	3.5	27.0	0.0037	53.
Ca(++)	0.25	2.5	36.0	0.0035	50.
Ca(++)	0.10	1.3	36.8	0.0018	25.
K(+)	0.30	3.2	31.5	0.0040	55.
Na(+)	0.30	2.2	32.5	0.0028	36.
Fe(+++)	0.30	5.7	4.5	0.0003	3.5
Mg(++)	0.30	2.0	18.5	0.0015	19.
None (raw)	--	10.8	17.6	0.0075	70.
A.W. (HCl)	--	4.5	2.4	0.0004	3.

Figure 5 SURFACE AREAS OF 700°C CHARS EXPOSED TO AIR

from $240 \text{ m}^2/\text{g}$ to $22 \text{ m}^2/\text{g}$. It is suggested that the loss of surface area is due to chemisorption of oxygen. Chemisorption reduces the effective size of pore openings, resulting in some of the pores becoming inaccessible to nitrogen at 77°K . Area would decrease as a function of the amount chemisorbed because pore restrictions would be a function of chemisorption. The original area can be restored by heating in an inert atmosphere. The extent of regeneration is dependent on the maximum reheat temperature and the time that the char is exposed to that maximum temperature. The effect of maximum reheat temperature and soak time on area regeneration can be seen in Table 9. Areas of 800°C and 900°C chars prepared from the 28 x 48 mesh size fraction of the raw coal aged in air for three months, reheated to various temperatures, and held for several hours are listed. In all cases the regenerated area increases with an increase in reheat temperature. Areas also increase with increased soak time at maximum reheat temperature. When the char is reheated, sufficient energy is supplied to the surface oxygen complexes to gasify the carbon site producing carbon monoxide and/or carbon dioxide and allowing accessibility to the interior pores. Some identical runs are included in Table 9 to show reproducibility. Nitrogen areas are within $20 \text{ m}^2/\text{g}$ of one another.

Interestingly, carbon dioxide areas of the chars were not affected by prolonged exposure to air or high temperature outgassing conditions. The constant carbon dioxide areas for chars are indicated in Figure 5 by a horizontal line at $730 \text{ m}^2/\text{g}$.

5.3.2 Carbon Dioxide Areas, Densities, and Porosities

Properties of chars (700°C , 800°C , and 900°C) prepared from a (28 x 48 mesh) $\text{Ca}(++)$ exchanged coal [1.2 mmoles/g of coal (daf)],

TABLE 9

SURFACE AREAS OF CHARS AGED IN AIR FOR THREE MONTHS AND
REHEATED TO DIFFERENT TEMPERATURES FOR DIFFERENT TIMES

Original Charring Temperature (°C)	Maximum Reheat Temperature (°C)	Soak Time At Maximum Temperature (hrs)	Nitrogen Area (daf) (m ² /g)
700	650	2	120
700	650	4	150
700	650	6	240
700	650	8	240
800	None	None	10
800	650	2	120
800	650	2	140
900	None	None	10
900	650	2	35
900	750	2	140
900	750	2	150
900	850	2	210
900	850	4	160
900	750	6	230

as well as from the raw and demineralized coals are listed in Table 10. As expected, ash contents increase with increased heat treatment temperature for the chars prepared from the raw and exchanged coals. As more volatile matter is evolved, the ash becomes a greater portion of the residue char.

Carbon dioxide areas increase with increased heat treatment temperature for chars prepared from the raw and $\text{Ca}(++)$ exchanged coals. However, surface areas are independent of heat treatment for chars produced from the demineralized coals ($680 \text{ m}^2/\text{g}$). The results imply that metal cations present naturally or deliberately introduced, play a major role in surface area development in the char. As discussed in Section 2.4., surface area development reflects changes in the nature of the porosity. Such changes are a result of the evolution of volatile matter and structural changes in the coal as it is charred. The cations may alter the release of volatiles or change the gradual rearrangement of the carbonaceous material which results in a more open structure and, thus, makes more area available for adsorption.

Density changes brought about by heat treatment result in pore volumes and porosities increased over the pore volumes and porosities of the parent coals. Pore volumes and porosities of the chars prepared from the raw, demineralized and $\text{Ca}(++)$ exchanged coals are essentially independent of heat treatment temperature. Since mineral matter may affect porosity development during charring and its removal creates additional porosity, the effect of demineralization on the development of pore volume during charring can be complex. Essentially no difference in porosity development can be distinguished between equivalent chars prepared from raw, demineralized and $\text{Ca}(++)$ exchanged

TABLE 10
 PROPERTIES OF CHARs PREPARED FROM 28 x 48 MESH RAW,
 DEMINERALIZED, AND Ca(++) EXCHANGED COALS

Treatment of Coal	Raw			Demineralized			Ca(++) Exchanged [1.20 mmoles/g of coal (daf)]		
Heat Treatment Temperature, °C	700.	800.	900.	700.	800.	900.	700.	800.	900.
CO ₂ Surface Area (daf) (m ² /g)	730.	800.	860.	680.	680.	680.	770.	800.	860.
He Density (mmcb) (g/cc)	1.92	1.97	2.00	1.74	1.88	1.89	1.92	2.04	2.01
Hg Density (mmcb) (g/cc)	1.33	1.33	1.37	1.20	1.18	1.20	1.33	1.33	1.37
Pore Volume (mmcb) (cc/g)	0.23	0.24	0.23	0.27	0.27	0.26	0.23	0.26	0.23
% Porosity (mmcb)	31.	32.	31.	32.	37.	37.	35.	35.	32.

chars. Particle size determinations by sieve analyses and Rosin-Rammler plots indicate no change in size with heat treatment temperature.

5.3.3 Effect of Calcium Loading on Char Properties

Table 11 lists properties of the 800°C chars prepared from coals containing varying amounts of calcium. Only the surface areas and helium densities vary consistently with calcium concentrations in the char. However, the increase in helium density with loading can be attributed to the increase in calcium in the chars.

The carbon dioxide surface area increases with increasing loading. Clearly, calcium addition to the coal promotes area development during charring. Figure 6, a plot of carbon dioxide surface area of the char as a function of calcium loading in the coals from which the char was prepared, shows a distinct relationship between calcium present in the parent coal and area development. It is suggested that the presence of calcium cations in the coal leads to changes in the mechanism of volatile matter release and to structural rearrangement as pyrolysis occurs.

5.3.4 Effect of Exchange of Various Cations on Char Properties

Properties of the 800°C chars prepared from various cation exchanged [Ca(++), Fe(+++), Mg(++), K(+), and Na(+)], 28 x 48 mesh coals are listed in Table 12. The properties of the 800°C chars prepared from the 28 x 48 mesh raw and demineralized coals are listed for reference. In general, the type of cation exchanged has little effect on most of the properties measured for the resulting chars. Apart from the char prepared from the demineralized coal, mercury densities are essentially constant (values ranged from 1.28 g/cc to 1.33 g/cc). Likewise, variations in helium densities can be accounted

TABLE 11

PROPERTIES OF 800°C CHARs PREPARED FROM Ca(++) EXCHANGED 28 x 48 MESH COALS

Amount of Cation Exchanged [mmole/g of coal (daf)]	2.14	1.20	0.95	0.66	0.56	0.45	0.32	0.32	0.25	0.10
% Ash (dry)	23.8	16.0	13.2	12.5	11.9	7.1	6.2	5.5	4.6	3.6
CO ₂ Surface Area (daf) (m ² /g)	850.	800.	780.	770.	760.	755.	760.	750.	740.	720.
He Density (mmcb) (g/cc)	2.02	2.04	2.01	2.03	1.97	1.98	1.96	1.95	1.97	1.93
Hg Density (mmcb) (g/cc)	1.36	1.33	1.35	1.37	1.33	1.35	1.34	1.33	1.35	1.30
Pore Volume (mmcb) (cc/g)	0.24	0.26	0.24	0.24	0.24	0.32	0.30	0.21	0.23	0.25
% Porosity (mmcb)	33.	35.	32.	33.	32.	32.	33.	29.	31.	33.

Figure 6 CARBON DIOXIDE SURFACE AREA OF 800°C CHARS PREPARED FROM Ca(++) EXCHANGED COALS

TABLE 12

PROPERTIES OF 800°C CHARs PREPARED FROM VARIOUS CATION EXCHANGED 28 x 48 MESH COALS

Treatment of Coal	Raw	Dem.	Ion Exchanged Coals [0.3 mmole/g of coal (daf)]					
			K(+)	Na(+)	Ca(++)	Fe(+++)	Mg(++) ^a	Mg(++) ^b
% Ash (dry)	14.3	0.5	5.8	4.0	5.5	8.0	4.0	3.8
CO ₂ Surface Area (daf) (m ² /g)	800.	680.	400.	450.	750.	800.	570.	600.
He Density (mmcb) (g/cc)	1.97	1.88	1.95	1.90	1.95	2.07	1.93	1.95
Hg Density (mmcb) (cc/g)	1.33	1.18	1.28	1.27	1.33	1.33	1.28	1.29
Pore Volume (mmcb) (cc/g)	0.24	0.32	0.27	0.26	0.21	0.27	0.26	0.26
% Porosity (mmcb)	32.	37.	34.	32.	29.	36.	34.	34.

a) Coal prepared from a magnesium acetate solution.

b) Coal prepared from a magnesium nitrate solution.

for by differences in the composition and amount of inorganic species present. One parameter which did vary markedly was carbon dioxide surface areas. Only the char prepared from Fe(+++) exchanged coal produced a surface area equal to that for the char of the raw coal. The order of surface area developed in the chars is: raw = Fe > Ca > Dem. > Mg > Na > K. It is suggested that changes in surface areas are due to the inorganic phases affecting the rearrangement and decomposition of the organic phase during heat treatment. Changes in the mechanism of volatile release or structural rearrangement would be expected to lead to shifting of pore size distributions.

5.3.5 Effect of Exchange Conditions on Char Properties

A possibility existed that exchange at different pH might cause cations to exchange on carbon sites of different configurations. Different sites might make the cations more or less active during charring and thus cause differences in the properties of chars prepared from coals exchanged at different pH. Table 13 lists the properties of chars prepared from coals exchanged at different pH. The properties do not vary with pH of exchange during loading. Either exchange at different sites does not take place to any appreciable extent or the exchange at different sites does not affect pore development.

For chars prepared from the Mg(++) exchanged coals, the anionic solution from which exchange took place did not alter the properties of the char to any large extent (Table 12).

5.4 Burn-off in Steam

5.4.1 Extent of Burn-offs

The volume percentages of carbon monoxide and carbon dioxide in

TABLE 13

PROPERTIES OF 800°C CHARS PREPARED FROM COAL EXCHANGED
WITH Ca(++) AT VARIOUS pH LEVELS

Properties	End pH		
	7.5	9.5	11.5
% Ash (dry)	15.9	16.0	16.5
CO ₂ Surface Area (daf) (m ² /g)	795.	800.	800.
He Density (mmcb) (g/cc)	2.10	2.04	2.09
Hg Density (mmcb) (g/cc)	1.37	1.33	1.39
Pore Volume (mmcb) (cc/g)	0.25	0.26	0.24
% Porosity (mmcb)	35.	35.	33.

the product gases from steam gasification did not change over the duration of each run made, but the percentages did vary from one run to another. For the reaction of chars produced from the raw and Ca(++), Na(+), and K(+) exchanged coals, carbon monoxide concentrations were about 3% of the total product gas concentration and carbon dioxide concentrations were about 32%. The balance was hydrogen. However, product gas for the reaction of chars prepared from the demineralized and Mg(++), and Fe(+++) exchanged coals with steam consisted of about 35% carbon monoxide, 10% carbon dioxide, and 55% hydrogen. As will be discussed, calcium, sodium, and potassium species are active catalysts for the water gas shift reaction.

The amount of carbon lost during burn-off can be calculated from the following equation:

$$W_c(t) = (\% \text{ CO}_2 + \% \text{ CO}) [V(t)] \left(\frac{12}{22.4} \right) \left(\frac{T_o}{T_R} \right) \quad (5.2)$$

where:

$W_c(t)$ = the cumulative weight of carbon loss at time, t , (g)

$V(t)$ = the cumulative volume of product gas (NTP) produced
at time, t , (cc)

$\% \text{ CO}_2$ = percentage of carbon dioxide in product gas

$\% \text{ CO}$ = percentage of carbon monoxide in product gas

12 = grams of carbon per mole of carbon

22.4 = molar volume at STP (l/mole)

T_o = standard temperature (273°K)

T_R = room temperature (K°).

5.4.2 Mass Balances

By weighing the amount of solid before and after reaction, measuring ash yields, and calculating the amount of carbon gasified from gas analysis, overall carbon and ash balances were calculated. An overall mass balance on carbon and ash showed very small losses apparently due to fine particulate elutriation during reaction for the chars prepared from the 28 x 48 mesh coal. Since no means was employed to measure the amount of fines, the ash and carbon mass balances always indicated net losses. Typical balances indicated a range of up to 1.0% solid loss. Thus, for 20 grams of char about 0.2 gram was lost as fines. In some cases (for chars prepared from 48 x 60 and 60 x 100 mesh Tyler coals) as much as 0.5 gram in 20 grams was lost. Hence, unreliable data were obtained and further work in these size fractions was not pursued. In addition, for some runs in which burn-offs exceeded 50% for chars prepared from 28 x 48 mesh coal, 2 to 3% of the total carbon and ash was lost. One additional factor which would contribute to losses in the mass balance is the removal of sulfur during gasification. A hydrogen sulfide odor was detected in the outlet stream.

Errors in measurement of the carbon monoxide and carbon dioxide concentrations could account for 2% difference in the overall carbon balance. It should be noted that mass balances were very sensitive to changes in ash content. A 1% error in ash yields resulted in a 15% error in the ash mass balance (while 0.1 gram loss of sulfur represented approximately a 10% error in the ash balance).

Oxygen and hydrogen mass balances were dependent on the steam input rate. The input rates were measured to ± 125 cc/min of gas at

STP. All runs were conducted at a flow rate of 1000 to 1250 cc/min of gas at STP. Uncertainty in steam input rate resulted in large errors in hydrogen and oxygen mass balances.

5.4.3 Equilibrium Considerations

The activity quotients for the carbon-steam reaction can be expressed as:

$$K_a = \frac{a_{CO} a_{H_2}}{a_{H_2O} a_C} \quad (5.3)$$

where: K_a = activity quotient

a_{CO} , a_C , a_{H_2} , a_{H_2O} = activity of the carbon monoxide, carbon, hydrogen, and water.

Assuming that the fugacity (activity) of the gas phase is proportional to the partial pressures of gases and that the activity of the solid char is unity, gas product quotients can be calculated:

$$K_p = \frac{P_{CO} P_{H_2}}{P_{H_2O}} \quad (5.4)$$

where: K_p = pressure quotient

P_{CO} , P_{H_2} , P_{H_2O} = the partial pressures of the gases.

Equilibrium pressure quotients are available for the steam-carbon reaction (12). At 650°C, $\log_{10} K_p$ is -0.17, and at 750°C $\log_{10} K_p$ is 0.56. Similarly, the pressure quotients for the water gas shift reaction can be expressed as:

$$K_p = \frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}} \quad (5.5)$$

Again equilibrium values of K'_p can be obtained at desired temperatures

(5). At 650°C $\log_{10} K'_p$ are 0.35 and at 750°C $\log_{10} K'_p$ is 0.14.

Ratios of K'_p are calculated from experimental product gas concentrations, K'_p , and from equilibrium values give, in turn, values for the extent of approach to equilibrium during reaction. Table 14 lists calculated K'_p values and the extent to which equilibrium is approached during reaction of the ion exchanged chars. In this study, calculation of product quotients from gas concentrations indicate that equilibrium was not approached closely for the carbon-steam reaction. For example, even for reaction of the most highly exchanged calcium-containing char at 650°C, the experimental K'_p was 1.0×10^{-5} , or 0.2% of the equilibrium value.

On the other hand, the water gas shift reaction reached equilibrium in the cases of the reaction of highly loaded calcium-containing chars. Results are summarized in Table 14. The water gas shift reaction, when raw coal char was gasified at 650°C, proceeded to 30% of the equilibrium concentrations. For the water gas shift reaction at 650°C in the presence of chars prepared from calcium exchanged coals, the K'_p values ranged from 14 to 98% of equilibrium. Product gases from the reaction of chars prepared from sodium and potassium exchanged coals (0.3 mmole/g) were 27 and 42% of equilibrium. K'_p 's for the product gases at 650°C of chars prepared from Mg(++) and Fe(+++) exchanged coals were only 5 and 10% of equilibrium values, respectively. In the case of the water gas shift reaction during the gasification of chars prepared from demineralized coal, approach to equilibrium was negligible. These results indicate that calcium, potassium, and sodium species catalyzed

TABLE 14

APPROACH TO EQUILIBRIUM OF CARBON-STEAM AND WATER GAS SHIFT
 REACTIONS FOR ION EXCHANGED CHARS REACTED AT 650°C WITH STEAM

Cation Exchanged	Amount of Exchange [mmole/g of coal (daf)]	Pseudo Equilibrium Constant		Approach to Equilibrium	
		$K'_p(C-H_2O) \times 10^5$	$K'_p(CO-H_2O)$	$C-H_2O$ (% $\times 10^3$)	$CO-H_2O$ (%)
Ca	2.14	1.0	2.20	1.4	98
Ca	1.20	0.4	1.08	0.60	48
Ca	0.95	0.4	1.02	0.60	45
Ca	0.66	0.4	1.00	0.60	44
Ca	0.56	0.3	0.93	0.50	41
Ca	0.45	0.3	0.85	0.50	32
Ca	0.37	0.4	0.70	0.60	31
Ca	0.32	0.3	0.64	0.30	28
Ca	0.25	0.1	0.57	0.15	25
Ca	0.10	0.2	0.32	0.30	14
K	0.30	0.3	0.94	0.50	42
Na	0.30	0.2	0.60	0.30	27
Mg	0.30	0.02	0.11	0.30	5
Fe	0.30	0.06	0.22	0.90	10

the water gas shift reaction markedly. Iron and magnesium salts were not as effective catalysts.

5.5 Burn-off Curves and Reactivities

5.5.1 Calculations of Reactivities

As discussed in section (5.3), the amount of carbon burn-off can be calculated from monitoring product gas concentrations and volume of the product gas. Percentages of carbon gasified can be expressed as follows:

$$\% \text{ B.O.} = \frac{W_g}{W} (100) \quad (5.6)$$

where: W_g = weight of carbon gasified at given time (g)

W = total weight of original carbon on dry ash free basis (g).

As described previously, the reactivity of chars in oxidizing atmospheres can be expressed in the following form:

$$R_T = \frac{1}{W} \frac{dW_g}{dt} \quad (5.7)$$

R_T = reactivity of char at given temperature (g/g hr)

W = original weight of char (g) (daf)

dW_g/dt = rate of carbon gasified cation (g/hr).

Thus, by taking the slope of the burn-off curve (dW_g/dt) reactivity can be calculated as a function of burn-off.

As will be seen, not all burn-off curves were linear with time. Since all chars were reacted past 10% burn-off, that level of burn-off was chosen as a standard level to measure reactivity. For most reactions, it was found that reactivity decreased by only a small amount

as burn-off increased. However for some samples (especially iron-containing chars) reactivity changes were marked. They will be discussed later.

5.5.2 Reaction of Raw Coal Chars with Steam

Burn-off curves at 650°C for heat treated chars (700°C, 800°C, 900°C) prepared from the 28 x 48 mesh size fraction of raw coal are given in Figure 7. Each curve is very slightly concave downward. These slightly concave curves may be a result of one of several factors. First the active catalysts may change state as reaction proceeds. For example, if the active species for the reaction was CaSO_3 or CaSO_4 , a slow reduction of the calcium phase to CaO and removal of sulfur to the gas phase in the form of hydrogen sulfide may cause a reduction in the concentration of active catalysts. Secondly, catalysts may have vaporized during the reaction. This is unlikely since Watt (14) reported no significant vaporization of sodium and potassium salts in porous carbon below 850°C. Third, the catalysts might slowly sinter decreasing dispersion and lowering catalyst unit activity. A further possibility is that as the exterior of the char particle is gasified away, the catalyst agglomerates on the surface decreasing dispersion. Also, the catalyst may lose contact with the exterior surface of the char as particle density decreases. Or, the total number of active carbon sites per unit weight of starting material might decrease as reaction progresses and as carbon weight remaining decreases. The above discussion lists factors which might influence char reactivity, and it suggests different possibilities which can influence the behavior of catalysts in these reactions.

Figure 7 BURN-OFF CURVES AT 650 °C OF CHARS PREPARED FROM THE 28 x 48 MESH SIZE FRACTION OF RAW COAL

Reactivities at 10% burn-off for reaction temperatures of 650°C, 700°C, and 750°C for heat treated chars (700°C, 800°C, 900°C) prepared from 28 x 48 mesh raw coal are listed in Table 15. At all reaction temperatures, reactivity decreases with increasing heat treatment temperature. Similar observations have been made previously (6). For reaction at 650°C, the reactivity for the raw char prepared at 800°C is only slightly less reactive than that prepared at 700°C. However, as heat treatment increases to 900°C reactivity decreases sharply. At higher reaction temperatures 700°C and 750°C, marked differences in reactivities between 800°C and 900°C chars are also observed. A decrease in the number of active sites as crystallites within the chars increase in size with increasing heat treatment temperatures is expected to cause decreases in reactivity (71). As seen from Table 10, it is true that total surface area of the chars produced from the raw coal increases with increasing heat treatment temperature. However, this has been attributed to an increased accessibility into the pore structure as a result of increased volatile matter removal. Total surface area can increase but still the fraction of this total area which is active area can decrease sufficiently rapidly as a result of increasing crystallite size to result in an over-all lowering of active surface area. Active surface areas were not measured in this thesis. Usually this is done by oxygen chemisorption at around 300°C. Sintering, vaporization, and change of state of catalysts with increasing heat treatment temperature will also cause reduced reactivity. Kamishita (51) has recently suggested that upon heat treatment volatiles may crack over catalytic sites and deactivate the catalysts. It is probable that all

TABLE 15

REACTIVITIES IN STEAM OF HEAT TREATED CHARs PREPARED FROM
RAW, DEMINERALIZED, AND Ca(++) EXCHANGED COALS

Heat Treatment Temperature, °C	Reaction Temperature, °C	Reactivity (10% B.O.) (g/g hr) (daf)		
		Raw	Dem.	Ca I.E. [1.2 mmolco/g of coalo (daf)]
700	650	0.057	0.0062	0.68
800	650	0.050	0.0050	0.43
900	650	0.020	0.0046	n.d.
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.

these effects do not occur in isolation. Changes in reactivity reported probably reflect a combination of all phenomena.

5.5.3 Reactions of Chars Prepared From Demineralized Coals With Steam

Reactivity plots for demineralized coal chars (700°C, 800°C, 900°C) are shown in Figure 8. Comparing these curves to those for the raw coal chars (Figure 7) it can be seen that rates are much slower. Clearly inorganic constituents originating in the raw coal catalyze strongly the steam-char reaction. In some cases, times in excess of 12 hours were required to reach 10% burn-off. Because of the length of time involved, gasification of these unreactive chars was stopped after 10% burn-off. Curvature of these plots is significantly less than that found for the raw coal chars (Figure 7) and becomes essentially linear after a small initial burn-off. Non-linearity in the initial phase may be due to removal of active sites by selective gasification. The linearity indicates that reactivity in this limited region remains essentially constant with time. It should be remembered that small amounts of impurities remained after demineralization, which may have some catalytic activity.

Halogens remaining after demineralization might retard burn-off (12), although Almagro (98) reported that the halogens are removed rapidly in steam at reaction temperatures of 650°C. Thus, if halogens (present as a result of demineralization) retarded gasification, their effect should decrease as burn-off proceeds. Such was not found to be the case.

Reactivities (at 10% burn-off), as listed in Table 15, show that all values for reactivities of demineralized coal chars are very much

Figure 8 BURN-OFF CURVES AT 650°C OF CHARS PREPARED FROM DEMINERALIZED, 28 x 48 MESH COAL

lower than those for raw coal chars (in some cases as much as an order of magnitude). The decrease in reactivity with increasing heat treatment of the demineralized coal chars is noted. Again the same factors as discussed previously can be responsible for this decrease. However, since the decrease in reactivity is not as marked as for the raw coal chars, the main effect of increasing heat treatment temperature on the reactivity of the raw coal chars seems to be enhanced deactivation of catalytic impurities.

A fully detailed study of pore structure as a function of burn-off is beyond the scope and objectives of this investigation. However, since pore structure does change as gasification proceeds, selected chars have been reacted to different burn-off levels and their porosities examined. A few generalizations can be made about structural properties as a function of burn-off. Table 15 lists properties of 700°C chars derived from the 28 x 48 mesh raw and demineralized coals and reacted in steam at 650°C to different amounts of burn-off. The char prepared from the raw coal was reacted from 10.3 to 55.8% burn-off. Properties of 800°C chars prepared from 28 x 48 mesh raw coal and reacted in steam at 750°C from 10 to 55.2% burn-off are listed in Table 17. As char is reacted, gasification of carbon sites leads to a reduction of pore restrictions and thus, increasing surface area. However, reaction of sites on pore walls will decrease the amount of solid between pores and eventually leads to pores joining together. This phenomenon will produce a decrease in surface area. In the early stages of burn-off, opening of porosity will dominate, and in the later stages of burn-off, collapsing of pores will dominate. The net result is that surface area will go through a maximum during burn-off. The

TABLE 16

PROPERTIES OF 700°C CHARS PREPARED FROM 28 x 48 MESH RAW AND
DEMINERALIZED COALS AND REACTED IN STEAM AT 650°C

Treatment	Raw							Demineralized			
% Burn-off (daf)	10.3	16.1	30.6	31.5	41.3	45.7	55.8	3.	4.5	7.	10.8
% Ash (dry)	13.9	14.7	14.9	15.6	17.8	17.8	27.8	0.7	0.6	0.7	0.7
CO ₂ Surface Area (daf) (m ² /g)	930.	980.	870.	860.	850.	840.	830.	710.	750.	820.	950.
He Density (mmcb) (g/cc)	1.94	2.01	2.	2.02	2.06	2.1	2.11	1.84	1.85	1.86	1.87
Hg Density (mmcb) (g/cc)	1.16	1.12	1.05	1.02	1.	0.97	0.78	1.16	1.15	1.1	1.07
Pore Volume (mmcb) (cc/g)	0.35	0.4	0.45	0.49	0.51	0.55	0.84	0.32	0.33	0.37	0.4
% Porosity (mmcb)	40.	44.	47.	50.	51.	54.	66	37.	38.	41.	43.

maximum burn-off level is dependent on many variables including reaction conditions and type of surface area measured. Torikai (99) reported that for activation of bituminous cokes in carbon dioxide at 850°C and 950°C, the carbon dioxide surface area went through a maximum of around 780 m²/g between 15 and 20% burn-off and decreased slowly thereafter.

TABLE 17

PROPERTIES OF 800°C CHARs PREPARED FROM 28 x 48 MESH RAW
COAL AND REACTION IN STEAM AT 850°C

Burn-off (daf)	10.6	21.4	30.2	38.8	55.2
% Ash (dry)	15.4	17.0	20.7	21.9	2.42
CO ₂ Surface Area (daf) (m ² /g)	710.	780.	940.	930.	910.
He Density (mmcb) (g/cc)	1.94	2.02	2.04	2.09	2.13
Hg Density (mmcb) (g/cc)	1.15	1.08	1.00	0.96	0.82
Pore Volume (mmcb) (cc/g)	0.35	0.43	0.51	0.57	0.74
% Porosity (mmcb)	41.	47.	51.	55.	61.

Carbon dioxide surface areas of the 700°C raw coal char reacted at 650°C (10.3 to 55.8% burn-off) show a comparatively small decline with increasing burn-off (Table 17), suggesting that the maximum area for this char occurred below 10% burn-off. For the 800°C raw coal char reacted at 750°C (10.6 to 55.2% burn-off), a maximum area was

reached between 30 to 40% burn-off. For the 700°C demineralized coal char, the carbon dioxide surface area increased significantly up to 10% burn-off.

As observed by Torakai, helium densities increase and mercury densities decrease with increasing burn-off. The increase in helium density is due to opening of closed porosity and to increasing ash content as reaction proceeds. Mercury densities decrease with increasing burn-off as carbon is gasified from the interior of the particles. The density changes result in increasing pore volume and porosity with increasing burn-off.

5.5.4 Reactions of Chars Prepared From Ca(++) Exchanged

Coals With Steam

Burn-off curves at 650°C for 800°C chars prepared from various calcium loaded ion exchanged coals, Figure 9, are nearly linear. However, some curvature is noted for the highest loaded sample. The burn-off curves for the chars derived from the raw and demineralized coals are included in this figure for comparison. As noted, the burn-off curve for the most highly loaded char (12.9%) is slightly concave downward. This curvature is probably due to two factors. One, catalyst dispersion decreased with increasing burn-off as a result of sintering. Sintering was more pronounced in the sample of highest calcium loading since the calcium species were in closest proximity in this sample. A second factor might be that increased reaction rate increased the hydrogen partial pressure within the char particles, thus, causing changes in the phase of the active catalysts species. X-ray diffraction profiles of the reacted char indicated that the major mineral phase

Figure 9 BURN-OFF CURVES AT 650°C OF 800°C CHARS PREPARED FROM Ca(++) EXCHANGED COALS

present was highly crystalline (a sharp peak intensity) CaCO_3 . Large crystallite size normally results from growth in particle size as a result of sintering.

Reactivities of chars as a function of $\text{Ca}(++)$ loading are listed in Table 18. The 8.5% calcium loaded char is the same 800°C char shown in Table 15. Reactivities show a marked dependence on calcium content. If reactivity at 10% burn-off is plotted as a function of calcium loading in the char, Figure 10, a linear relationship results. This plot indicates that the rate of reaction at 10% burn-off is directly proportional to the amount of calcium contained in the char, showing that the species evolved from the $\text{Ca}(++)$ exchanged cations plays a major role in catalysis of the char-steam reaction. As a catalyst is added to a char, the rate of reaction is expected to increase. Walker et al (13) report that for each additional incremental increase in loading, the incremental increase in reaction rate is usually smaller. A parameter, the utilization factor, may be defined as the reaction rate per unit weight of catalyst. In the case for chars prepared from $\text{Ca}(++)$ exchanged coals, the utilization factor at 10% burn-off is constant. That the utilization factor is constant over such a wide range of loading (1.1 to 12.9% calcium) suggests that the catalyst is highly dispersed and that the catalyst is not sintered markedly during heat treatment. Reactivity of the 800°C char derived from the raw coal falls below the straight line as shown in Figure 10 (i.e. it is less reactive than an equivalent $\text{Ca}(++)$ exchanged coal char). This suggests that some of the calcium in the raw coal is in a less active form (presumably a mineral such as calcite or gypsum). Reactivity of the demineralized char falls on the line in Figure 10, indicating

TABLE 18

REACTIVITIES IN STEAM AT 650°C OF 800°C CHARS PREPARED

FROM Ca(++) EXCHANGED COALS

Amount of Exchange [mmoles/g of coal (daf)]	% CaO In Char	% Ca In Char	Reactivity (10% B.O.) (g/g hr) (daf)
2.14	17.9	12.9	0.63
1.29	12.7	9.1	0.45
1.20	11.8	8.5	0.43
1.15	11.7	8.4	0.40
0.95	9.8	7.0	0.33
0.66	7.4	5.3	0.30
0.56	6.3	4.5	0.23
0.45	4.3	3.1	0.20
0.37	3.7	2.6	0.17
0.32	3.2	2.1	0.14
0.25	2.6	1.9	0.13
0.10	1.6	1.1	0.11

Figure 10 REACTIVITIES IN STEAM AT 650°C OF 800°C CHARS PREPARED FROM Ca(++) EXCHANGED, RAW, AND DEMINERALIZED COALS AND SELECTED NITRIC ACID TREATED CHARS

that the small amount of calcium present catalyzes the char-steam reaction to some extent.

Various chars (700°C, 800°C, 900°C) were prepared from a Ca(++) exchanged coal [1.2 mmoles/g of coal (daf)]. Results in Table 15 show that reactivities decrease with increasing heat treatment temperature, as previously found for the chars produced from raw and demineralized coal.

Completing our examination of Table 15, it is interesting to note the effect of reaction temperatures between 650°C and 750°C on reaction rates for the 800°C chars. Arrhenius plots of reaction rate versus $1/T$ have not been made to estimate activation energies, but it is seen by comparing rate increases between 650°C and 700°C with those between 700°C and 750°C that the apparent activation energy decreases with increasing reaction temperature. There are at least two reasons which can be put forward to explain this result. First, with increasing temperature and reaction rate, the reaction is more likely to be controlled, at least in part, by diffusion of reactants in and products out of the internal pore system of the char particles. Second, higher reactivity means that more product hydrogen is produced and hydrogen is a marked inhibitor for the carbon-steam reaction (12).

A further indication that the diffusion step can limit the gasification rate is seen by comparing the effect of reaction temperature on gasification rates for the chars produced from the demineralized coal, increase in gasification rate in going from 650°C to 750°C is about twelve times; whereas for the char produced from the Ca(++) exchanged coal, the increase in gasification rate is less than three times. That is, for the char having the highest reactivity, diffusion

limitation of gasification is more marked; and, hence the change in reactivity with temperature less marked.

Portions of the demineralized coal were exchanged with approximately 1.2 mmoles $\text{Ca}(++)$ /g of coal (daf) at pH levels of 7.5, 9.5, and 11.5. As discussed earlier, pH may affect the location of sites on which ions exchange and thus affect the activity of the catalyst. It was concluded from observation of results in Table 13 that variation in pH during ion exchange on the coal did not have a significant effect on the structure of the char produced. Figure 11 shows that variation in pH also has no detectable effect on the extent of catalysis of the carbon-steam reaction. The burn-off curves are almost identical and appear to be essentially linear. The linearity suggests a highly dispersed, non-sintered, stable catalyst and a structure which contains a constant concentration of active sites over the burn-off range followed.

5.5.5 Effect of Addition of Various Cations to Coal on Subsequent Char Reactivities

Burn-off curves of chars prepared from various cation [$\text{Ca}(++)$, $\text{Mg}(++)$, $\text{Fe}(+++)$, $\text{K}(+)$, and $\text{Na}(+)$] exchanged coals loaded to 0.3 mmole/g of coal (daf) are shown in Figure 12. Again, curves for the 800°C chars prepared from the raw and demineralized coals and reacted at 650°C are included for reference. Plots for most chars are linear over the burn-off range measured. One exception, is the curve for the reaction of the iron-containing char, which shows marked curvature (as reaction proceeds, the rate gets slower). Apparently, as reported by McKee (18), the iron is undergoing a change in state.

Figure 11 BURN-OFF CURVES AT 650°C OF 28 x 48 MESH 800°C CHARS PREPARED FROM Ca(++) EXCHANGED COALS WITH SIMILAR CALCIUM LOADING BUT VARIED END POINT pH

Figure 12 BURN-OFF CURVES AT 650°C OF 800°C CHARS PREPARED FROM VARIOUS CATION EXCHANGED CHARS

X-ray diffraction patterns of the partially reacted iron-containing char confirmed the presence of a high concentration of Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$. The exchanged iron was likely to have formed FeO and CO_2 in the presence of a steam atmosphere. At reaction temperatures, FeO is expected to be further oxidized, as confirmed from x-ray diffraction results. McKee (18) has concluded that iron oxides are not very active as catalysts for the carbon-steam reaction. On the other hand, metallic iron is a most active catalyst.

The curves for chars containing alkali metals are essentially linear. Rates are larger for these chars than for the rate of the demineralized char, showing the catalytic activity of these species. The linearity of these curves indicates that the active catalyst species are not changing and rates are not affected by changes in the pore structure of the char over the burn-off range followed. No major components could be identified by x-ray diffraction for the partially reacted sodium or potassium-containing chars. Many minor peaks were observed close to the background intensity, indicating that many different phases of the alkali species existed including silicates (formed from SiO_2 left after demineralization), sulfates, sulfites, sulfides, and carbonates. The burn-off curve of the calcium char (1.1% Ca) was discussed in a previous subsection. The curve was linear and CaCO_3 was present. The magnesium-containing char was very unreactive; its burn-off curve is lower than the curve of the char prepared from the raw coal. X-ray diffraction of the partially reacted magnesium-containing char showed a magnesium oxide phase of small crystallite size. Apparently this phase is relatively inactive, though the rate of gasification of the magnesium containing char is higher than for the demineralized char.

Thermodynamic calculations (Appendix), using free energies, showed that FeCO_3 , MgCO_3 , and CaCO_3 , should decompose to the oxide when heat treated to 800°C or above in an inert gas. However, under reaction conditions, calculations showed that the CaCO_3 phase could reappear. The product carbon dioxide concentration is too small to convert the other oxides (MgO and Fe_3O_4) to carbonates. Unfortunately, the carbonate salts can not be confirmed as the active catalysts because CaSO_4 , Na_2SO_4 , and K_2SO_4 are present for calcium and the alkali containing chars. Magnesium sulfate will not form rapidly at temperatures under 1300°C (14). For iron-containing chars, Fe_3O_4 is the most stable phase under the reaction conditions encountered (oxidizing atmosphere), while MgO is the most likely form of magnesium.

To check the effect of the addition of different anions, magnesium exchanged coals were prepared from two different solutions, acetate and nitrate. Both coals were loaded with equal amounts of magnesium [0.3 mmole/g of coal (daf)]. The coals were charred under the same conditions and reacted in steam at 650°C . Burn-off curves of the resulting char are given in Figure 13. Results for the two chars can be correlated by the same reaction plot, at least out to 10% burn-off.

Reactivities at 650°C at 10% burn-off for 800°C chars prepared from various cation exchange coals are listed in Table 19. The potassium-containing char was the most reactive, the magnesium-containing char was the least reactive. The order of reactivity at 10% burn-off level for 0.3 mmole/g of coal (daf) loading was: $\text{K} > \text{Na} = \text{Fe} = \text{Ca} > \text{Mg}$. However, at higher burn-offs, the rate of reaction

Figure 13 BURN-OFF CURVES AT 650°C OF 800°C CHARS PREPARED FROM Mg(++) EXCHANGED COALS

of the iron-containing char decreases markedly. Above 15% burn-off, its reactivity falls below that of the calcium-containing char.

TABLE 19
REACTIVITIES IN STEAM AT 650°C OF CHARS PREPARED
FROM VARIOUS CATION EXCHANGED COALS

<u>Cation</u>	<u>Loading of Cation [mmoles/g of coal (daf)]</u>	<u>Reactivity (10% B.O.) (g/g hr) (daf)</u>
K	0.3	0.18
Na	0.3	0.13
Fe	0.3	0.12
Ca	0.3	0.14
Mg ^a	0.3	0.03

a) Reactivity is the same for coal prepared from magnesium nitrate solution and magnesium acetate solution.

5.5.6 Reaction of Ion Exchanged Thermally Stable Chars

With Steam

Pore development during heat treatment could cause differences in reactivity. The pore development may be dependent on the type of impurities present as discussed (section 5.5.3 and 5.5.4). Kamishita (51) suggested that the cracking of hydrocarbon volatiles during charring affected the activity of catalysts. Thus, as the project progressed, the desirability of monitoring the effect of ion exchange on reactivity of a thermally stable structure (chars which would not change pore structure if reheated) became apparent. To provide a

thermally stable medium, raw coal was charred to 800°C and 900°C, demineralized, and treated with concentrated nitric acid to add COOH groups to the char surface (107). Portions of the 800°C char were exchanged in 0.4 molar solutions of sodium, calcium, and magnesium acetates, and ferric nitrate. These chars were reheated to 800°C prior to their being reacted at 650°C. The 900°C char was exchanged with calcium acetate and reheated to various temperatures (650°C, 700°C, 750°C, 800°C, and 850°C). Reactions of these reheated chars in steam were followed in order to determine the effect of reheat temperature on reactivity. In this subsection these chars will be referred to as exchanged coal chars.

The amount of cation exchanged was determined from chemical analyses of the ash of these samples. These data along with ash and chemical analyses for the 800°C, demineralized, nitric acid treated chars and various cation exchanged chars prepared from this thermally stable structure are listed in Table 20. About 0.2 mmole of cation/g of 800°C nitric acid treated char (daf) and 0.4 mmole of Ca(++)/g of 900°C nitric acid treated char (daf) was exchanged. The difference in the level of exchange may reflect the ease at which the chars are oxidized with nitric acid.

Ash yields of the demineralized chars are higher than those found when the coal is demineralized prior to charring. During heat treatment minerals change phase and sinter. Both changes can make the resulting species more impervious to acid attack. The iron species appears to be especially difficult to remove after heat treatment, probably because the iron species sinters extensively. It could also be that the state of the iron changes. Aluminum and calcium species

TABLE 20

CHEMICAL ANALYSES OF ASH OF DEMINERALIZED, NITRIC ACID TREATED CHARs

Original Char Temperature, (°C)	Char Treatment	Amount of Exchange [mmoles/g of char (daf)]	% Ash	Oxides (% by weight)						
				SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	SO ₃
800	--	--	3.6	4.0	19.5	24.2	20.5	5.1	0.60	14.0
900	--	--	3.3	4.0	19.5	22.0	22.5	4.3	0.35	17.2
800	Ca I. E.	0.2	4.6	n.d.	n.d.	n.d.	40.5	n.d.	n.d.	21.2
800	Na I. E.	0.2	3.2	n.d.	n.d.	16.8	13.6	3.2	19.4	8.9
800	Fe I. E.	0.2	7.4	n.d.	n.d.	39.3	15.1	n.d.	0.4	12.6
800	Mg I. E.	0.2	3.9	n.d.	n.d.	n.d.	12.3	26.0	0.6	12.5
900	Ca I. E.	0.4	6.0	n.d.	n.d.	n.d.	47.3	n.d.	n.d.	29.8

also have a tendency toward becoming more difficult to remove. Other species do not seem to be affected, and they are removed efficiently by HCl/HF treatment of the char. Not all possible elements were analyzed for. Other components commonly found in coal ash, such as TiO_2 , were not analyzed for. Thus, the analyses do not add to 100 percent.

Properties of the exchanged chars are listed in Table 21. Little effect of ion exchange on physical properties is noted. Mercury and helium densities increase slightly due to the addition of the cations. The effect of subsequently reheating the chars between 650°C and 800°C on physical properties can be seen by comparing data listed in Tables 21 and 22. This heat treatment produces significant changes in helium and mercury densities and an accompanying large increase in pore volume and porosity. This is primarily the result of substantial carbon gasification being produced as the carboxyl groups in the chars thermally decompose. Somewhat surprisingly, this heat treatment did not produce any significant change in surface area.

Figure 14 shows reactivity plots for the various reheated $\text{Ca}(++)$ exchanged chars. Reactivity results taken from Figure 14 are summarized in Table 23. Again, heat treatment has an effect on reactivity. Referring back to Figure 10, it is seen that the addition of calcium to the char instead of the raw coal yields chars which are somewhat more reactive. This is true even for the char which was heated to 900°C prior to calcium addition. It was more reactive to steam at 650°C than the char produced by heating calcium-exchanged coal to only 800°C . Of course this may be due to the fact that the demineralized

TABLE 21

PROPERTIES OF DEMINERALIZED, NITRIC ACID TREATED, CATION EXCHANGED CHARS

Heat Treatment Temperature, °C	800.	900.	800.	800.	800.	800.	800.
Ion Exchanged			Na(+)	Fe(+++)	Ca(++)	Mg(++)	Ca(++)
% Ash (dry)	3.6	3.3	3.2	7.4	4.6	3.9	6.0
CO ₂ Surface Area (daf) (m ² /g)	740.	740.	740.	740.	740.	740.	740.
He Density (mmcb) (g/cc)	1.95	2.02	1.99	2.04	1.97	2.01	2.07
Hg Density (mmcb) (g/cc)	1.32	1.37	1.35	1.36	1.37	1.39	1.33
Pore Volume (mmcb) (cc/g)	0.24	0.23	0.24	0.24	0.22	0.22	0.27
% Porosity (mmcb)	32.	32.	32.	33.	30.	31.	36.

TABLE 22

PROPERTIES OF REHEATED CHARs PREPARED FROM 800°C AND 900°C, CATION EXCHANGED CHARs

Original Heat Treatment Temperature, °C	800.	800.	800.	800.	900.	900.	900.	900.	900.
Reheat Temperature, °C	800.	800.	800.	800.	650.	700.	750.	800.	850.
Cation Exchanged	Na(+)	Fe(+++)	Ca(++)	Mg(++)	Ca(++)	Ca(++)	Ca(++)	Ca(++)	Ca(++)
% Ash (dry)	3.6	8.7	4.8	4.3	7.6	7.6	7.3	7.6	7.8
CO ₂ Surface Area (m ² /g) (daf)	740.	740.	740.	740.	740.	740.	740.	740.	740.
He Density (mmcb) (g/cc)	2.03	2.04	2.03	1.99	2.16	2.12	2.16	2.16	2.13
Hg Density (mmcb) (g/cc)	1.05	1.04	1.08	1.07	1.12	1.12	1.13	1.13	1.12
Pore Volume (mmcb) (cc/g)	0.46	0.47	0.43	0.43	0.45	0.44	0.42	0.42	0.44
% Porosity (mmcb)	48.	49.	47.	46.	50.	49.	48.	48.	50.

Figure 14 BURN-OFF CURVES AT 650°C OF REHEATED Ca(++) EXCHANGED CHARs.

char had a higher ash yield than the char produced from demineralized coal. That is, at least some of the other inorganic species found would be expected to have catalytic activity. The constant utilization factor obtained for various loadings of calcium exchanged coal chars suggested that sintering was not marked at temperatures below 800°C. If it is assumed that catalyst sintering during reheating of the nitric acid treated char would be no greater than catalyst sintering during charring of the coal, the reactivity decreases observed in Figure 14 suggest a change in state or phase of the catalyst. Until the active catalyst species is identified, explanation of the decreases in reactivity with heat treatment temperature is difficult.

TABLE 23
REACTIVITIES IN STEAM AT 650°C OF 900°C Ca(++)
EXCHANGED, REHEATED CHARs

Reheat Temperature (°C)	Amount of Exchange [mmoles/g of acid treated char (daf)]	Reactivity (10% B.O.) (g/g hr) (daf)
650	0.4	0.39
700	0.4	0.23
750	0.4	0.24
800	0.4	0.24
950	0.4	0.17

Burn-off curves measured at 650°C for chars to which various cations were added are shown in Figure 15. The original char was prepared at 800°C, and following cation addition, it was again heated

Figure 15 BURN-OFF CURVES AT 650°C OF VARIOUS EXCHANGED CHARS

to 800°C. The calcium and iron containing chars exhibit burn-off curves which decrease with time. The curve for the iron-containing char decreases at a more rapid rate. The curves for the comparatively slow reacting magnesium-containing char and the rapidly reacting sodium-containing char are nearly linear with time, as were the reactivity curves for the chars prepared from the ion exchange coals. The calcium curve became linear after about 5% burn-off. It is suggested that the catalyst underwent some initial change in state and then stabilized as a slightly less active species.

Reactivities of these chars are listed in Table 24. The reactivity order at 10% burn-off was: Na = Fe > Ca > Mg. The above order was the same as that for the chars prepared from the cation exchanged coals.

TABLE 24
REACTIVITIES IN STEAM AT 650°C OF CATION EXCHANGED,
800°C REHEATED CHARs

Cation Exchanged	Amount of Exchange [mmoles/g of acid treated char (daf)]	Reactivity (10% B.O.) (g/g hr) (daf)
Na(+)	0.2	0.11
Fe(+++)	0.2	0.11
Ca(++)	0.2	0.09
Mg(++)	0.2	0.03

6. SUMMARY AND CONCLUSIONS

6.1 Summary of Work

A 28 x 48 size fraction of a Darco, Texas lignite, PSOC 140, was demineralized by treatment with HCl and HF. Some of the demineralized coal was ion exchanged with various cations [Mg(++), Fe(+++), K(+), and Na(+)] to 0.3 mmole/g of coal (daf), while other portions of the demineralized coal were exchanged with 0.10 to 2.14 mmoles of calcium/g of coal (daf). Demineralized coal was exchanged with two magnesium salt solutions and in calcium acetate solution at three different pH levels.

Raw, demineralized, and Ca(++) exchanged [1.2 mmole/g of coal (daf)] coals were heat treated to 700°C, 800°C, and 900°C, using a heating rate of 10°C/min in a nitrogen atmosphere. The other cation exchanged coal samples were heated to only 800°C. To produce a thermally stable pore structure for comparison, fractions of the 800°C and 900°C chars produced from the raw coal were demineralized to remove inorganic impurities and treated with nitric acid to add carboxyl groups. The 800°C char was then exchanged to 0.2 mmole cation/g of char and reheated to 800°C. The 900°C char was exchanged with 0.4 mmole/g of char and reheated to 650°C, 700°C, 750°C, 800°C, and 850°C.

All the above chars were gasified at 650°C in one atmosphere of steam. Some chars [800°C and 900°C chars prepared from raw and demineralized coal and the 800°C char prepared from a calcium exchanged coal (1.2 mmoles/g of coal)] were also gasified at 700°C and 750°C. In addition, a 900°C char prepared from the exchanged coal (1.2 mmoles/g

of coal) was gasified at 700°C. Reactivities were calculated for all gasification runs.

All solid samples were characterized by carbon dioxide adsorption, densities from helium and mercury displacements, particle size distributions from sieve analysis, and ashing at 650°C. Ashing constituents were determined using atomic absorption spectroscopy. X-ray diffraction profiles were used to characterize the inorganic phase in some of the cation exchanged samples following some char gasification.

6.2 Summary of Results

Demineralization of the coal markedly increased carbon dioxide surface area. Ion exchange of various cations [Na(++), K(+), Fe(+++), Mg(++), and 10 levels of Ca(++)] on the demineralized coal did not affect pore structure of coals.

Pore structure varied with heat treatment temperature in a complex manner. Type of cation added to the coal affected its carbon dioxide surface area development during heat treatment. Coals loaded with Fe(+++) and Mg(++) resulted in the largest surface areas, while coals loaded with Na(+) and K(+) resulted in the smallest surface area developed. Heat treatment of raw coals resulted in chars with surface areas as large as that developed from the Fe(+++) exchanged coal. The demineralized coal led to the smallest area development upon heat treatment. Increased Ca(++) exchange on the coal led to increased carbon dioxide surface area upon heat treatment. Pore volumes and porosities developed in the chars were essentially independent of the starting precursor.

Demineralization and nitric acid treatment of the raw coal chars did not alter porosities significantly. Ion exchange by cations [Na(+), Fe(+++), Mg(++), and Ca(++)] or reheating of the exchanged chars did not affect pore structure of the char.

Upon gasification, the surface area of most chars increased to a maximum with increasing burn-off and then decreased. The burn-off at which maximum area occurred and the value of the surface area at the maximum varied with the nature of the starting char. Increased burn-off monotonically increased pore volume and porosity. Optimum conditions for activation or best precursor for activation were not explored.

Reactivities of chars measured at 10% burn-off decreased with increasing heat treatment temperature for all samples, but the amount of decrease was variable. Decreases in reactivity were attributed to changes in the chemical and/or physical structure of the catalyst and changes in pore structure of the chars upon heat treatment. Reactivities were directly proportional to the amount of calcium in the char (in the range studied). The kind of cation exchanged on the coal from which the char was prepared also affected reactivity. Catalyst activity following gasification of the char to 10% burn-off was in the order: $K > Na = Fe = Ca > raw > Mg > Dem.$ Char reactivity varied as a function of burn-off. The extent of change of reactivity with time of reaction varied from char to char. In particular, reactivities of the highest loaded calcium char and the iron-containing char markedly decreased with reaction time. Reactivities of the lesser loaded calcium chars and the alkali containing chars were essentially constant over the range of burn-offs studied. Analysis of x-ray diffraction profiles

of the partially reacted iron-containing char revealed that the iron was a highly ordered, highly oxidized $\gamma\text{Fe}_2\text{O}_3 - \text{Fe}_3\text{O}_4$ phase. Increasing the extent of oxidation of the iron decreased its catalytic activity and thus char reactivity to steam. The decrease in reactivity of the iron-containing char resulted in the reactivity order at 15% burn-off changing to: $\text{K} > \text{Na} = \text{Ca} > \text{raw} > \text{Fe} = \text{Mg} > \text{Dem}$.

Interpretation of changes in reactivity with burn-off for the calcium-containing chars was more complex. Calcite was identified by x-ray diffraction as the major species present in the partially reacted char having the highest calcium loading. The calcite phase was highly crystalline, suggesting that particle agglomeration and/or some sintering of the calcium phase occurred during char gasification. X-ray diffraction studies identified the major phase for the magnesium-containing char as MgO. X-ray diffraction of the sodium and potassium-containing char indicated that the major phases were poorly crystalline. They could not be identified. Reactivities of chars prepared from raw and demineralized coal decreased with reaction time. Again those reactivities appeared to be a complicated function of changes in catalytic activity of impurities and structure of the char as gasification proceeds. End pH of exchange and anionic solution from which coal was exchanged did not affect reactivities of the resulting chars.

6.3 Conclusions

The following conclusions can be drawn from data discussed:

1. Cations can be exchanged under various conditions to various amount on a demineralized lignite. Increasing temperature of exchange,

increasing pH of exchange, and increasing concentration of exchange solution increases the amount of cation exchanged.

2. Demineralization opens some previously closed pores or enlarges existing pores slightly by removal of minerals and thus increases carbon dioxide surface area of coals.

3. Cation exchange did not significantly alter the pore structure of the lignite.

4. Heat treatment of the various lignite samples produced complex changes in their pore structure.

5. Impurities and especially highly dispersed species can affect carbon dioxide surface area development during heat treatment but do not radically alter the total pore volume calculated from helium and mercury densities of resulting chars.

6. Final pH of exchange and anionic component (acetate or nitrate) of exchange do not affect properties of resulting chars.

7. Lignite chars chemisorb oxygen when exposed to moist air at room temperature. Chemisorption of oxygen decreases nitrogen uptake at 77°K. If the chars are outgassed at elevated temperatures prior to adsorption measurement, maximum nitrogen uptake is restored.

8. Cations in coals have the ability to fix sulfur in the ash when the coals are oxidized in air at 650°C. Iron impurities do not fix sulfur significantly but may aid other species in sulfur fixation by catalyzing the oxidation of SO_2 to SO_3 .

9. Char reactivities decreased with increasing heat treatment temperature for chars prepared from the raw, demineralized and Ca^{++} exchanged coals. It is suggested that the temperature a char is exposed to prior to reaction should be held as low as possible if char reactivity

is to be maximized. Decrease in reactivity with increasing heat treatment temperature is, at least in part, thought to be due to decreases in catalyst dispersion.

10. Cation addition to the coal leads to production of highly reactive chars. Reactivities of chars prepared from Ca(++) exchanged coals of various loadings are directly proportional to the extent of calcium loading. Inorganic species resulting from heating sodium and potassium exchanged coals to 800°C and reacting in steam at 650°C are highly dispersed, catalyze the carbon-steam reaction markedly, and are not identifiable from x-ray diffraction studies. Potassium was the most active catalyst. It was found that Fe_3O_4 , Fe_2O_3 , and MgO result when coals exchanged with Fe(+++) or Mg(++) are heated to 800°C in nitrogen and reacted in steam at 650°C. The above states of iron and magnesium are poor catalysts for the char-steam reaction at 650°C.

6.4 Recommendations

Reactivities for a series of chars produced from different lignite coals of varying exchange capacities should be measured and compared with values predicted from the plot of calcium loading versus reactivity.

Second, work is needed to determine the feasibility of adding catalysts to raw lignites. The effect of loading of K(+) and Na(+) on reactivity should be explored to determine if reactivity of chars prepared from these coals would be directly proportional to loading. Since exchange can take place under conditions resembling the mixing of sea water and demineralized coal, it would be of interest to determine

if exchange of sea water on raw coal could take place and if increased reactivities of the chars would result. The ocean is one possible source of catalyst. To be able to use sea water as a catalyst source in commercial gasification plants, the feasibility of exchange needs to be shown. In addition, effects of $H(+)$ and $Cl(-)$ in the system would need evaluation.

Third, the effect of heating rate in going from coal to char was not studied in this investigation. Rapid devolatilization of the ion-exchanged coal may result in chars of unique properties. As such, these chars would be of extreme interest to processes employing rapid devolatilization.

One final area of study which requires pursuing would be mineral matter characterization during or after charring and reaction. A basic understanding as to the effect of process conditions on the inorganic constituents and how these constituents can add or detract from a process is needed.

Active catalytic species were not determined in all cases. Certainly this area should be explored. Such a study might elucidate the mechanism of carbon-catalyst interaction, the manner in which sulfur is released to the gas phase, or the safe operation temperatures for full utilization of catalysts in gasification schemes.

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APPENDIX

A change of standard Gibbs free energy of a reaction can be calculated from standard Gibbs free energies of formation of compounds involved in the reaction. The change in standard Gibbs free energy of a reaction is the sum of Gibbs free energy of formation of the products minus the sum of the Gibbs free energy of formation of the reactants. Table A-1 lists the Gibbs free energy of formation of various metal carbonates at 800°C and energy of formation of their decomposition products (metal oxides and carbon dioxide). Data was obtained from JANAF Tables (108). Free energy changes for the following carbonate decomposition reactions were calculated:

and are listed in Table A-2. The following is a sample calculation used to determine changes in the Gibbs free energy for the carbonate decomposition reaction at 800°C for K_2CO_3 :

TABLE A-1

GIBBS FREE ENERGIES OF FORMATION OF METAL CARBONATES,
METAL OXIDES, AND CARBON DIOXIDE

<u>Compound</u>	<u>Free Energy of Formation at 800°C (Kcal/mole)</u>
CO ₂	-94.5
CaCO ₃	-218.0
CaO	-115.1
K ₂ CO ₃	-198.0
K ₂ O	-50.1
Na ₂ CO ₃	-195.9
Na ₂ O	-65.7
MgCO ₃	-215.2
MgO	-116.0
FeCO ₃	-226.5
FeO	-120.1

TABLE A-2
CHANGES IN GIBBS FREE ENERGY FOR CARBONATE
DECOMPOSITION REACTIONS

<u>Reaction Number</u>	<u>Standard Free Energy Change (Kcal/mole)</u>
A.1	53.4
A.2	35.7
A.3	8.4
A.4	-14.7
A.5	-12.0

$$\Delta G^\circ = \epsilon \Delta G_{\text{products}} - \epsilon \Delta G_{\text{reactants}}$$

$$\Delta G^\circ = [(-50.1) + (-94.5)] - (-198.0) \quad (\text{A.6})$$

$$\Delta G^\circ = 53.4$$

A positive ΔG° indicates that the reaction is unfavorable in the forward direction. Carbon dioxide pressure at which the carbonate will decompose can be calculated from the following equation:

$$\Delta G^\circ = - RT (\ln K_p) \quad (\text{A.7})$$

where K_p is simply the partial pressure of carbon dioxide in the system (assuming the solids have activities of unity). Clearly, Na_2CO_3 and K_2CO_3 are stable at 800°C . If the carbon dioxide pressure drops below about 10 torr the calcium carbonate will decompose. Carbon dioxide pressures during charring are likely to fall below that level. However, during reaction of chars with steam, carbon dioxide pressures would exceed that level. Thus, during charring calcium would exist as CaO , but during reaction it would exist as CaCO_3 . Iron and magnesium would exist as oxides during charring and reaction.