

CATALYTIC EFFECTS OF ALKALI METAL SALTS IN THE GASIFICATION OF COAL CHAR

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INTRODUCTION

Coal is a complex and variable carbonaceous rock which is composed basically of two types of materials. The macerals or carbonaceous remains of plants constitute the organic fraction of coal, with the remainder comprising minerals or inorganic impurities present in the parent vegetation or deposited subsequently. The major mineral components of coal include clays, alkaline carbonates, metallic sulfides, oxides and quartz,⁽¹⁾ but the minor and trace impurities may include most of the elements of the Periodic Table.

The reactivity and properties of coal can be profoundly influenced by these inorganic impurities.⁽²⁻⁴⁾ Currently, there is interest not only in the effects of mineral matter on the chemical behavior of coal but also in the possibility of adding catalysts to coal in order to lower the temperature required for gasification processes. For example, it has been known for over one hundred years that the reactivity of coal and char towards steam is promoted by the addition of alkalis, such as caustic soda or lime.⁽⁵⁾ There are a number of processes under development today which utilize the catalytic properties of alkali carbonates to improve the reactivity of coal in the gasifier.⁽⁶⁻⁸⁾ Earlier work has shown that the carbonates and oxides of the alkali and alkaline earth metals are among the most active catalysts for the gasification of carbonaceous materials in steam and carbon dioxide.⁽⁹⁻¹¹⁾ However, there is still no generally accepted explanation for these catalytic effects.⁽¹²⁾

This paper describes the results of a continuing study of the catalytic behavior of salts of the alkali metals in the gasification of coal char by steam and CO_2 . The main purpose of this work is to investigate possible mechanisms of the catalysis and to elucidate the effects of mineral impurities on the reactivity of coal char. For this purpose the behavior of a typical char and a pure graphite powder have been compared in the presence and absence of added alkali catalysts. In a companion paper (13), the effects of char pyrolysis temperature, surface area and mode of catalyst addition are described.

EXPERIMENTAL

Materials

The char used in this work was prepared from a large sample of Illinois #6 HVB bituminous coal from Inland Mine #1, Sessor, Illinois. Proximate and ultimate analyses of this coal sample are given in Table I. The results of x-ray diffraction on ash residues after low temperature ashing (LTA) showed major amounts of kaolinite and minor amounts of quartz and pyrite.

Initially the coal was coarse ground, homogenized, vacuum dried at 105°C and then stored in a vacuum desiccator. In some cases salt catalysts were added to coal samples before pyrolysis. Thus, about 15 g. of the dried coal was micronized in a nitrogen-driven fluid grinding mill to give a particle size of the order of several microns. A known amount, generally 5 percent, of the dried powder salt, e.g., K_2CO_3 , CH_3COOK , was then added to the coal and the mixture rolled for four hours in a rolling mill. The doped samples were then placed in alumina crucibles and pyrolyzed in nitrogen at 700°C for 2 hours. Observed weight losses of the coal

samples during this pyrolysis were of the order of 30 percent. In other cases the catalysts were added after charring at 700°C by mixing weighed amounts of salts and char together in a Fisher Minimill. The char samples had surface areas of approximately 280 m²/g., as determined by CO₂ adsorption at 195°K.

Spectroscopic grade graphite powder (-325 mesh, Type UCP-2^R, highest purity) was obtained from Ultra Carbon Corp. This material had an initial surface area of 7.5 m²/g., as determined by nitrogen adsorption at -195°C.

The salt additives were Analytical Reagent or Certified ACS Grade materials and were used without further treatment. The gaseous atmospheres used included Linde Instrument Grade carbon dioxide and Linde Ultra-High Purity Grade helium. For experiments in steam (water vapor), the helium was passed through a distilled water bubbler at 25°C to give a water vapor pressure of 23 mm. (3.1 kPa) in the gas stream.

Proximate Analysis

	<u>% Moisture</u>	<u>% Ash</u>	<u>% Volatiles</u>	<u>% Fixed C</u>	<u>BTU/lb</u>
As Received	0.72	9.68	39.45	50.15	12979
Dry Basis	-	9.75	39.74	50.51	13073

Free Swelling Index = 5

Ultimate Analysis

	<u>% Moisture</u>	<u>% C</u>	<u>% H</u>	<u>% N</u>	<u>% Cl</u>	<u>% S</u>	<u>% O (diff.)</u>
As Received	0.72	73.06	5.04	1.68	0.39	1.20	8.23
Dry Basis	-	73.59	5.08	1.69	0.39	1.21	8.29

Table I: Analyses of Illinois #6 Coal Sample

Procedure

Thermogravimetric studies and measurements of the isothermal kinetics of the catalyzed gasification of char and graphite in CO₂ and water vapor were carried out in the Mettler Thermoanalyzer-2 automatically recording balance as previously described.⁽¹⁴⁾ Kinetic measurements at a series of constant temperatures between 600 and 1000°C were made on 200 mg. samples of the doped carbons, using flowing CO₂ at 1 atm. (1.02 x 10⁵ kPa) and a flow rate of 200 ml.min⁻¹. Gasification in water vapor was accomplished in a water vapor-saturated helium stream (23 mm. H₂O, 3.1 kPa) at a flow rate of 300 ml.min⁻¹. Kinetic data were generally plotted in the form of Arrhenius plots (rates vs. 1/T°K), the gasification rates at each temperature being derived experimentally from the relation,

$$\text{Rate (min}^{-1}\text{)} = \frac{dW/dt}{W_0}$$

where W₀ is the initial weight of the sample. In all cases, in order to minimize the effects of changing surface area and catalyst concentration, the total weight loss during gasification of each sample was kept below 15 percent.

Some thermogravimetric measurements of the reactions between the salts and the carbons and between the salts and selected minerals were carried out by heating appropriate mixtures in the thermobalance at a linearly increasing temperature of $10^{\circ}\text{Cmin}^{-1}$ using flowing atmospheres of pure dry helium or carbon dioxide.

RESULTS

Catalyzed Gasification in Steam

As expected, the carbonates of the alkali metals proved to be effective catalysts for the gasification of both char and graphite in steam. In the case of the char, the addition of 5 percent by weight of the salts resulted in slightly more active chars when the catalysts were introduced prior to charring at 700°C rather than physically mixed with the char after charring (13). In general, the reactivity of the doped chars in steam decreased on successive thermal cycles and with time at a constant gasification temperature. This effect will be discussed in more detail below. Figure 1 shows Arrhenius plots (gasification rates vs. $1/T^{\circ}\text{K}$) for the 700°C char doped with 5 percent by weight of alkali carbonates after charring. These data were obtained during the second thermal cycle in each case. A similar order of catalytic activity was observed previously for graphite, although in this case Na_2CO_3 was slightly less active than K_2CO_3 . Pure graphite was considerably less reactive than the uncatalyzed char sample, however the catalytic effects of the added salts were more marked in the former case, so that the catalyzed gasification rates in steam were quite similar for both graphite and char over the $600\text{-}900^{\circ}\text{C}$ temperature range. Gasification rates for graphite doped with 1 and 5 wt. percent of the alkali salts were about the same, whereas with the char a progressive increase in rate was observed with increasing carbonate concentration up to 20 weight percent, as shown in Figure 2. This marked difference in behavior between graphite and char was probably related to the large difference in surface area between the two materials although the active site area was not known in either case. However, with a series of chars, prepared in the presence and absence of added catalysts, there was no significant correlation between reactivity and surface area. In fact, surface areas were generally somewhat smaller for catalyst-doped samples than for uncatalyzed chars. Also there was little difference in gasification rates when the char particles were ground from ca. 1 mm. size to ca. $1\ \mu\text{m}$. (13) These results indicate that surface areas and particle size are not important parameters in determining char reactivity, at least for chars of the same type and the same heat treatment history. In the steam environment, Li_2CO_3 was clearly the most active catalyst, with Na_2CO_3 and K_2CO_3 exhibiting somewhat lower activity. Other additives, such as KNO_3 and K_2SO_4 , also showed substantial catalytic activity, whereas KCl was somewhat less active.

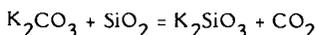
As noted above, the catalyzed char samples showed a progressive loss in reactivity towards steam during the experiments. This phenomenon, which was not observed with graphite, was studied in some detail. Figure 3 shows kinetic data obtained with a char sample doped with 5 weight percent K_2CO_3 during three successive thermal cycles. The initially high gasification rates in steam fell by a factor of about two on the second cycle with progressively smaller deactivation effects on subsequent cycles. Figure 4 shows the results of isothermal rate measurements obtained at 800°C for char samples initially doped with 2, 5 and 10 percent K_2CO_3 . In all three cases a rapid drop in gasification rate occurred during the first hour with more gradual decreases during the subsequent four hours of the experiments. In the case of the sample containing 10% K_2CO_3 , the gasification rate was so high that the rate began to decrease after about 3 hours because of loss of contact between the catalyst phase and the residual char substrate.

In steam (water vapor) catalyst deactivation was observed for every catalyst additive tested, regardless of whether the salt was added before or after charring. Figure 5 shows data obtained from a char sample to which 5 wt. % potassium acetate had been added before

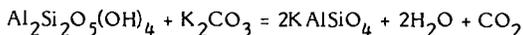
charring at 700°C. Again a marked progressive loss in activity was found on successive thermal cycles, accompanied by an increase in the apparent activation energy from 18 to 51 Kcal/mole during the four cycles shown.

As it was found that this progressive deactivation did not occur during the catalyzed steam gasification of graphite, it appeared unlikely that the effect was due to sintering, agglomeration or vaporization of the salt catalyst. It seemed more probable that catalyst deactivation was related to reaction of the alkali salts with minerals such as quartz, clay, kaolin, and pyrite present in the char samples. Some experiments were therefore carried out in the thermobalance, using mixtures of K_2CO_3 with these mineral species, to determine if solid state reactions might occur at temperatures in the gasification range (600-1000°C).

Figure 6 shows thermograms (weight change vs. temperature) for 200 mg. pure K_2CO_3 (dashed curve) and for a mixture of 200 mg. K_2CO_3 and 200 mg. powdered quartz (solid curve) on heating in a stream of dry helium during a linear temperature rise of 10°C/min. Following an initial dehydration at 100-150°C, the pure salt showed no further weight loss on heating to 980°C and a slight loss at higher temperatures due to vaporization above the melting point. On the other hand, the mixture of salt and quartz lost weight rapidly at temperatures above 750°C, probably as a result of evolution of CO_2 by reactions of the type



A variety of silicate-forming reactions are in fact possible. The extent of these reactions at a given temperature and the temperature of inception of the solid state reactions would be expected to depend on the particle size and interfacial contact area between the solid phases. Also the presence of CO_2 in the gas phase would tend to suppress these reactions. Similar thermogravimetric data for (A) 200 mg. pure K_2CO_3 , (B) 200 mg. of powdered illite clay, and a mixture of 200 mg. K_2CO_3 and 200 mg. illite, are shown in Figure 7. The curve labelled (A+B) is the sum of curves (A) and (B) and represents the weight changes expected for a salt-illite mixture if no reaction occurred between the two phases. It is evident from the lower solid curve in Figure 7 that a reaction between the clay and the salt took place above 700°C with a continuous loss in weight of the sample, probably as a result of liberation of CO_2 . The composition of the mineral illite, a complex aluminosilicate, is, however, indefinite, so no equation can be written for this reaction. Illite, however, is an important major mineral constituent in many coals. Similar data for kaolin- K_2CO_3 mixtures are shown in Figure 8. A comparison of curve (A+B) for kaolin + K_2CO_3 with no reaction and curve C, the experimental thermogram for the mixture, indicates that a reaction between the mineral and the salt took place at temperatures above 700°C with the loss of a volatile product, most likely CO_2 . In a CO_2 atmosphere, this reaction was inhibited (curve D), but even in this case a marked loss in weight occurred above 900°C. A possible reaction between the salt and the kaolin is



The expected weight loss for the completion of this reaction is 60 mg, which corresponds closely to the experimental loss in weight of the kaolin-salt mixture between 650 and 1100°C. The reaction of potassium salts with the mineral constituents of fly ash to produce the water-insoluble mineral kalsilite ($KAlSiO_4$) has been reported by Karr et. al. to occur in the presence of steam at 850°C. (16)

Catalyzed Gasification in CO_2

As expected, the alkali metal carbonates were found to be active catalysts for gasification of coal char in CO_2 . Results for the catalyzed gasification of graphite have been reported previously. (14) With coal char the kinetic data were much more reproducible in CO_2

than in steam. Figure 9 shows data obtained for a char-5% K_2CO_3 (the same sample as that used in Figure 3) on gasification in 1 atm. CO_2 between 600 and 900°C. In this case, during four successive thermal cycles the kinetic data were remarkably constant, with only a slight decrease in rates between the first and second cycles. The apparent activation energy for this series of experiments was 49.3 Kcal/mole. Similar data for a char sample to which 5% K_2CO_3 had been added before the 700°C charring step are shown in Figure 10. Again, following a small reduction in gasification rates between the first and second cycles, the reactivity on further cycling was reproducible, with an apparent activation energy of 53.8 Kcal/mole. Comparison with Figure 9 indicates that the catalytic effect of the K_2CO_3 was similar regardless of whether the salt was added before or after charring. Similar data for a CH_3COOK -doped char sample are shown in Figure 11. In this case also, following a slight reduction in reactivity between cycles 1 and 2, subsequent kinetic data were quite reproducible. Comparison with Figure 5 shows the marked difference in behavior of this doped char sample in the two gaseous environments.

Gasification data in CO_2 for char doped with 5% Li_2CO_3 , Na_2CO_3 and K_2CO_3 (added prior to charring) are shown in Figure 12. In this environment there was no significant difference in activity between the three salts when compared on a weight % basis. The effect of increasing concentration of K_2CO_3 (added prior to charring) on the CO_2 gasification kinetics is illustrated in Figure 13. Reactivity generally increased with K_2CO_3 concentration, at least up to the 20% level, however, the effect on apparent activation energy was small.

Reaction between Alkali Carbonates and Carbon

When K_2CO_3 is heated with carbon in an inert atmosphere, a solid state reaction takes place between 600 and 900°C, depending on the particle size and extent of physical contact between the two phases. The products of this reaction are CO and potassium vapor which sublimates into the cooler parts of the apparatus. Figure 14 shows thermograms (weight changes vs. temperature) for K_2CO_3 -char and K_2CO_3 -graphite mixtures on heating in dry helium in the thermobalance at an increasing temperature of 10°C/min. In the case of graphite, loss in weight became marked above 800°C and the reaction was essentially completed at 1000°C. The char had a much larger surface area than the graphite and reaction with the salt began at about 600°C. This solid state reaction, which takes place in the gasification range, is believed to play an important role in the gasification of carbon with CO_2 or steam in the presence of the K_2CO_3 (10,14) as discussed in the next section.

DISCUSSION

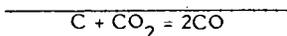
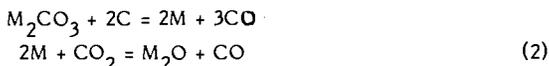
The reactivities of coal chars are obviously strongly influenced by a number of factors such as charring temperature and thermal history, pore size distribution and the presence of ubiquitous mineral impurities. However, the catalytic behavior of additives such as the alkali metal carbonates is similar for char and graphite and the same mechanisms probably operate in both cases.

The main effect of the salt catalysts (Figures 1,2,12,13) in both gasification reactions is to increase the pre-exponential factor of the rate equation. Changes in the apparent activation energy are small from catalyst to catalyst and on increasing the salt concentration. The most likely explanation of this effect is that the salt reacts with the char substrate to produce active sites on the surface where gasification can proceed. Increasing the amount of salt present increases the effective concentration of these active sites up to the point at which the surface becomes saturated.

A plausible mechanism which has been proposed previously (10,14,15) to account for the catalytic effects of Na_2CO_3 and K_2CO_3 in these reactions is shown in Table II. A common first

step, reaction (1) is suggested for both reactions, with the subsequent steps being different for CO_2 and H_2O as the gaseous oxidant.

C - CO_2 REACTION



C - H_2O REACTION

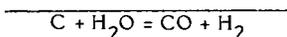
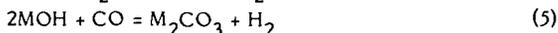
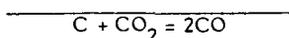


Table II: Carbon Gasification Catalyzed by Na_2CO_3 or K_2CO_3

Although reaction (1) possesses a positive free energy change at temperatures in the 600-1000°C range, at low partial pressures of CO the reaction can proceed rapidly, as shown by the TGA data in Figure 15. Figure 15 shows the equilibrium stability regions of K_2CO_3 and K(g) for reaction (1), calculated from free energy data, as functions of temperature and the partial pressures (in atmospheres) of K(g) and CO. The sloping lines at each temperature separate the region of stability of K_2CO_3 (upper left) from that of K(g) (lower right). An overall gasification rate of $5 \times 10^{-3} \text{ min}^{-1}$ (about the maximum attained in this study at 900°C) would give an ambient partial pressure of CO of about 10^{-3} atm. above the gasifying char sample. At this value of P_{CO} , and with a similar value of P_{K} , Figure 15 indicates that reaction (1) would be thermodynamically possible for all temperatures above about 800°C. At a temperature of 600°C the measured gasification rate, and the ambient value of P_{CO} , are about two orders of magnitude less than at 900°C and Figure 15 shows that reaction (1) is again possible for $P_{\text{K}} = P_{\text{CO}} = 10^{-5}$ atm. The steady state values of P_{K} reaction will in fact be much less than P_{CO} because of the occurrence of reactions (2) and (4). Direct evidence that reaction (3) does occur has recently been obtained by Wood et al.,⁽¹⁶⁾ using high temperature Knudsen cell mass spectrometry. On heating K_2CO_3 and carbon together at temperatures of 500°C and above, the evolution of K vapor and CO could be measured. Thus, reaction (1), which is inhibited by increasing amounts of CO in the gas phase, is probably the rate determining step in the case of the gasification reactions catalyzed by Na_2CO_3 and K_2CO_3 . Reactions (2) and (3) and also (4) and (5) have large negative free energy values at gasification temperatures and are thus favored thermodynamically, although little is known about their kinetics.

A somewhat different pathway probably operates in the case of the reactions catalyzed by Li_2CO_3 as Li_2O is more stable than the oxides of Na and K, also Li_2CO_3 is more easily hydrolyzed to hydroxide than the carbonates of Na and K. A possible sequence of reactions that might be involved in the catalysis process in the case of Li_2CO_3 is shown in Table III below. Evidence for the occurrence of these individual reactions is still, however, indirect and future efforts will be directed to exploring the catalytic process by the aid of isotopic tracers and in determining the relative rates of the elementary steps involved in the catalyzed gasification process.

C - CO₂ REACTION



C - H₂O REACTION

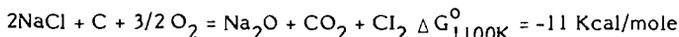


Table III: Carbon Gasification Catalyzed by Li₂CO₃

The above mechanistic schemes, although feasible for the alkali carbonates, cannot readily explain the observed catalytic activity of the alkali halides in these reactions. Such salts as KF, NaF and LiCl have been found to be moderately active catalysts for the gasification of both char and graphite in steam and CO₂. The route by which the alkali halides function as catalysts in these reactions is not clear at this point. Direct reduction of these salts to alkali metal by reaction with the carbon substrate seems unlikely on thermodynamic grounds. However, although the direct hydrolysis reaction



has a positive free energy change at gasification temperatures, appreciable and catalytically active concentrations of KOH might be formed in a flowing gas in which the partial pressure of HF is low. KF-char mixtures have, in fact, been observed to evolve appreciable amounts of HF during steam gasification,⁽¹⁸⁾ hence dissociation and hydrolysis of the KF salt evidently does occur in the presence of carbon and steam. In CO₂, the mechanism of catalysis by KF cannot be interpreted on this basis. It is interesting, however, that the alkali halide salts are also moderately active catalysts for the oxidation of carbon by molecular oxygen.⁽¹⁹⁾ On heating a mixture of graphite powder and pure KF in air at 900°C until the carbon was completely gasified, the residue was found by analysis to contain appreciable amounts of K₂O (2.4% by weight). A similar experiment with pure NaCl produced lower (0.4%) amounts of Na₂O. As no oxides could be detected in the original halide salts, the catalytically active alkali oxides may have resulted from the oxidation of the halides during the gasification of the carbon, possibly by a reaction of the type



though other halogenated species, such as HX, COX₂, HOX and the like could be formed in low concentrations.

CONCLUSIONS

The catalytic effects of alkali carbonates and other salts in the gasification of coal char and graphite in steam and CO₂ have been studied. Although the patterns of catalytic activity for the various additives were similar for both char and graphite, the reactivity of the char was influenced by factors such as charring temperature, porosity and the presence of mineral impurities.

On increasing the charring temperatures from 700°C to 900°C, there was a marked decrease in reactivity towards both steam and CO₂, presumably due to loss in porosity of the

char or annealing of active sites at the higher temperature. Non-porous graphite had a much lower surface area than the char and a lower reactivity, in the absence of catalysts. However, within a series of char samples prepared at the same temperature, there was no significant correlation between reactivity and surface area. In fact, surface areas were slightly reduced when salt catalysts were added to char samples, even though the reactivity was increased considerably. Also, the reactivity of the catalyzed samples proved not to be strongly dependent on the mode of addition of the catalyst and physical mixing of the salt with the pre-carbonized char was almost as effective as adding the catalyst prior to charring.

An observation of important practical implication was the progressive and rapid initial loss in catalytic activity during gasification at constant temperature and on thermal cycling between gasification temperatures and ambient. This effect, which was much more marked in steam than in CO_2 , appeared to be the result of reaction of the salt additives with mineral matter in the char to form stable inert silicates and aluminosilicates.

Thermodynamically feasible mechanisms for the alkali carbonate catalysts which involve sequences of oxidation/reduction reactions with the intermediate formation of alkali metal or oxides have been discussed. The moderate catalytic activity of certain alkali halide salts is however difficult to explain on this basis.

ACKNOWLEDGEMENT

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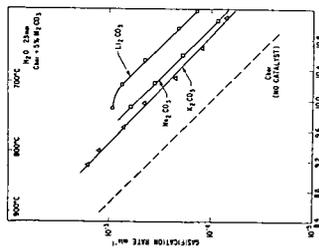


Figure 1 Catalytic effects of alkali metal carbonates on the gasification of coal char in water vapor. 3% salt added after charring at 700°C. Second cycle rate data vs. 1/T-K.

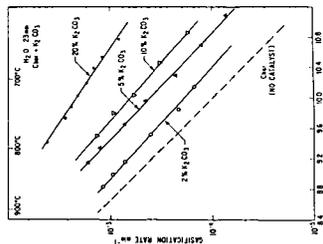


Figure 2 Effect of K_2CO_3 concentration on the rate of gasification of coal char in water vapor. Salt catalyst added after 700°C charring. Second cycle rate data vs. 1/T-K.

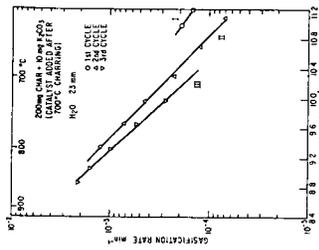


Figure 3 Gasification kinetics (rate vs. 1/T^oK) in water vapor for a 5% K_2CO_3 -doped char (salt added after charring), for three successive thermal cycles.

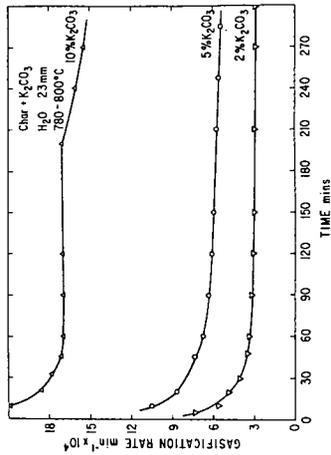


Figure 4 Gasification rates in water vapor vs. time at 800°C for a char with various concentrations of added K_2CO_3 .

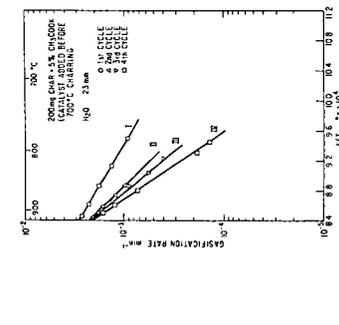


Figure 5 Gasification kinetics (rate vs. $1/T^{\circ}K$) in water vapor for a char containing initially 5% CH_3COOK (salt added before 700°C charring). Rates measured during four successive thermal cycles.

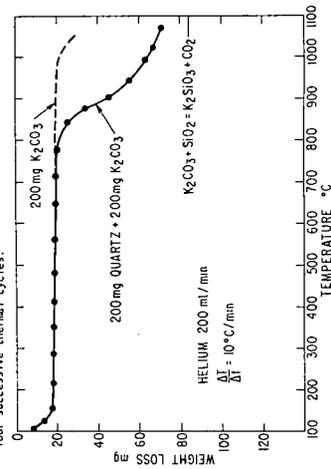


Figure 6 Thermograms (weight loss vs. temperature) for K_2CO_3 and a 1:1 quartz- K_2CO_3 mixture on heating in helium at 10°C/min.

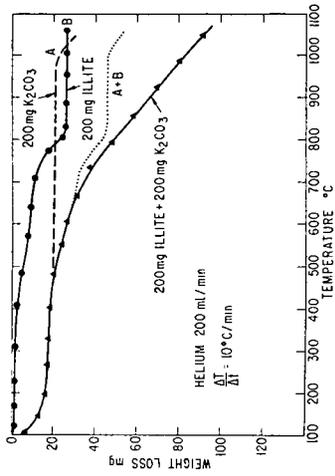


Figure 7 Thermograms (weight loss vs. temperature) for (A) K_2CO_3 , (B) Illite and an Illite- K_2CO_3 mixture on heating in helium at 10°C/min.

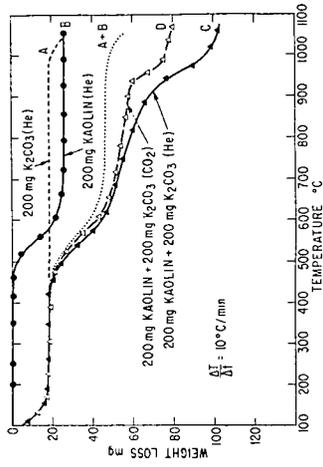


Figure 8 Thermograms (weight loss vs. temperature) for (A) K_2CO_3 , (B) kaolin and a kaolin- K_2CO_3 mixture on heating in helium (C) and CO_2 (D) at 10°C/min.

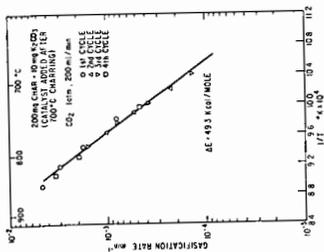


Figure 9 Gasification kinetics (rate vs. $1/T^{(0K)}$) in CO_2 for a char with 5% K_2CO_3 added after charring. Rates shown for four successive thermal cycles.

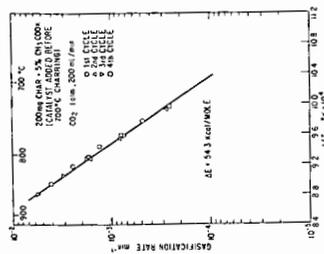


Figure 11 Gasification kinetics (rate vs. $1/T^{(0K)}$) in CO_2 for a char containing initially 5% K_2CO_3 (salt added before 700°C charring). Rates shown for four successive thermal cycles.

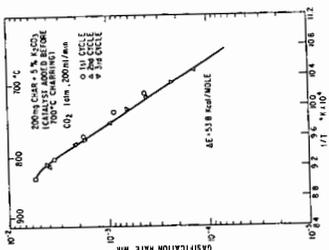


Figure 10 Gasification kinetics (rate vs. $1/T^{(0K)}$) in CO_2 for a char containing initially 5% K_2CO_3 (salt added before 700°C charring). Rates shown for three successive thermal cycles.

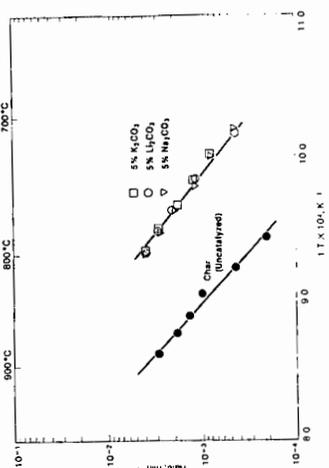


Figure 12 Gasification kinetics (rate vs. $1/T^{(0K)}$) in CO_2 for chars doped with 5% Li, Na and K carbonates (added prior to 700°C charring).

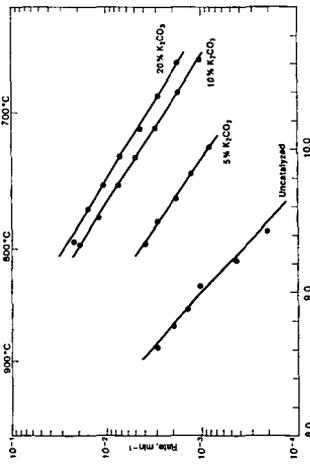


Figure 13 Gasification kinetics (rate vs. $1/T^2$) in CO_2 for chars doped with 5%, 10%, and 20% K_2CO_3 (added prior to 700°C charring).

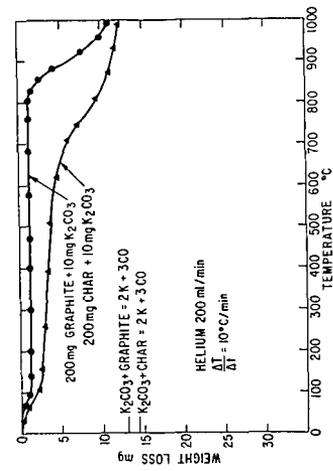


Figure 14 Thermogram (weight loss vs. temperature) for graphite-5% K_2CO_3 and char-5% K_2CO_3 , on heating in helium at 10°C/min.

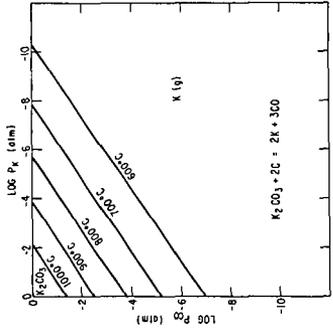


Figure 15 Equilibrium stability regions of $\text{K}(g)$ and $\text{K}(l)$ for the reaction $\text{K}_2\text{CO}_3 + 2\text{C} = 2\text{K} + 3\text{CO}$, as functions of temperature, P_{CO} and P_{K} .