Gasific.....n Rates as Related to Coal Properties

P. L. WALKER, Jr.
Department of Material Sciences, The Pennsylvania State University,
University Park, Pennsylvania

ABSTRACT

Workers in this laboratory have studied the reactivity of chars produced from a wide variety of U. S. coals varying in rank from Pennsylvania anthracites to western lignites. Over a 100 times increase in char reactivity is found as the rank of coal from which the chars are produced is decreased.

This major difference in char reactivity is explained on the basis of the prime factors promoting high carbon gasification rates, that is, high concentration of active carbon sites, good accessibility of the sites to the reactive gas, and substantial catalysis of the gasification reaction by inorganic impurities. Each of these factors is more favorable to the higher reactivities of lignite chars than the reactivities of chars produced from most eastern coals.

Approaches at increasing the reactivity of coals, such as using preoxidation, enhanced heating rates, lower charring temperatures, catalyst addition, and smaller particle size, are considered.

In this laboratory we have studied the reactivity of chars produced from a wide variety of U. S. coals varying in rank from Pennsylvania anthracites to western lignites. The coals usually have been heated to some maximum temperature at a heating rate of $10°C$ min^{-1} in an inert atmosphere, converting them to a char, prior to measuring gasification rates at a lower temperature.

In our studies we have measured the reactivity of chars, produced at $1000°C$, to 1 atm of air at $500°C$ (Ref. 1) and to 1 atm of CO_2 at $900°C$ (Ref. 2). Figure 1, summarizing these results, shows that char reactivity increases sharply as the carbon content (rank) of the
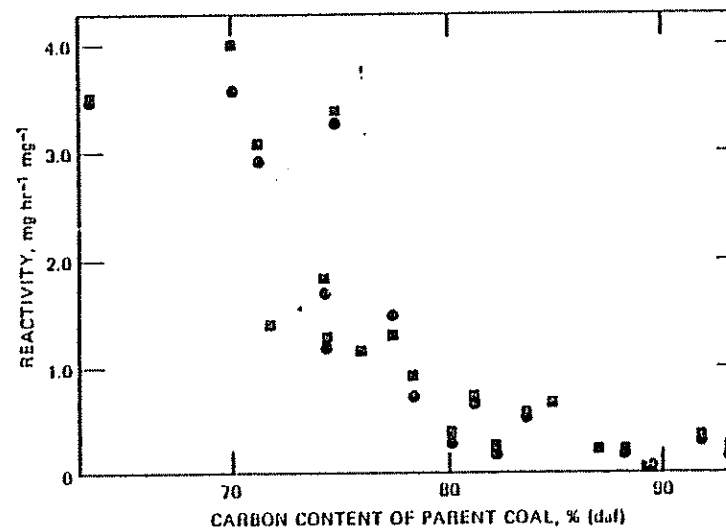
Fig. 1   Variation of reactivity of $1000°C$ chars produced from coals of different rank. ●, CO_2 at $900°C$.■, air at $500°C$.

parent coal decreases. The most reactive char, produced from a Montana lignite, gasified at a rate roughly 200 times greater than that for a char produced from a low volatile (Pennsylvania) bituminous coal. Figure 2 shows the correlation between char reactivity and the amount of CaO present in the char, strongly suggesting that gasification was being catalyzed by the presence of calcium.

It is instructive now to back off and consider the prime factors that promote high carbon gasification rates: (1) high concentration of active carbon sites, (2) good accessibility of the sites to the reactive gas, and (3) substantial catalysis of the gasification reaction by inorganic impurities.[3,4] Each of these three factors can be considered briefly.

Coals are composed of aromatic and hydroaromatic building blocks, containing more or less cross-links between the building blocks and functional groups at their periphery. Upon their heating to gasification temperatures, functional groups are removed as volatile matter, some cross-links are broken, and hydroaromatic building blocks are converted first to additional aromatic building blocks and then to small carbon crystallites. Breakage of cross-links permits improved alignment of the building blocks. Whether the char particles remaining have a more open or less open pore structure than that in the original coal depends upon a balance between additional
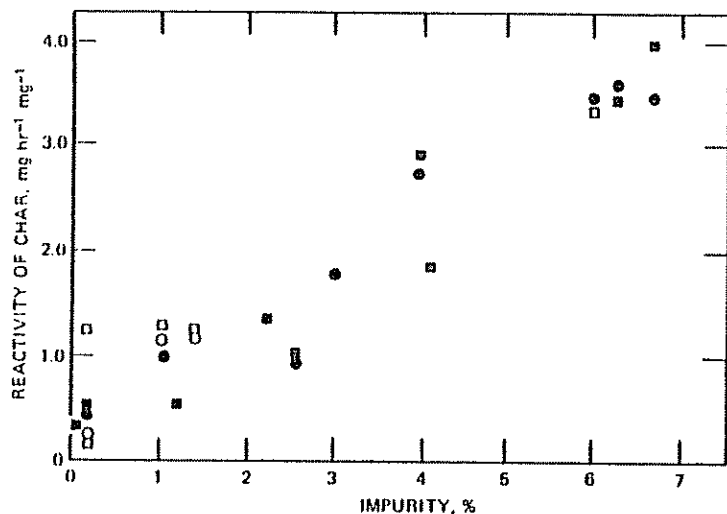
Fig. 2 Plot of CO_2 and air reactivities of $1000°C$ chars versus percentages (by weight) of CaO present in the chars. Closed and open symbols represent chars from original and acid-washed coals, respectively. ●○, CO_2 at $900°C$. ■□, air at $500°C$.

Fig. 3 The graphite crystal structure.

pore volume created by volatile matter release and loss of pore volume caused by enhanced alignment of the planar building blocks. The balance is a function of the rank of the starting coal, maximum heat-treatment temperature (HTT), and heating rate to maximum temperature, as we will see.

The first factor, that of *active sites*, on the small carbon crystallites, or those sites most reactive to gasification, is understandable from extensive studies on the reactivity of graphitic carbon. Figure 3 shows the graphite crystal lattice. The carbon atoms that are reactive to oxygen, CO_2, steam, and H_2 are those located at the edges of the basal planes. The ratio of such sites to the total number of carbon sites in the structure obviously increases as the crystallite (or building-block) size decreases.

Once the concentration of active sites in a char is established by the choice of starting coal and heating conditions, it is then of concern as to how well the sites will be utilized in gasification. The second factor, that of *active site utilization* in heterogeneous reactions, has been well developed as a concept by a number of workers and particularly considered for the gasification of porous particles of carbonaceous solids by Walker, Rusinko, and Austin.[3] The utilization factor, η, varies from zero to 1, where a value of 1
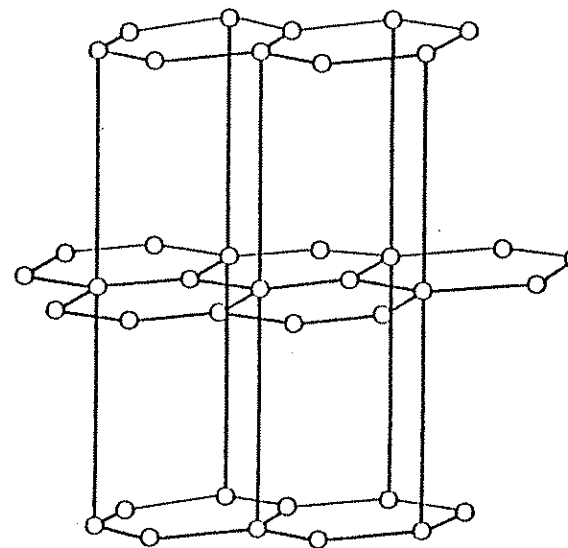
indicates complete utilization of active sites. That is, all active sites are "bathed" in the same concentration of reactive gas as that which exists in the main gas stream outside of the particles. It is obviously desirable for η to approach 1 as closely as is possible (and economically feasible). Its value is a balance between the resistance to the inherent chemical rate of the gasification reaction and the resistance to the mass transport rate of the reacting gas into the pores of the carbonaceous particle. The smaller the ratio of these two resistances, the smaller will be the value of η. This concept is shown quantitatively in Fig. 4 for the Arrhenius plot of log (reaction rate) versus reciprocal of temperature. The slope of the plot decreases with increasing temperature (as η also decreases) since the resistance to mass transport increasingly controls the overall gasification rate.

The third factor, that of *catalysis of the gasification reaction by inorganic impurities*, has a pronounced effect on gasification rates in the presence of inorganic impurities in the carbonaceous matrix. Many inorganic impurities are effective catalysts for dissociating molecular species into atomic or free radical species and thus enhance gasification rates. That is, the rate of gasification of an active carbon site is much more rapid in the presence of atomic oxygen or hydrogen than in the presence of molecular species containing these elements.
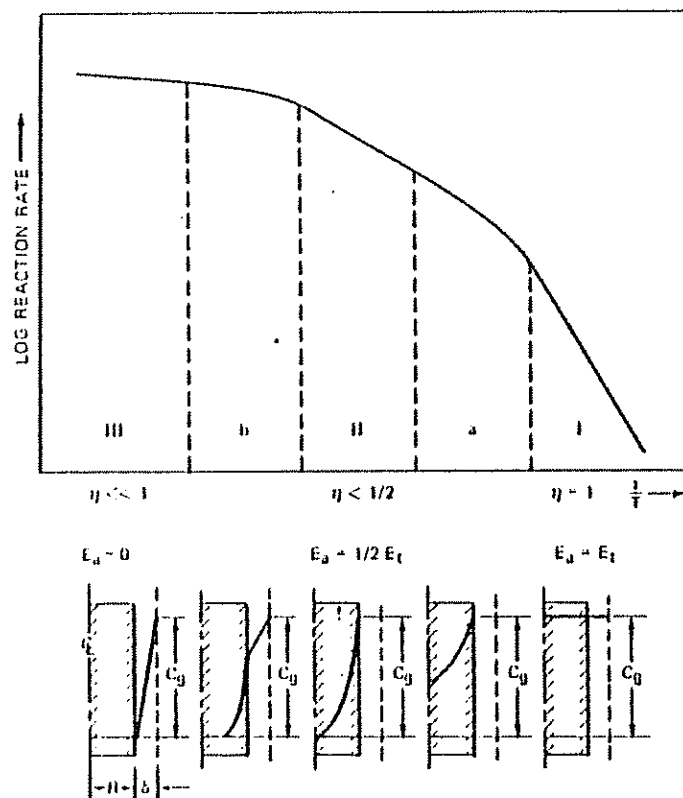
Fig. 4 Ideally the three zones representing the change of reaction rate of a porous coal char with temperature.

Considering the three prime factors affecting carbon gasification, it is now understandable why the reactivity of western lignite chars is much greater than that of chars produced from eastern (Pennsylvania) coals: First, it has been shown that the size of the building blocks decreases as the rank of coal decreases.[5] Thus, upon heat treatment, the size of the carbon crystallites in the lignite char is expected to be smaller than that found in chars produced from higher rank coals. As a result, the active site concentration should be a maximum in lignite chars. Second, as the rank of coal decreases, the amount of volatile matter released upon heat treatment generally increases. This results in a maximum increase in porosity within the chars and enhanced accessibility of the reactive gas to active sites. Thus the utilization of active sites (η) is increased. Increased accessibility to the internal porosity of chars with decreasing rank of

coal from which the char is produced is shown dramatically in Fig. 5, where specific surface areas as measured by N_2 adsorption at $77^{\circ}K$ are given. Third, as seen in Fig. 6, the CaO content of chars increases sharply as the rank of the precursor coal decreases. This results in enhanced reactivity for chars produced from low-rank coals, as was seen in Fig. 2.

In light of the above discussion, what can be done to enhance reactivities of chars produced from higher rank coals? We can consider briefly such possibilities as using: (i) higher gasification temperatures and reactive gas pressures, (ii) preoxidation, (iii) lower
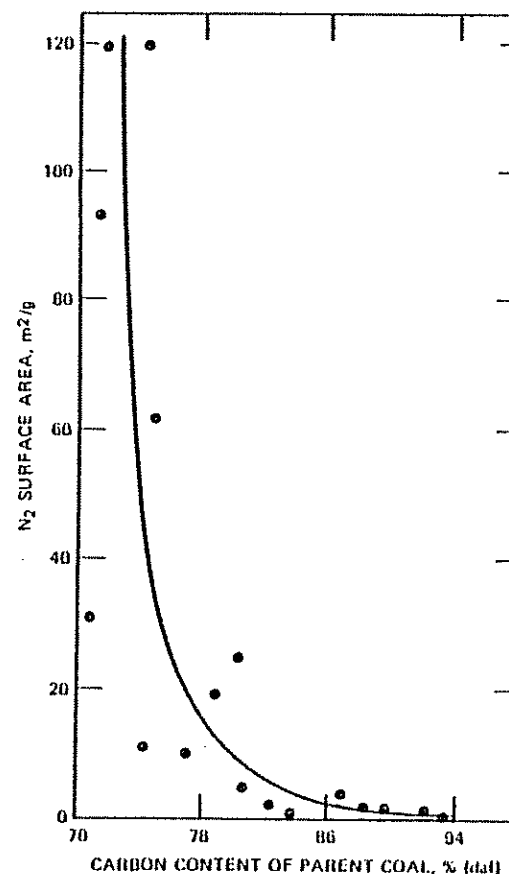

Fig. 5 Correlation between the N_2 surface areas of chars ($77^{\circ}K$) and the carbon content of the parent coals.
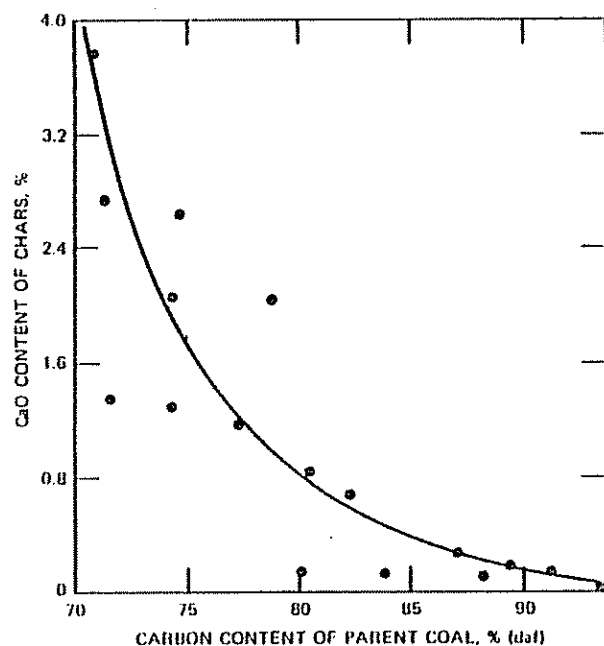
Fig. 6 Correlation between CaO content of chars and the carbon content of the parent coals.

charring temperatures, (iv) enhanced heating rates, (v) catalyst addition, and (vi) smaller particle size.

Consider possibility (i). The activation energies involved in the chemical step of carbon (char) gasification are substantial;[3] therefore increasing the reaction temperature is obviously a possible approach to be used to enhance gasification rates so long as the reaction is not limited primarily by mass transport or equilibrium. The only gasification reaction limited by equilibrium at reasonable temperatures is hydrogasification. At least up to some pressure(s), rates of gasification can also be increased by operating at higher reactive gas pressures.[3]

From the standpoint of costs of capital equipment and operation, however, it is desirable to conduct gasification reactions at as low a temperature and as close to atmospheric pressure as possible. The use of possibilities (ii) to (vi), which are discussed below, will enable us to do just that.

Consider possibility (ii). Many of the eastern coals behave as thermoplastic precursors when heated to 400 to 500°C. That is, the coals soften and their building blocks have high mobility to align,

resulting in much loss of surface area and active site concentration. The primary reason for the softening of the coals is thought to be that these coals have a low concentration of cross-links between the planar building blocks and/or the particular cross-links have relatively low thermal stability to breakage. Preoxidation of these coals in air at low temperatures (about 200 to 250°C) adds oxygen (ether) cross-links to the coal structure, producing a solid that behaves as a thermosetting material when taken to higher temperatures. The result is expected to be the production of chars with more open structures and higher reactivities.

Consider possibility (iii). Jenkins, Nandi, and Walker[1] have shown that coal char reactivity decreases as the HTT is increased. Such results are summarized in Fig. 7 for three chars. This phenomenon is attributed to a combination of decrease of accessibility of active sites, decrease in volatile matter content, and decrease in catalytic activity of inorganic impurities as a result of their sintering as HTT is increased. Thus it is important that chars not be taken to a temperature any higher than necessary if their reactivity (at some fixed temperature) is to be maximized.

Consider possibility (iv). Ashu has recently shown that the use of very high heating rates up to pyrolysis temperature can lead to substantial subsequent increases in char reactivity.[6] He studied the reactivity in air at 500°C of chars produced from a North Dakota lignite, following its heating at rates of 10°C min^{-1} and 8×10^3°C sec^{-1}. The results are summarized in Table 1. The use of the rapid heating rate to 800°C almost doubled subsequent char reactivity over that found when the slow heating rate was used. In fact, rapid heating to 800°C more than counterbalanced the use of slow heating to only 500°C, insofar as subsequent reactivity was concerned. Ashu found that rapid heating produced chars of higher surface areas, as measured by N_2 (77°K) and CO_2 (298°K) adsorption. However, the overall enhancement in reactivity is thought to be attributable to a combination of factors (including an increase in active surface area and in site accessibility) which are not completely understood at this time.

Consider possibility (v). Hippo has recently shown that the reactivity of chars produced from a Texas lignite can be further enhanced by the addition of more calcium.[7] Calcium was added to demineralized lignite (following its treatment in HCl and HF to remove most inorganic impurities) by exposing it to a solution of calcium acetate in water. Exchange occurs between the hydrogen of the carboxyl group on the lignite and the calcium ion. The amount of exchange was controlled by the molarity of the solution and its pH. Calcium was also added to the char produced from the
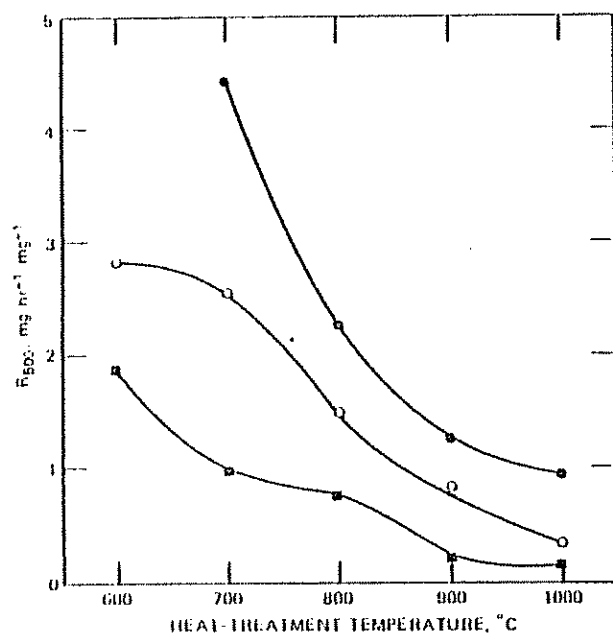
Fig. 7 Effect of temperature of heat treatment of selected chars on their air reactivity at 500°C. ●, char produced from lignite. ○, char produced from HVB bituminous. ◼, char produced from HVA bituminous coals.

TABLE 1

REACTIVITY OF PSOC-246 CHAR IN AIR AT 500°C FOLLOWING DIFFERENT HEAT TREATMENTS

Heat treatments	Reactivity, g hr^{-1} g^{-1}
10°C min^{-1} to 500°C	3.85
10°C min^{-1} to 800°C	2.79
8 x 10^{3}°C sec^{-1} to 800°C	5.17
10°C min^{-1} to 800°C followed by 8 x 10^{3}°C sec^{-1} to 800°C	3.10
10°C min^{-1} to 500°C followed by 8 x 10^{3}°C sec^{-1} to 800°C	4.89

demineralized lignite, following the addition of carboxyl groups to the char by its exposure to HNO_3. Figure 8 summarizes the results for the reactivity of chars in 1 atm of steam at 650°C following calcium addition. The 800°C char produced from the raw Texas lignite contained 2.3 wt.% calcium. Loadings on the char up to 12.9 wt.% calcium were effected. It is seen that char reactivity increased essentially linearly with an increase in calcium addition and that the maximum reactivity achieved was some 12 times greater than that of the char produced from the raw lignite.
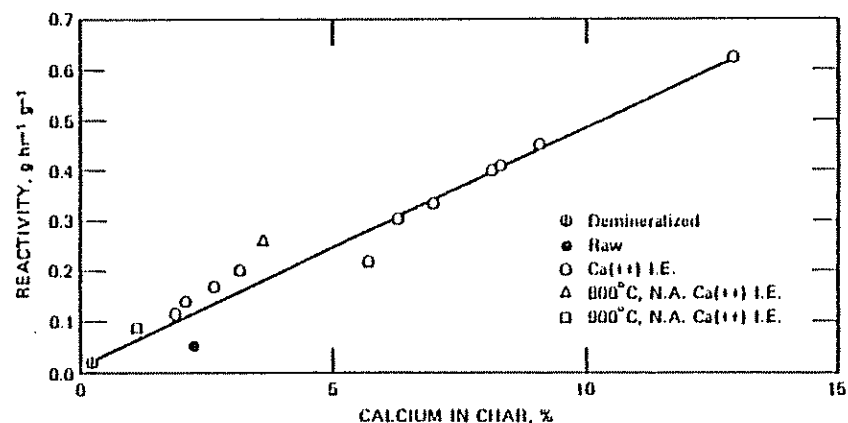

Fig. 8 Reactivities in steam at 650°C of (1) 800°C char prepared from calcium exchanged, raw, and demineralized coals and (2) 800 and 900°C chars prepared from selected nitric acid-treated chars.

Eastern coals lack the carboxyl group concentration onto which cation exchange can be easily accomplished. However, catalysts can be added to these coals by the adsorption of inorganic species onto the internal surface of the coal from salt solutions. In addition to catalyzing gasification, the added inorganic impurity may also act to tie up (during gasification) a portion of the sulfur present in the original coal.

Consider possibility (vi). It is well known that the limitation which mass transport can impose on gasification rates can be minimized by using increasingly smaller particle sizes in the reactor. For example, Hippo and Walker[2] show that the rates of gasification of a low volatile bituminous coal to CO_2 at 900°C can be significantly increased by reducing the particle size from 40 by 100

to 200 by 325 mesh. The gasification of ultrafine ground coals in entrained bed reactors could take advantage of this phenomenon.

As an extra bonus, the conduction of coal gasification concurrently with coal comminution may be attractive. That is, it is known that highly active sites are produced at the instant of particle breakage. The presence of a significant steady-state concentration of such sites could be expected to enhance the rate of gasification if it occurs simultaneously with particle breakage.

ACKNOWLEDGMENTS

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