The Scientific Base of Coal Gasification

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Editor's Note:

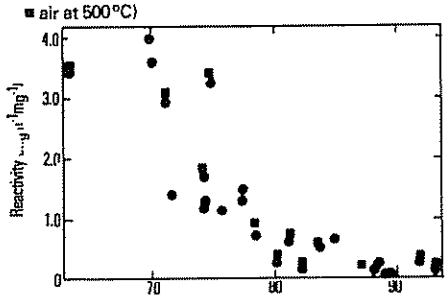
The Seminar on Combustion Technology that is conducted biennially at Pennsylvania State University by acknowledged experts in the field provides one of the most complete overviews on this subject. Organized and directed by Dr. Howard B. Palmer, in conjunction with outstanding associates, the Seminar, comprising selective in-depth material presented in a carefully planned week of activities at the Pennsylvania State University campus, is a rich and rewarding experience for all participants. The appropriate mix of assembled technological data, fundamental information from active researchers, and valuable pertinent operating practice from managers in industry, together with the interchange of experiences by those in attendance, refreshes one's point of view and stimulates new ideas that can be put into actual practice.

The recent seminar, July 25-29, with emphasis on coal combustion technology was particularly timely and significant. One of the valued contributions on the fundamentals of coal was made by P.L. Walker, Jr., Head of the Department of Material Sciences. Based on laboratory studies, Dr. Walker presented an extremely revealing paper on the principal factors that influence coal gasification. Because of the increasingly practical relevance of the structure of coal, his discussion of atomic changes and the potential advantages of controlling these changes through regulation of composition (such as calcium) and other factors (temperatures, heating rates, pressures and particle size and shape) should be of vital interest to all concerned with energy independence.

The reactivity of chars produced from a wide variety of U.S. coals varying in rank from Pennsylvania anthracites to Western lignites have been studied in the laboratory of the Department of Material Sciences. The coals usually have been heated to some maximum temperature at a heating rate of 10 °C/min in an inert atmosphere, converting them to a char, prior to measuring gasification rates at a lower temperature.

In these studies measurements have been made of the reactivity of chars, produced at 1000 °C, to 1 atm of air at 500 °C[1] and 1 atm of CO_2 at 900 °C.[2] A summary of these results, Fig. 1, shows that char reactivity increases sharply as the carbon content (rank) of the 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. Fig. 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.

Fig. 1 Variation of reactivity of 1000°C chars produced from coals of different rank. (• CO_2 at 900°C, ■ air at 500°C)



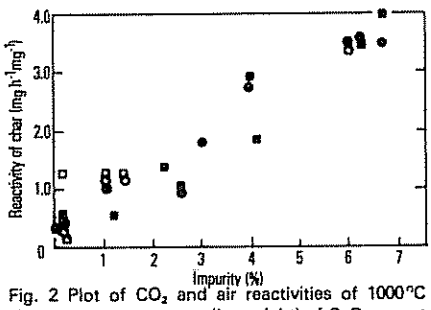


Fig. 2 Plot of CO_2 and air reactivities of 1000°C chars versus percentages (by weight) of CaO present in the chars. Closed and open symbols represent chars from original and acid-washed coals respectively. (• ○ CO_2 at 900°C, ■ □ air at 500°C)

Factors Promoting High Rates of Carbon Gasification

The prime factors promoting high carbon gasification rates are 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.[3,4]

Carbon Concentration

Coals are composed of aromatic and hydroaromatic building blocks, containing more or less crosslinks between the building blocks and functional groups at their periphery (Fig. 3). Upon their heating to gasification temperatures, functional groups are removed as volatile matter, some crosslinks are broken, and hydroaromatic building blocks are converted first to additional aromatic building blocks and then to small carbon crystallites. During devolatilization, rates of gasification are at their maximum (Fig. 4).[5] Breakage of crosslinks permits improved alignment of the building blocks. Whether the char particles remaining have a more open pore structure than that in the original coal depends upon a balance between additional 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.

Active Carbon Sites

The concept 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. Fig. 5 shows the graphite crystal lattice. The carbon atoms which 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 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 concept of **active site utilization** in heterogeneous reactions has been well developed by a number of workers and particularly considered for the gasification of porous particles of carbonaceous solids by Walker and co-workers.[3] The utilization factor, η, varies from zero to one, where a value of one 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

growth to 150 GWe in 1985; Japan expects to reach 50 GWe in 1985 and 90 GWe in 1990; in 23 less developed countries, growth may reach 150 GWe by 1990 and 350 GWe in 2000. In 1975, including reactors in the U.S. there were about 160 nuclear reactors generating almost 70 GWe. The total world-wide nuclear commitment in 1975, was over 600 reactors representing about 500 GWe. Clearly the demand for nuclear electric generation is already severe. Future world-wide nuclear energy needs emphasizes the fallacy of the U.S. to expect to rely on advanced foreign expertise and capability in building a future large scale industrial-utility-technical base. It is apparent that it is not too soon for a collective bringing together of minds to focus on ways to achieve successful LMFBR commercialization.

In addressing leaders in the steel industry at the 85th General Meeting of American Iron and Steel Institute, Robert C. Seamans, Jr., urged the recognition of nuclear energy as a well developed technology that must be used extensively. He also stated that the Government might be helpful in easing the steel industry energy burden in these areas: experimenting with coal-oil slurries to reduce steel industry combustion of petroleum and in improving current coal-gasification processes to produce fuel to be used in steel processing.

Synthetic Fuels — A Current Solution

Dr. Henry R. Linden, President Institute of Gas Technology, also believes that it is risky to abandon nuclear fission or "to even allow it to stagnate for a period" because it is a demonstrated alternative to crude oil and natural gas. However, he feels to gain sufficient lead time to develop longer range alternatives, full development of the world's coal and other solid fossil fuel resources and their utilization in environmentally acceptable ways through direct combustion and in the form of synthetic fuels and electricity is an essential although difficult step.

According to Institute of Gas Technology's new study and analysis of U.S. and world non-renewable energy sources, coal accounts for 84% of U.S. proved and current recoverable fossil fuel resources. Futhermore, U.S. coal reserves of 4.75Q considerably exceed the proved oil reserves of the Middle East, which are estimated to be 1.86 to 2.08Q. Various methods of using coal, especially for production of synthetic fuels,should be encouraged.

It is encouraging to hear of increasing industrial ventures into synthetic fuels; such as, the Conoco plant to be built in eastern Ohio; the design and engineering of a coal gasification plant by Dravo Corp.; Pittsburgh, Pa., being built by the Illinois Coal Gasification Group; the experimental coal to oil conversion plant built by Foster-Wheeler Corp. near existing ERDA facilities in South Park, Pittsburgh, Pa.; the coal to oil plant to be designed by Hydrocarbon Research Inc. and to be built in Catlettsburg, Ky.; and the Surface Div., Midland-Ross Corp., process for methanation of low Btu gas from gasification plants; etc.

The technology for use of gas from coal in industrial burners exists; ironically some of this knowledge was gained in U.S. work involved with the 2 billion dollar synthetic fuels facilities being built in South Africa.

Guidelines for Overall Energy Program

A large part of the difficulty in moving toward energy independence lies in chinks in the armor of a U.S. energy plan. It must be designed to overcome both government roadblocks and perils that could arise from special interest groups. The populace must recognize the danger of relying on oil imports; surely the adverse effect on U.S. economy and threat to independence is realized. There must be incentives for the oil and gas industry to spur production and greater exploration efforts. There must be rewards for investing in risk-laden drilling. Free market rates for energy must prevail. Private industry must recognize that only Government can provide the total resources and incentives required to stimulate capital risk. And emphasis must be shifted from conservation to new energy processes.

To guide President Carter and Congress in forging a national energy strategy, a 60-member panel of business and education leaders forming the Research and Policy Committee of the nonpartisan Committee for Economic Development (CED) recently offered these key elements: "(1) increased supply and greater conservation should be dual energy goals; (2) primary reliance should be placed on the market system; (3) the nation should expand its coal and nuclear power capacity; (4) work must be stepped up now in technologies for the next century; (5) energy-environment conflicts must be settled promptly and sensibly and (6) international cooperation should be strengthened".

Implications of Worldwide Energy Needs

According to Dr. Linden, and most qualified people in this field, conservation can only be important from the standpoint of providing some additional time delay for avoiding the inevitable crises. "No degree of politically tenable self-denial by the industrialized world will provide for the rapidly growing energy needs of the world". In the case of energy, no one country can afford to be independent.

The satisfying of world energy needs rather than American conservation is the significant consideration if the end of the world's golden age, stemming from soaring raw materials costs, exhaustion of oil and gas and governmental bankruptcies by 2070 (as depicted by Terry Dale of the Washington Post) is to be circumvented. Full development of the world's coal and other solid fossil fuel resources is crucial. Free industrialized nations must consider energy budgets similar to what is now invested in defense. Energy is defense!

One must face reality. In the past, shortages of critical commodities, energy among the foremost, has lead to war. To avoid a time inevitable holocaust, a solution to the world's growing energy needs must be provided. The United States with its existing technology, natural resources and capabilities can lead the way.

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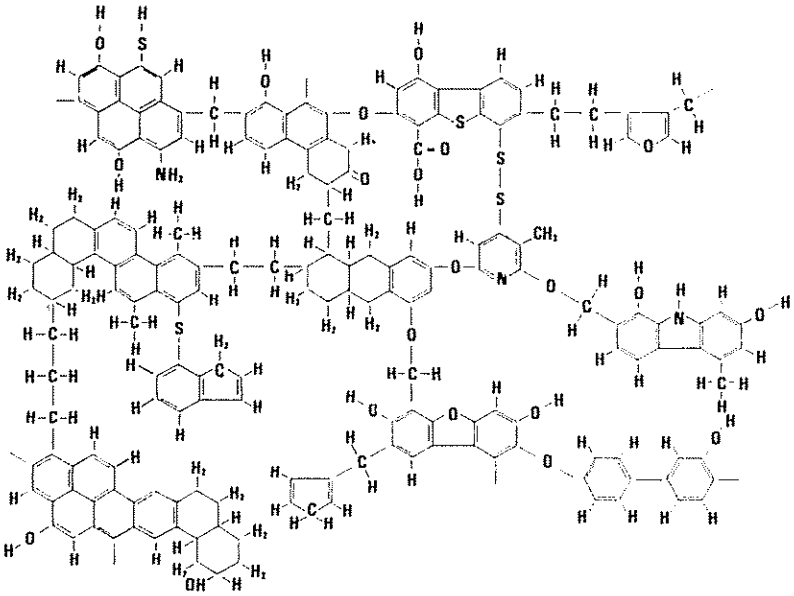


Fig. 3 A representation of bituminous coal structure.

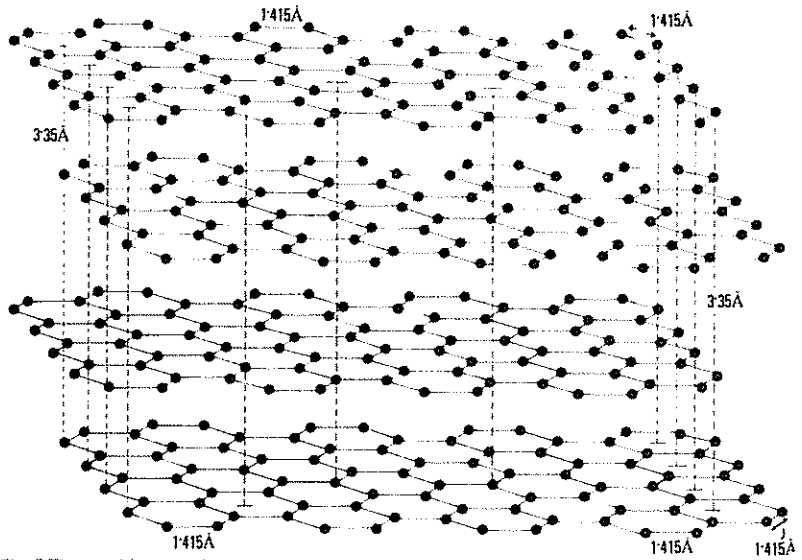


Fig. 5 The graphite crystal structure.

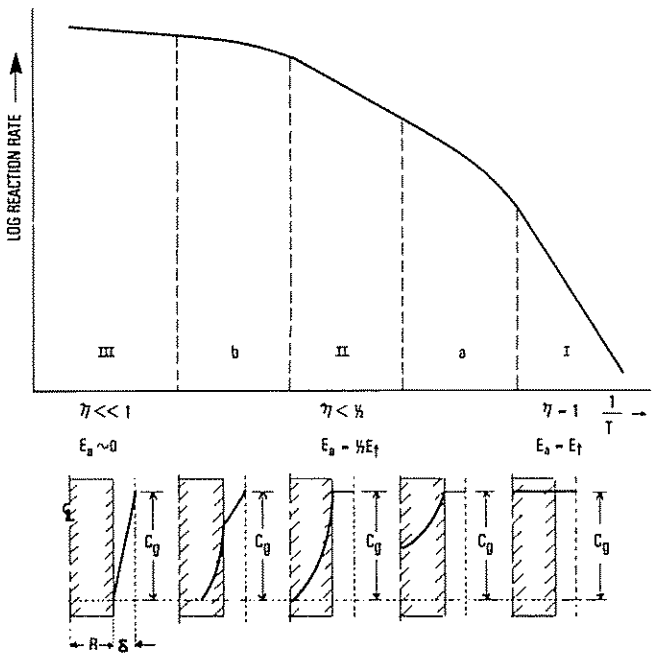


Fig. 6 Ideally, the three zones representing the change of reaction rate of a porous coal char with temperature.

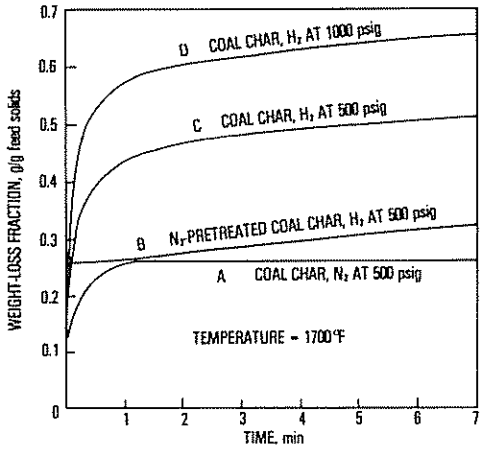


Fig. 4 Typical weight-loss curves obtained when a bituminous coal is injected rapidly into H_2 and N_2 atmospheres at 1700°F.

particles. It is desirable for η to approach one 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. 6, 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), as the resistance to mass transport increasingly controls the over-all gasification rate.

Impurities

The third factor which has a pronounced effect on gasification rates is 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, thereby, enhancing 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.

Summary of Influences of Prime Factors

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 (carbon content) of coal decreases.[6] 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. 7, where specific surface areas as measured by N_2 adsorption at 77 °K are given. **Third**, as seen in Fig. 8 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.

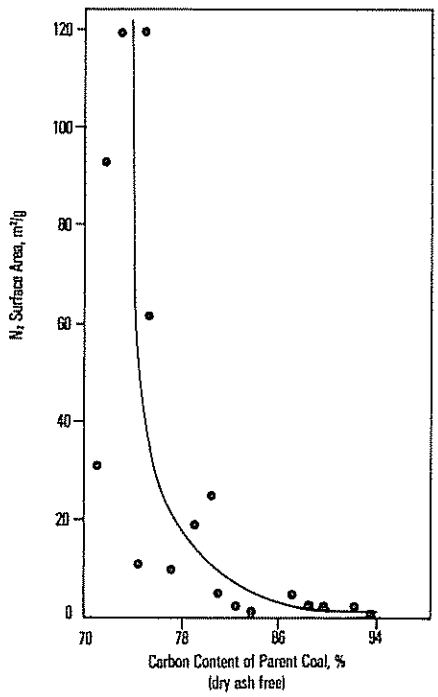


Fig. 7 Correlation between the N_2 surface areas of chars (77 °K) and the carbon content of the parent coals.

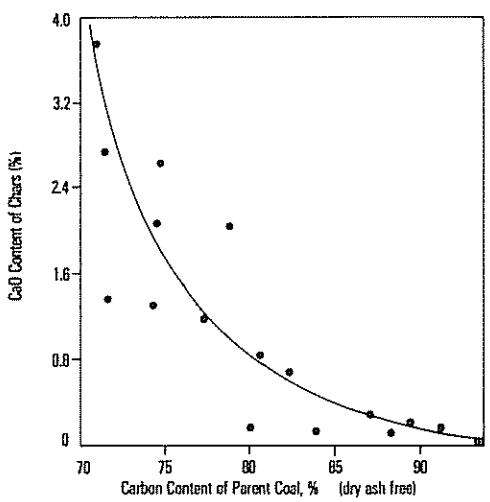


Fig. 8 Correlation between CaO content of chars and the carbon content of the parent coals.

Improving Reactivity

In light of the above discussion what can be done to enhance reactivities of chars produced from higher rank coals? Briefly considered below are such possibilities as using: (1) high gasification temperatures and reactive gas pressures, (2) preoxidation, (3) lower charring temperatures, (4) enhanced heating rates, (5) catalyst addition, and (6) smaller particle size.

(1) The activation energies involved in the chemical step of carbon (char) gasification are substantial;[3] and, therefore, increasing 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 hydro-gasification. 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 (2) - (6), will enable operation under these favorable conditions, as discussed in the following paragraphs.

(2) Many of the Eastern coals behave as thermoplastic precursors when heated to 400-500 °C. That is, they soften and their building blocks have high mobility to align, resulting in much loss of surface area and active site concentration. The primary reasons for their softening are thought to be that these coals have a low concentration of crosslinks between the planar building blocks and/or the particular crosslinks have relatively low thermal stability to breakage. Preoxidation of these coals in air at low temperatures (about 200-250 °C) adds oxygen (ether) crosslinks to the coal structure, producing now a solid which behaves as a thermosetting material (not conducive to change) when taken to higher temperatures. The result is expected to be the production of chars with more open structures and higher reactivities.

(3) Jenkins and co-workers[1] have shown that coal char reactivity decreases as the HTT is increased. Such results are summarized in Fig. 9 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.

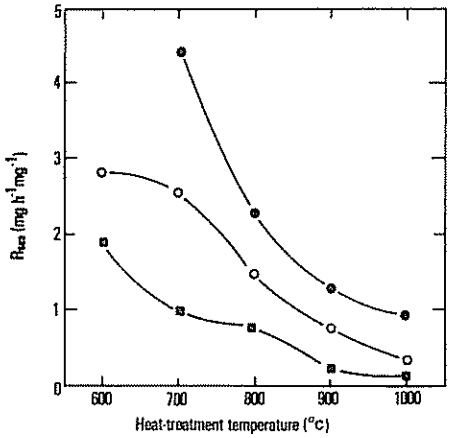


Fig. 9 Effect of temperature of heat treatment of selected chars on their air reactivity at 500 °C. Chars produced from • lignite, O HVB bituminous, ▣ HVA bituminous coals.

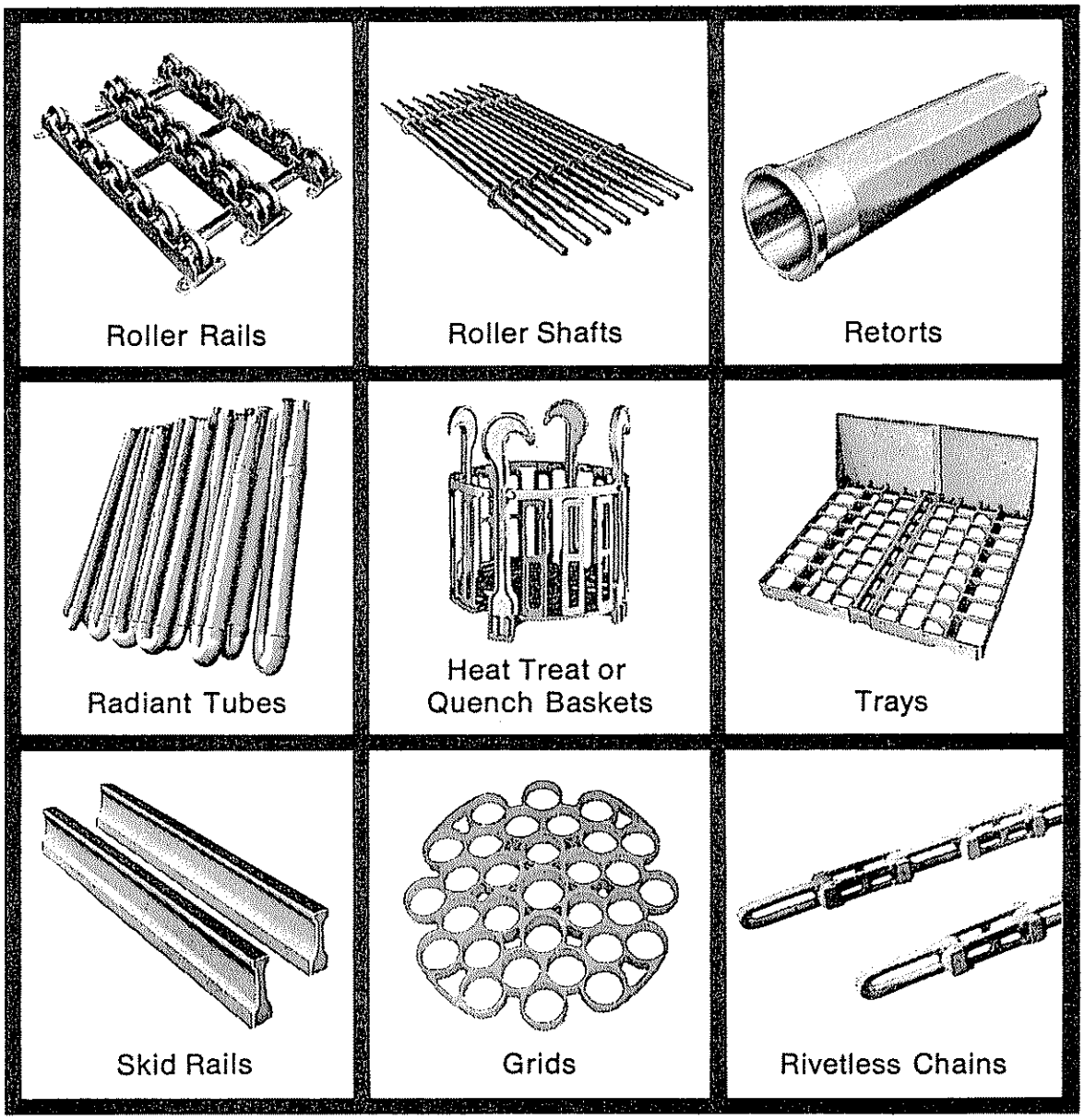
(4) Recently, Ashu has shown that the use of very high heating rates up to pyrolysis temperature can lead to substantial subsequent increases in char reactivity.[7] He studied the reactivity in air at 500 °C of chars produced from a North Dakota lignite, following its heating at rates of 10 °C/min and 8×10^3 °C/sec. Results are summarized in Table I. 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. But the over-all enhancement in reactivity is thought to be attributable to a combination of factors (including increase in active surface area and site accessibility) which are not completely understood at this time.

Table I
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 to 500°C	3.85
10°C/min to 800°C	2.79
8×10^3°C/sec to 800°C	5.17
10°C/min to 800°C followed by 8×10^3°C/sec to 800°C	3.10
10°C/min to 500°C followed by 8×10^3°C/sec to 800°C	4.89

(5) Recently, Hippo has shown that the reactivity of chars produced from a Texas lignite can be further enhanced by the addition of more calcium.[8]

Heat Treat Equipment Parts For Temperatures Up To 2300°F



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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 demineralized lignite, following the addition of carboxyl groups to the char by its exposure to HNO_3. Fig.10 summarizes results for 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% calcium, by weight. Loadings on the char up to 12.9% calcium, by weight, were effected. It is seen that char reactivity increased essentially linearly with 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.

Eastern coals lack the carboxyl group concentration on to 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.

(6) It is well known that the limitation which mass transport can impose on gasification rates can be minimized by using increasingly smaller 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 reduction of particle size from 40x100 to 200x325 mesh. Advantage of this phenomenon could be taken by gasification of ultra-fine ground coals in entrained bed reactors.

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.

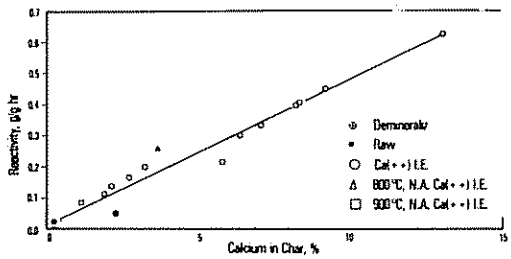

Fig. 10 Reactivities in steam at 650°C of 800°C char prepared from calcium exchanged, raw, and demineralized coals and selected nitric-acid treated 800°C and 900°C chars.

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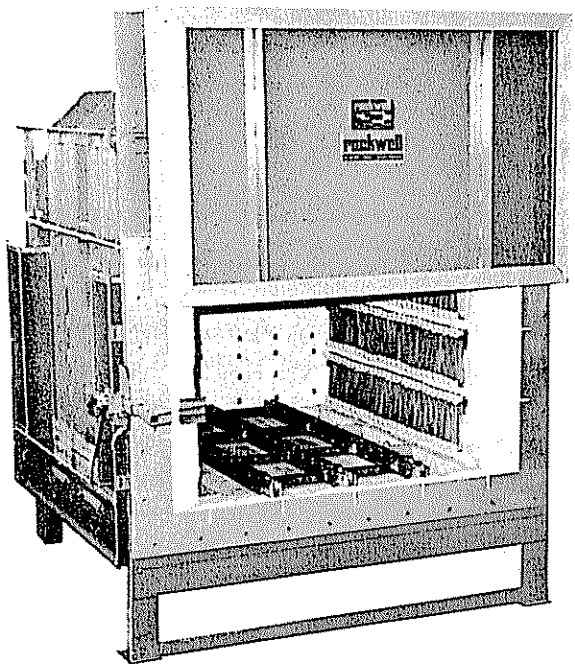

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