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REACTIVITY OF HEAT TREATED CHARS

Technical Report 8

Prepared by

O.P. Mahajan and P.L. Walker, Jr.
at
THE PENNSYLVANIA STATE UNIVERSITY

ENERGY RESEARCH & DEVELOPMENT ADMINISTRATION
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HEAT TREATED CHARS

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COAL RESEARCH SECTION
THE PENNSYLVANIA STATE UNIVERSITY
UNIVERSITY PARK, PENNSYLVANIA 16802

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ABSTRACT

Reactivities of a number of chars produced from American coals varying in rank from lignite to anthracite have been measured in air, CO_2, steam and H_2. The variables chosen for the study were: rank of the parent coal, inorganic matter content, particle size, reaction temperature and pressure as well as heat treatment conditions used during char preparation. In all gasification atmospheres studied, reactivity plots for different chars are essentially of the same general shape and have three distinct regions. The reaction rate first increases slowly with time. The plot then goes through a maximum in slope, followed by a lengthy region of decreasing slope as burn-off approaches 100%. The shape of the burn-off curves can be explained on the basis of what is known about the development of porosity and surface area in microporous chars as they undergo gasification. Using an adjustable time parameter, equations have been developed which successfully correlate the reactivity data.

Char reactivity decreases, in general, with increase in rank of the parent coal. Reactivities of chars in air, CO_2 and steam increase over 150-fold in going from a low volatile bituminous to a lignite parent coal; the spread in char reactivities in H_2 is only 30-fold. Removal of inorganic matter from coal precursors prior to their charring or from chars produced from the raw coals has a marked effect on char reactivity and surface area. Removal of inorganic matter (by acid washing) decreases, in general, reactivity of chars produced from lower rank coals, whereas reactivities of chars derived from higher rank coals increase. Reactivity in steam of chars produced from a lignite is further enhanced by the addition of exchangeable potassium, sodium and calcium ions. For the less reactive

higher rank chars, a decrease in particle size results in a significant increase in reactivity.

Reactivity of a char is higher the lower the maximum heat treatment temperature (HTT) used during carbonization of the precursor coal, the higher the heating rate to maximum HTT, and the shorter the soak time at maximum HTT. In order to maximize reactivity during the early stages of gasification, it is desirable to devolatilize coal in the presence of the reactant gas.

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PREFACE

As part of the present contract, we have been assigned the responsibility of measuring reactivities of coal chars to oxygen, steam, carbon dioxide and hydrogen and attempting to correlate reactivities with measurable physical and chemical properties of the chars. Thus, we have been concerned with the possible ways to measure reactivities and then how best to express the experimental results by a meaningful number. This is an on-going program; thus, this report represents our efforts at pointing out some of the problems and suggesting some meaningful measurements which can be made at this time.

During gasification from zero to complete carbon burn-off, the solid is constantly changing with time. That is, its total surface area, active surface area, total pore volume, pore volume distribution, and, possibly, the chemical and physical form of the inorganic impurities present are changing. Since the properties of the solid are changing with time, it is to be expected that the reactivity of the solid remaining is also changing with time. Therefore, not only is there a challenge in understanding why reactivities of coal chars vary with the rank of the precursor coal used, but a challenge also exists in understanding the change in reactivity of a given coal as it proceeds through a reactor (increasing burn-off). Such information is vital if mathematical modelling of coal gasifiers is to be successful.

Since coals and their coal chars are quite heterogeneous materials, both physically and chemically, not only does the reactivity of chars vary with degree of their burn-off, but also the relations between weight loss, composition of the gases produced, and heat of reaction vary. Thus, the authors conclude that more studies should be performed in which all these measurements are made on the same char-gas reaction. In this way, we have the best chance of understanding the gasification process and, hopefully, how to maximize reactivity by altering char structure and surface characteristics in a controlled way.

Lastly, the reader is urged to look carefully at under what conditions reactivities were measured when reported in the literature. They can be a function of char particle size, gas flow rate, as well as the extent of carbon burn-off.

I. INTRODUCTION

The importance of the conversion of coal to gaseous fuels has had a curious history in the United States. In the first half century, the production of low and medium BTU gas via reactions with steam, air, and CO_2 was of considerable importance as a source of energy for industry and the home. The coals primarily used were obtained from the bituminous and anthracite deposits. But with the abundance of cheap natural gas in the 1950's and 1960's, coal gasification plants became dormant.

Interest in coal gasification has suddenly been revived, initially because of interest in the production of synthetic natural gas and lately also because of the realization that industry will again need low and medium BTU gas produced from coal. The interest not only encompasses the coals of the eastern United States but also, in a most significant way, focuses on the western sub-bituminous and lignite deposits. Interest in the western coals is stimulated by their high reactivity as well as their abundance.

Ironically, perhaps, even though there was little interest in coal gasification processes and research between the 1950-1970 period, during this time we probably obtained our greatest understanding of the fundamentals of the gasification of carbon. The impetus for this understanding was concern about the gasification of moderator graphite used in high temperature gas-cooled nuclear reactors. These studies have given us the scientific base to better understand the gasification of more complex coal-derived chars. In fact, we now understand the major factors which affect gasification rates. In a later section we will consider approaches to measure gasification rates and then discuss how rates which are found to be widely different for coal-derived chars depend on measurable properties of the chars.

II. EXPERIMENTAL MEASUREMENT OF REACTIVITY

When microporous coals are thermally heated, they lose volatile matter, planar regions grow in size, and crosslinks are broken. The heat treatment of coals invariably results in the production of some kind of coke or char*. The structure of a char and, hence, its reactivity are influenced in a complex manner by a number of variables such as: heating rate, maximum heat treatment temperature (HTT), soak time at maximum temperature, atmosphere under which heating occurs, particle size, inorganic impurities present and their distribution in the coal precursor, maceral composition, and whether the coal behaves as a thermoplastic or thermosetting material. In order to have a meaningful comparison of char reactivities in different gasification atmospheres, we have used in this laboratory the same set of chars derived from the same size fraction (40x100 mesh) of coals of different rank. Non-caking coals were carbonized in a fluidized bed reactor, while the caking coals were carbonized in a horizontal tube reactor. In each case, coals were heated at a rate of 10°C/min to 1000°C. An inert atmosphere of N_2 was used during heat treatment. Soak time at 1000°C was 2 hr. Chars prepared from non-caking and weakly caking coals were used as such, whereas chars prepared from strongly caking coals were reground and 40x100 mesh fractions used for reactivity measurements.

When a thermobalance is used for reactivity measurements, the chars can be prepared from the coal precursors in the thermobalance itself.

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*If upon heating the coal precursor goes through a liquid state, the resulting solid is termed a coke. If, however, negligible softening occurs, the resulting solid is termed a char. For convenience, we have used the term char throughout this report.

Jenkins et al. (1973) found that the reactivity of a char to air (1 atm) at 500°C was essentially the same whether the char was prepared in the thermobalance or in a fluidized bed reactor under identical conditions. Chemisorption of oxygen on freshly prepared chars upon exposure to air, even at ambient temperature, can result in significant alteration of char pore structure, which in turn might affect its subsequent reactivity. Therefore, in order to desorb the chemisorbed oxygen, the chars prepared in the fluidized and horizontal tube reactors must again be heated, prior to reactivity measurements, in an inert atmosphere up to the maximum HTT used during the char preparation.

Reactivities of chars can be measured by the methods (techniques) discussed below.

A. By Weighing

There are a number of commerical Thermo Gravimetric Analyzer (TGA) units available to measure weight changes during chemical reactions. Each unit comprises basically two components--an electrobalance having a sensitivity in the microgram range and a linear temperature programmer. In this laboratory, we have used two different TGA units for reactivity measurements: a Fisher TGA unit, Series 300, and a DuPont 951 TGA unit. The two units can handle maximum loads of 2.5 and 1.0 gm, respectively. However, the starting weight of a char used for reactivity measurements is usually a few milligrams (<10 mg). This is because under the chosen experimental conditions,char reactivity should be independent of bed depth (weight). That is, resistance for diffusion of reactant gas molecules down through the bed should be minimal.

For most of the reactivity studies in this laboratory, we have used a Fisher TGA system. Therefore, we will describe in detail the experimental procedure followed for this particular unit. However, with minor modifications the procedure should be valid for other TGA units. For reactivity measurements, the char sample is contained in a platinum pan which in turn is supported by a nickel hangdown wire connected to one end of an electrobalance. The thermocouple can be adjusted manually; it is maintained at a fixed position, approximately 1 mm below the sample pan. To allow for a controlled atmosphere during the experimental run, a quartz tube is positioned around the hangdown wire and sample. For heating, a sample furnace is positioned around the quartz tube.

In the TGA unit, gases can be introduced through the conventional inlet which is located at the rear of the balance chamber (the chamber has a volume of about 4 ℓ) or through the conventional outlet which is located in the thermocouple assembly; this assembly can be connected to the quartz reactor through a ground glass joint. When the former flow system, referred to as downward flow system in the text, is used during reactivity measurement, the gasification rates obtained may be erroneous due to the following reason. During a reactivity run when N_2 (used during preheat treatment of the sample) is replaced by the reactant gas at the reaction temperature, a volume of about 4 ℓ of N_2 need to be displaced by the reactant gas. This means that until the outlet gas concentration equals the inlet reactant gas concentration, the char will be gasified at progressively increasing partial pressures of reactant gas. Since gasification rates are dependent upon partial pressures of reactant gas, as will be shown later in this chapter, the char reactivity measured in varying partial pressures of reactant gas will be different from that measured in the 'pure' reactant gas, that is, in the absence of dilution of reactant gas by N_2.

Due to the aforementioned considerations, Soledade (1976a) used the conventional gas outlet in the TGA unit as the inlet for introducing gases. Using this flow system (referred to as upward flow in the text), the volume of N_2 to be displayed by reactant gas, before the char sample 'sees' inlet pressure of reactant gas, is less than 50 cm^3/min. In our reactivity work, we have used a gas flow rate of 300 cm^3/min. Thus, when N_2 is replaced by reactant gas, it will take less than 1 min to displace N_2. The gases were vented off through a port located below the weighing chamber. During reactivity runs, N_2 is continuously passed through the weighing chamber to avoid any possible damage to the weighing mechanism from the hot and/or corrosive product gases; N_2 is vented off to atmosphere through the same port as that used for the reactant gas.

Soledade (1976a) used the following procedure to measure char reactivity. Prior to making reactivity runs, the system was flushed with N_2 (300 cm^3/min) for 30 min to displace the air present. The char sample was then heated (at a rate of 20°C/min) from ambient to the maximum HTT seen by the char during its preparation and held at this temperature until sample weight became essentially constant. During heat treatment, the char lost weight due to desorption of chemisorbed oxygen as CO and CO_2*. Following heat treatment, the char sample was cooled to reaction temperature at a rate of 20°C/min. The char was held at reaction temperature for 20 min to allow for temperature stabilization. Nitrogen was then replaced by the reactant gas at the same flow rate. Changes in sample weight due to gasification were then recorded on a strip chart recorder as a function of time.

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*During heat treatment, the char also showed an apparent weight loss due to buoyancy effects. Sample weights prior to onset of gasification at the chosen reaction temperature were corrected for buoyancy effects.

The effect of gas flow system used during reactivity measurements is illustrated by burn-off versus time plots (Figure 1) obtained for a Texas lignite char when it is reacted with air (1 atm) at 500°C. It is seen that at any stage gasification rate is appreciably greater when the upward gas flow system is used instead of the conventional flow system. These results bring out clearly the importance of using the proper gas flow system to obtain unambiguous gasification rates.

Because of the large effect of temperature on rates of char gasification, it is critical to always closely duplicate positioning of the thermocouple relative to the sample pan. Soledade (1976b) has suggested that the TGA system be calibrated by determining the temperatures corresponding to the decomposition of hydrated calcium oxalate ($CaC_2O_4 \cdot 2H_2O$) to CaC_2O_4, $CaCO_3$ and CaO.

The carbon-hydrogen reaction is thermodynamically the least favorable gasification reaction (Walker et al., 1959). Conversion to methane is enhanced at high pressures. In this laboratory, the char-hydrogen reaction was studied at 980°C and a H_2 pressure of 400 psi (Tomita et al., 1977). It was ascertained that under these conditions the reaction was not limited by equilibrium.

Tomita et al. (1977) used a DuPont 951 TGA balance, in conjunction with a 990 Thermal Analyzer, to monitor weight changes during the hydrogasification reaction. A schematic diagram of the balance and the gas flow system used is shown in Figure 2. A platinum pan (6x7x5 mm) containing about 10 mg of char was suspended from the quartz beam of the balance. The flexible end of the chromel-alumel thermocouple, which is attached to the balance housing, was placed in close proximity to the sample. The reactor was made of a quartz tube (25 mm, OD), with a

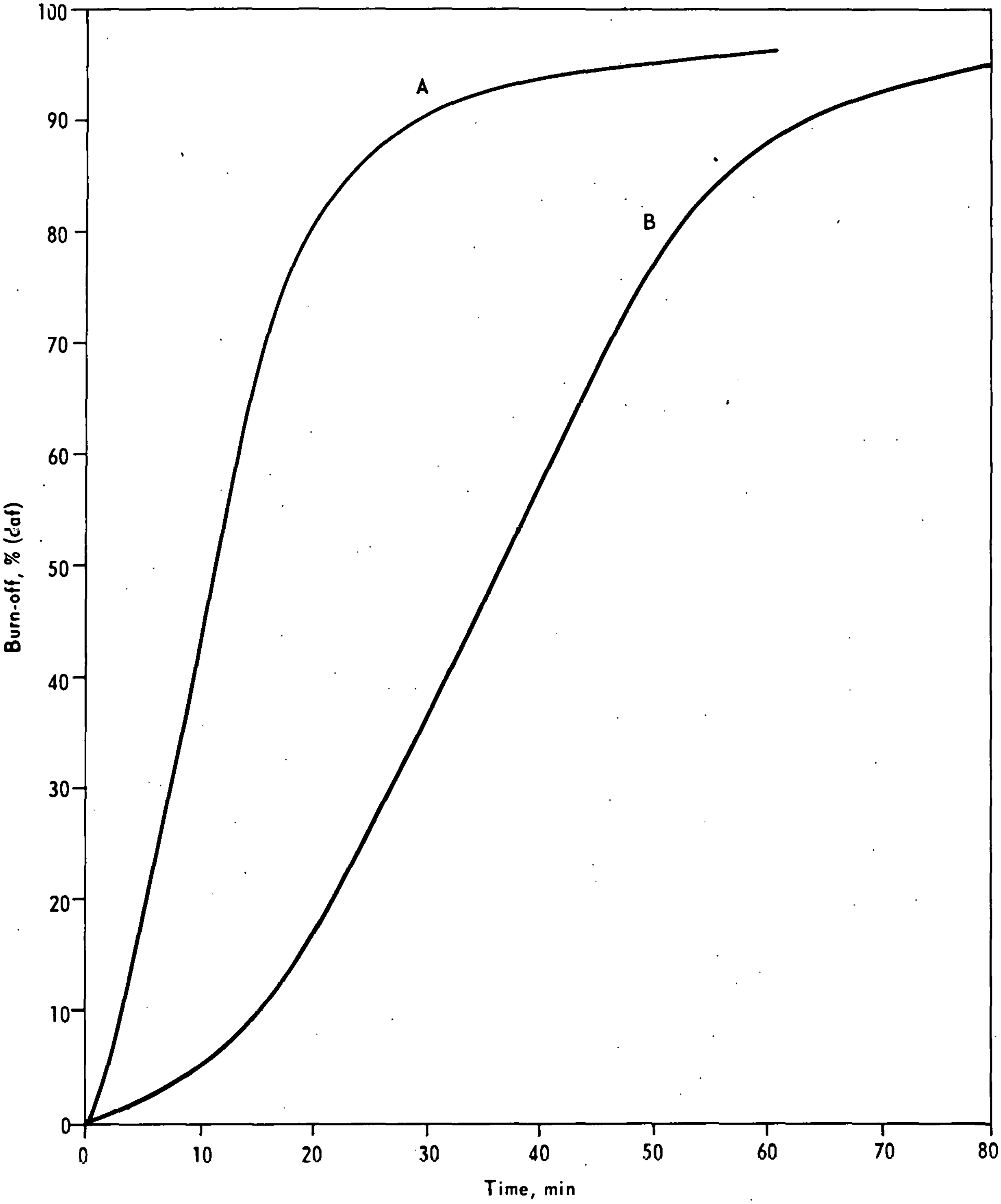

Figure 1. EFFECT OF GAS FLOW SYSTEM ON REACTIVITY OF A LIGNITE CHAR IN AIR AT 500°C AS MEASURED IN A TGA UNIT
A, upward flow; B, downward flow
Effect is related to amount of N_2 to be displaced before obtaining an air environment.
From Soledade (1976b)

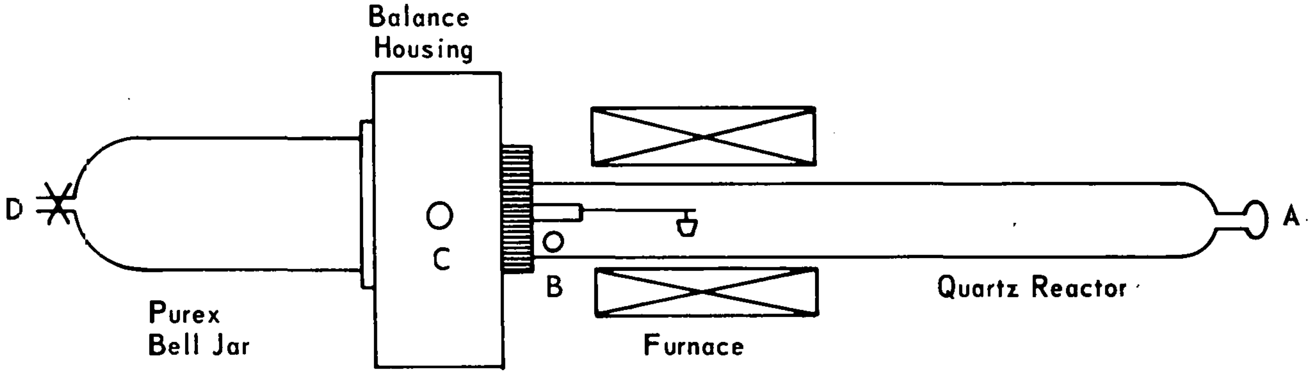

Figure 2. SCHEMATIC DIAGRAM OF A HORIZONTAL TGA BALANCE USED TO MEASURE GASIFICATION RATES AT ELEVATED PRESSURES IN AN AUTOCLAVE

reduced end on one side and an aluminum retainer ring on the other side, which fitted into the balance housing. The H_2 flow was divided into two parts. The gas entered through inlets A and C and was vented through outlet B; this outlet is a hole in the reactor tube near the metal ring. Outlet D was always kept closed. The volume of the quartz reactor tube was reduced to a minimum to ensure a rapid replacement of the inert atmosphere by H_2. The reactor tube was surrounded by a tube furnace* (wound with molybdenum wire) of ID only slightly greater than the OD of the reactor tube. The balance assembly along with the reactor and furnace were mounted in a carbon steel pressure vessel (built by Autoclave Engineers, Erie, Pa.) which was provided with a quick opening door with Conax pressure-seal outlets. After introducing the sample, the pressure vessel was closed and evacuated, following which it was pressurized with N_2 to 400 psi. Helium at 400 psi was introduced into the reactor at a flow rate of 1.2 ℓ/min (STP). After a period of 15 min, the furnace was activated to raise the sample temperature to 980°C for 15 min to ensure thermal stability. At this stage, helium in the reactor tube was replaced by H_2 at 400 psi at the same flow rate. Sample weight was then continuously recorded. The volume of the reactor tube was about 120 cm^3. Therefore, using a flow rate of 1.2 ℓ/min (STP) or 41 cm^3/min at 400 psi, it took about 3 min to displace helium by H_2 over the char sample. In all reactivity measurements, starting time for the reaction was considered to be when helium was displaced by H_2.

Tomita et al. (1977) ascertained in a few preliminary runs that the use of a quartz bucket for a given char gave essentially the same weight losses at different reaction times as the use of a platinum bucket,

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*The DuPont furnace (which is an integral part of the TGA system) is a low capacity furnace. It was found to be ineffective to raise the sample temperature to the desired reaction temperature, that is 980°C, at a H_2 pressure of 400 psi.

indicating that the platinum bucket catalyzed the hydrogasification reaction to a negligible extent.

Johnson (1974) used a thermobalance to study the kinetics of bituminous coal char gasification with gases containing steam and hydrogen at pressures between 1-70 atm and reaction temperatures in the range 815-1093°C. The apparatus is shown schematically in Figure 3. The coal sample (20x40 mesh) was contained in the annular space of a wire mesh basket bound on the inside by a hollow stainless steel tube and on the outside by a wire mesh screen. In order to facilitate mass and heat transfer between the carbon bed and the gaseous environment, the bed thickness was only two to three particle diameters. Sufficiently large gas flow rates were used in the reactor so that gas conversion during the reaction was minimal.

For determining reactivity, the following procedure was used. The wire mesh basket containing the coal/char particles was initially held in an upper cooled portion of the reactor in which a downward flow of an inert gas was maintained. When the desired temperature and pressure conditions were established in the lower portion of the reactor in the presence of the reactive gas, the basket was lowered into the heated reaction zone; this procedure took about 5-7 sec. The sample took about 2 min to attain reaction temperature. The sample was kept in the heated zone for different intervals of time while its weight was recorded continuously. The experimental run was terminated by raising the basket back to the upper cooled portion of the reactor. During an experimental run, Johnson measured the dry feed gas flow rates by an orifice meter and the dry product gas flow rates by a wet test meter. Samples of product gas were analyzed periodically by a mass spectrometer. Feed and product steam flow rates were measured gravimetrically.

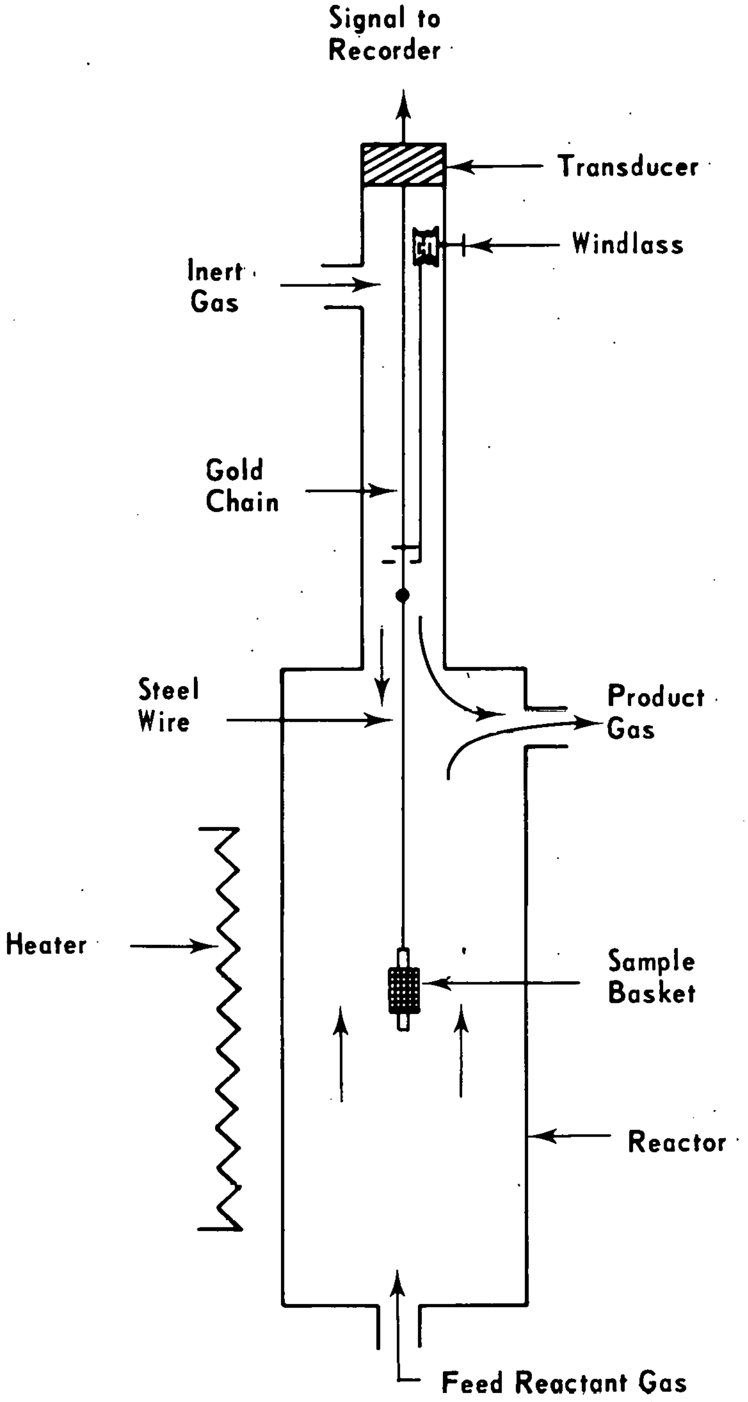

Figure 3. THERMOBALANCE REACTOR
From Johnson (1974)

B. By Gas Analysis

Perusal of the literature shows that a number of experimental approaches have been used to measure char reactivities by gas analysis. Among these approaches were those used by Ergun (1956), Daly and Budge (1974), Fuchs and Yavorsky (1975), Kayembe and Pulsifer (1976), and Hippo (1977). Basically in each of these approaches product gases are analyzed by suitable techniques such as gas chromatography, mass spectrometry, and infrared. From a material balance, the amount of carbon gasified at different time intervals can be calculated. A small fixed bed or a fluidized bed reactor is used under isothermal conditions; the fluid bed offers the advantage of more efficient heat and mass transfer between reactant and product gases and char particles.

Recently, Hippo (1977) used a fluidized bed reactor to measure reactivities in steam of chars derived from raw and calcium-exchanged lignite. A schematic diagram of the apparatus is shown in Figure 4. The gas inlet section consisted of a water feed system and a preheater. Water was contained in a steel feed tank (B). Helium was bubbled through water to remove dissolved O_2. Steam was vaporized in boiler (D) which was equipped with an automatic feed pump (C). The desired steam pressure was obtained by controlling the electrical power input. Steam left the generator through 1/4 in. copper tubing; excess steam was discharged into a drain pipe. The gas line from the steam generator to preheater E was wrapped with heating tapes. The preheater, filled with reduced copper turnings, was maintained at 600°C. This arrangement facilitated the removal of traces of oxygen present in the gas steam. From the preheater, the gases were passed through Pyrex tubing (wrapped with heating tape) to the Vycor fluidized bed reactor. The reactor was fitted with a Vycor fritted disk to support the char sample. A 10 mm ID Vycor inlet tube wrapped around the body of the reactor allowed preheated gas to enter the reactor through an opening in the bottom. A

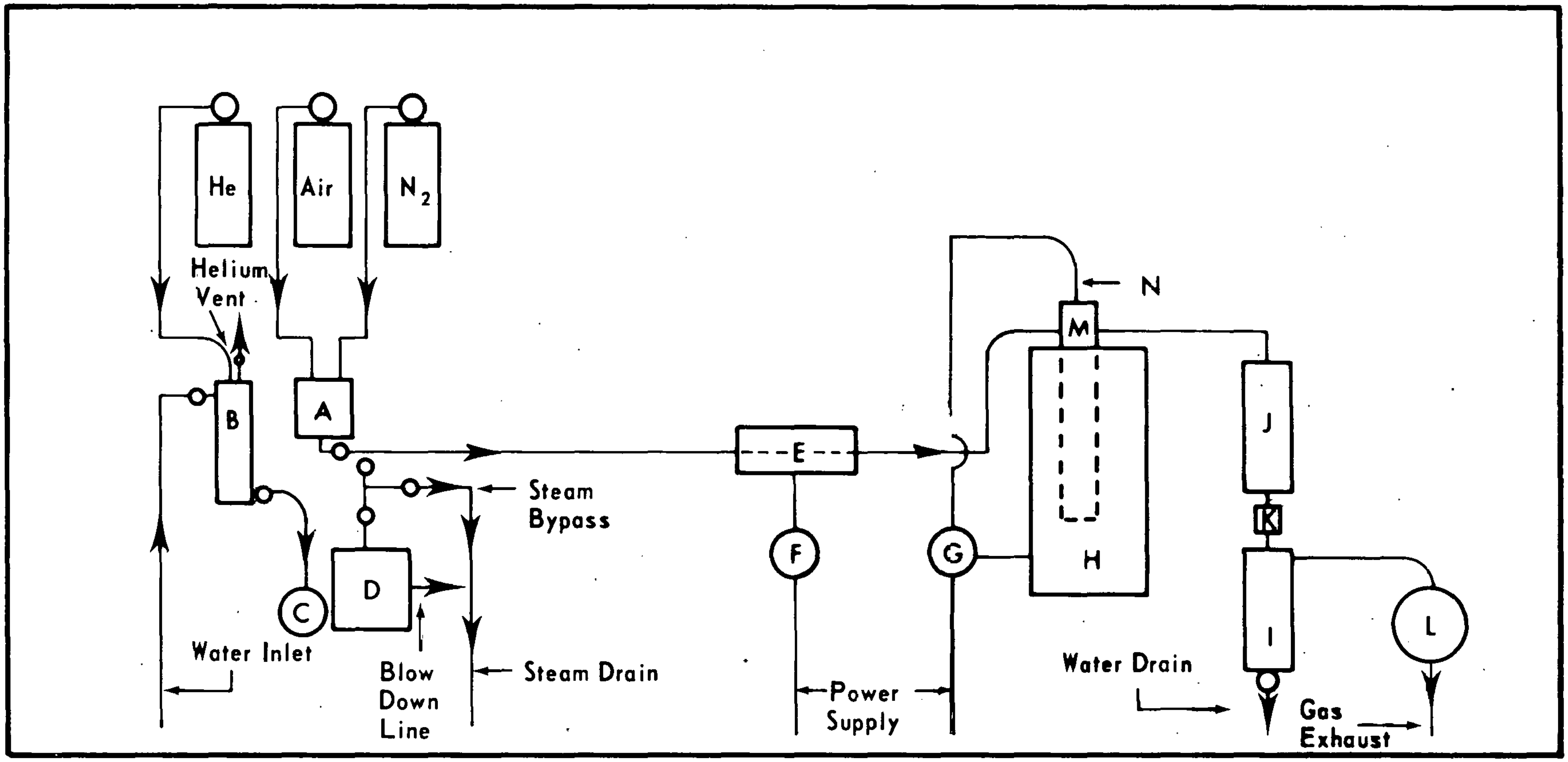

Figure 4. SCHEMATIC DIAGRAM OF CHAR-STEAM REACTION SYSTEM
A, rotameters; B, feed water storage tank; C, feed pump; D, steam generator; E, preheater; F and G, temperature controllers; H, furnace; I, water tap; J, condenser; K, sampling port; L, wet test meter; M, reactor; N, thermocouple
From Hippo (1977)

graded seal was used to connect the main body of the reactor to the top of the reactor, which in turn consisted of a ground glass joint which fitted inside the reactor cap. A 7 mm ID Vycor thermocouple well was connected to the reactor cap through a Pyrex-Vycor graded seal.

About 20 gm oven-dried (110°C) char were taken in the reactor. The reactor was placed inside the furnace (H). The temperature of the sample in the center of the bed was read by a chromel-alumel thermocouple (N). Prior to reactivity measurements, the reactor was flushed with N_2 to displace air. The furnace was then activated and the reactor brought to the desired reaction temperature. After thermal equilibrium was attained, N_2 was replaced by steam. Product gases coming out of the reactor at M were passed through a condenser (J). The condensate was collected in separating funnels. The gases were then passed through a wet test meter and then vented off into the atmosphere. After different reaction times, samples of product gases were taken and analyzed for CO, CO_2, CH_4 and H_2. A Fisher gas partitioner (FGP) was used to analyze CO, CO_2 and CY_4, whereas a Hewlett-Packard chromatograph (HPC) with a carbosieve B column was used to measure the concentration of H_2. Helium was used as a carrier gas in the FGP and Ar in the HPC. After the desired level of carbon burn-off was attained, the run was terminated. The residual sample was cooled in N_2 and finally weighed.

Fuchs and Yavorsky (1975) used a fluidized bed reactor to measure reactivities of chars in CO_2 and steam at high pressures (up to 70 atm). The reactor was made of stainless steel. Two disks of porous stainless steel confined the char sample within the reaction zone. The reactor was heated by direct resistance heating in which the reactor itself served as the heating element. At the bottom of the reactor a preheater (in the form of a ceramic rod containing a heating wire) raised the feed gas temperature. For the steam experiments, the preheater was insufficient to vaporize the water completely. In such cases, heating tapes were wrapped around the water feed line to maintain the temperature above the boiling point of water at the experimental pressure. For high pressure steam experiments, a water reservoir was pressurized with helium. In order to circumvent the possibility of back reactions, care was taken to prevent a build-up of product gas concentration near the particle surface.

C. By Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) is a thermal analytical technique in which the ordinate value of an output curve at any given temperature is directly proportional to the differential flow of heat between a sample and reference material and in which the area under the measured curve is directly proportional to the total differential caloric input. The term 'scanning' implies that the temperature of both the sample and reference material is increased during the experiment at a known heating rate.

Recently, Mahajan et al. (1976, 1977) have used the DSC technique for measuring the heats involved during pyrolysis and hydrogenation of a wide spectrum of coals. Although this technique has not yet been used for measuring reactivities of chars, it holds great potential as a fast analytical tool in this area. Therefore, it will be discussed in some detail in conjunction with studies being conducted on characterization of active surface area, which is an important consideration in carbon gasification. One of the prime factors governing gasification rates of carbons is the active surface area (ASA), or the concentration of carbon atoms located at the edges of layer plans. In coals, according to Cartz and Hirsch

(1960), the average layer diameter and number of atoms per layer increases with increasing coal rank, that is, ASA decreases with increasing coal rank. These characteristics of the coal precursors are thought to be carried over to the resultant chars. In this context, Diamond (1960) has reported that when chars are prepared from different coals at a given temperature, average layer diameter increases with increase in the carbon content of the parent coal. It will be discussed shortly that the reactivity of a char in different gasification atmospheres decreases, in general, with increase in the rank of the parent coal. Taken in the context of the work of Cartz and Hirsch (1960) and Diamond (1960), this means that char reactivity decreases with decrease in ASA of the coal precursor and hence, of the char derived from it.

It has not yet been established experimentally whether the ASA of a char, prior to gasification, is in any way a measure of or related to char reactivity during gasification. It will be shown later that ASA of relatively pure carbons can be determined by oxygen chemisorption. However, it is uncertain if ASA of 'impure' carbons such as chars which are invariably associated with inorganic impurities can be measured accurately. It is well known (Walker et al., 1968) that the first step in the overall gasification process is the dissociative chemisorption of the reactant gas at the active sites. Therefore, the heat released during chemisorption of oxygen on a unit weight of char may be related to its ASA and, hence, to its reactivity during gasification.

With the DSC technique, it is possible to measure quantitatively the magnitude of exothermic heat involved during chemisorption of oxygen on chars under controlled experimental conditions. In this laboratory, Ismail (1977) has measured the heat of chemisorption of oxygen on Saran char at 100°C (Saran is a copolymer of PVDC and PVC in the ratio of 9:1).

Saran char is highly microporous and has a structure similar to the coal-derived chars. For determining the heats, Ismail used the following procedure. About 10 mg char (150x250 mesh) were taken in an aluminum pan. It was ascertained that under the chosen experimental conditions no diffusional effects were involved. That is, the heat released was independent of bed height, char particle size and O_2 flow rate. The sample was heated in the DSC cell in an N_2 atmosphere at a rate of 20°C/min up to 700°C, which is the maximum attainable temperature. Soak time at 700°C was 30 min. The sample was then cooled in N_2 to 100°C. After temperature stabilization, N_2 was replaced by O_2 at the same flow rate (45 cm^3/min). The DSC output curve, that is the exotherm, was followed for 30 min. Heat released during the reaction was calculated from the following equation:

$$\Delta H = \frac{60ABE\zeta}{m} \tag{1}$$

where

ΔH = heat released (mcal/mg)

A = area of the exotherm ($in.^2$)

m = sample mass (mg)

B = time-base setting (min/in.)

E = cell calibration coefficient (dimensionless)

ζ = Y-axis sensitivity (mcal/sec/in.)

If, as is usually the case, the heat released is expressed per unit weight of gas chemisorbed, it is imperative to also determine the amount of oxygen chemisorbed during chemisorption. Ismail determined weight increase ocurring during chemisorption using a Cahn RG electrobalance under conditions simulating those in the DSC runs.

Mahajan et al. (1977) found that the heat released during the hydrogenation of coals of different rank, in the temperature range 200-570°C, could be used as a relative measure of reactivity of coals during their hydrogasification. In the light of this observation, it is probable that the heat released during the reaction of chars with gases, under conditions simulating those in the reactivity runs, may well be a measure of char reactivity during gasification. Furthermore, in designing gasification reactors, information is badly needed on heats involved during gasification. During gasification the char loses weight continuously. Mahajan et al. (1976) have argued that in such cases the DTA and DSC output curves are displaced (relative to the reference base line) due to both weight and thermal changes involved during the reaction. They have emphasized that unless the output curves are corrected for displacement due to weight changes it is not possible to estimate quantitatively the thermal effects involved during the reaction. These corrections cannot be made in the DTA technique but can be made in the DSC technique (Mahajan et al., 1976). Unfortunately, there appears to be no commercial equipment available at present to permit the DSC technique to be used above 700°C. Nevertheless, the work of Mahajan et al. shows that the DSC technique holds potential for measuring quantitatively thermal changes, and possibly reactivities as well, during char gasification.

III. SELECTED EXPERIMENTAL RESULTS

A. Burn-Off Versus Time Curves

Typical burn-off versus time plots obtained for the gasification in air at 405°C of four 1000°C chars derived from 40x100 mesh fractions of A (lignite), B (Sbb-A), C (HVC) and D (HVB) coals are shown in Figure 5. These plots are more or less typical of the plots found for all the chars reacted in other gasification media (CO_2, steam and H_2). Inspection of Figure 5

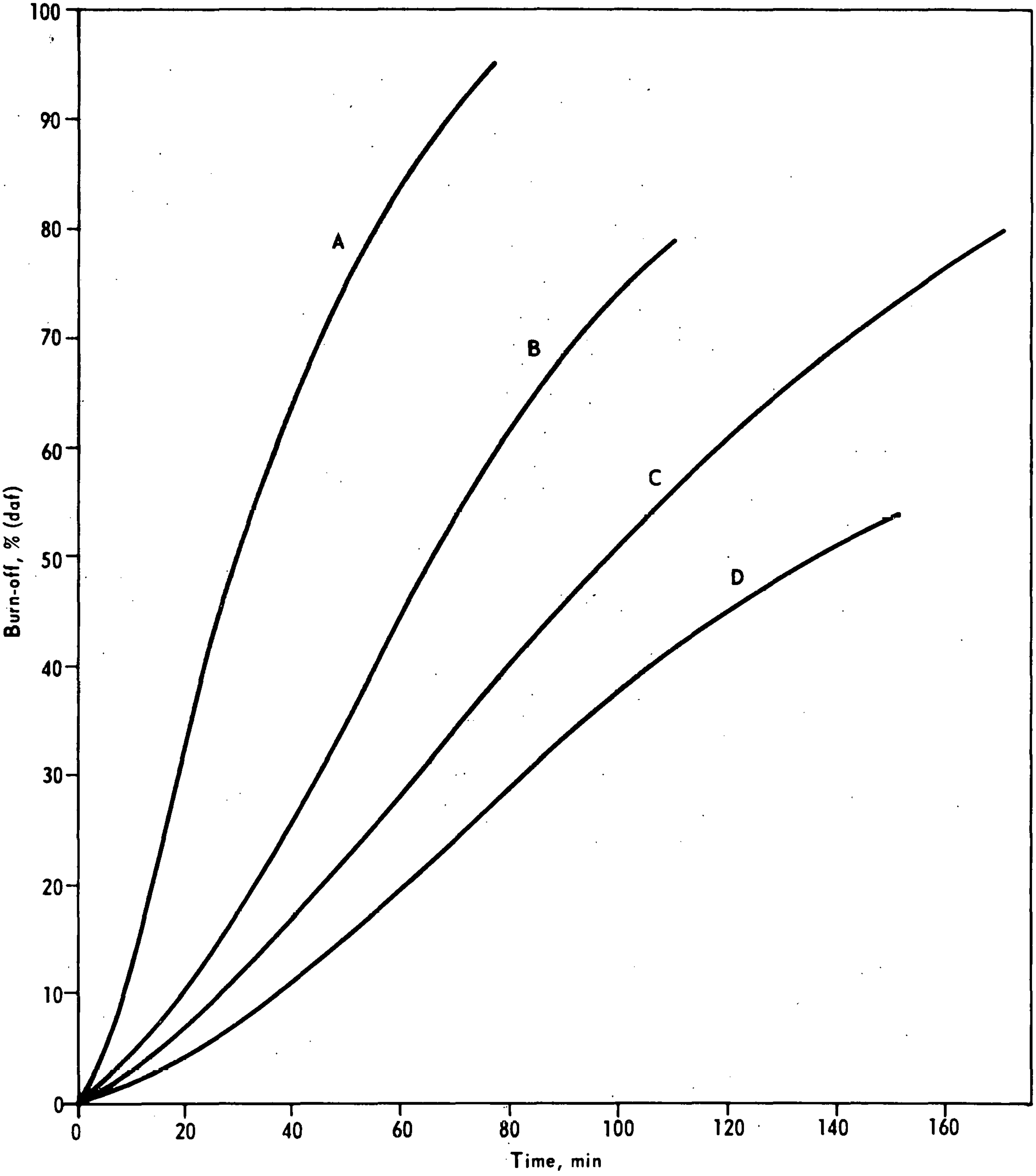

Figure 5. TYPICAL BURN-OFF VERSUS TIME CURVES IN AIR AT 405 °C
A, lignite; B, Sbb-A; C, HVC; D, HVB
From Soledade (1976b)

shows that all the plots are essentially of the same shape and that each curve has three distinct regions. The first region involves the so-called induction period; that is, the reaction rate increases slowly with time. The plot then goes through a maximum in slope, followed by a lengthy region of decreasing slope as burn-off approaches 100%.

Qualitatively, at this time, the shape of the burn-off curves in Figure 5 can be explained on the basis of what is known about the development of porosity and surface area in microporous chars as they undergo gasification. Chars before gasification contain closed porosity, that is, porosity inaccessible even to helium. With the onset of gasification, two important phenomena occur: i) enlarging of pores that were open in the unreacted char, and ii) opening up of closed pores. Since the total number of pores is increased as well as their average radius, specific pore volume and specific surface area increase with increasing carbon burn-off. The specific surface area increases sufficiently rapidly as reaction time increases so that the product of specific area and char weight remaining, that is, total area remaining, increases. The result is an increasing slope of burn-off versus time plot. At some point, depending upon the pore structure of the individual char, walls between existing pores are gasified away; and the total number of open pores commences to decrease. This leads to specific surface area ultimately going through a maximum as burn-off proceeds. This results in the slope of the burn-off versus time plot going through a maximum value and continuing to decrease out to complete burn-off.

Perusal of the literature shows that several parameters have been used to express reactivities of chars during gasification. In this laboratory, Jenkins _et al_. (1973) expressed reactivity as

$$R_T = \frac{1}{W} \cdot \frac{dW}{dt} \qquad (2)$$

where

R_T = reactivity (gm $hr^{-1}gm^{-1}$)

W = starting weight of char on a daf basis (gm)

dW/dt = maximum rate of reaction (gm hr^{-1})

Tomita et al. (1977) expressed reactivity as

$$R = \frac{1}{W_u} \cdot \frac{dW}{dt} \qquad (3)$$

where

W_u = weight (daf) of char unreacted at time t

dW/dt = slope of burn-off curve at the corresponding time t

Tomita et al. found that over a certain burn-off range the kinetics followed a first order rate expression with respect to the unreacted char.

B. Effect of Different Variables on Reactivity

1. General

The major factors which control the reactivity of carbonaceous solids to O_2, CO_2, H_2O and H_2 are known (Walker et al., 1959, 1968). They are: i) concentration of active sites; that is, carbon atoms located at the edges of crystallites or building blocks, ii) diffusional limitations on how rapidly the reactive gas molecules can reach active sites, and iii) presence of catalytic inorganic impurities. Char properties undergo dynamic changes during the gasification process. As gasification proceeds, ASA can change as a result of opening of closed porosity and enlarging of existing porosity. The extent of change in ASA during gasification depends in complex ways upon such variables as: the starting structure of the char, gasification temperature, reactive gas, nature and dispersion of inorganic impurities present, and the level of burn-off itself.

The majority of ASA in chars is located in micropores. Since most of the micropores in coal chars (prior to their gasification) are very small or of a size comparable to that of the reactant molecules, diffusion into these pores is activated (Walker et al., 1966). Diffusion rates increase very sharply with small amounts of gasification (Patel et al., 1972). Therefore, the utilization factor, η, that is, the extent of utilization of active sites, increases. η can vary 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 particles. During gasification, it is desirable for η to approach one as closely as possible (and economically feasible).

It is well known that most inorganic impurities catalyze carbon gasification (Walker et al., 1959, 1968). The extent to which an impurity is an active catalyst during gasification depends upon the amount present, chemical form (that is, a metal, an oxide, etc.) and degree of dispersion (particle size). For a given amount of catalyst, the greater the degree of its dispersion, the greater its specific catalytic activity is expected to be. In coal chars, there can be a wide range in the dispersion of impurities. Most of the inorganic impurities present as discrete minerals have a rather low dispersion, and their degree of dispersion is expected to change little during gasification. Conversely, most of the inorganic impurities present within the carbon matrix or associated with functional groups at the edges of the matrix are highly dispersed. This degree of dispersion would be expected to decrease markedly during gasification. The extent of change will depend upon the impurity, its original degree of dispersion, the reactant atmosphere and reaction temperature. These parameters determine the degree of mobility of impurities and, therefore, the possibility of their coalescence into larger particles (Ruckenstein and Pulvermarcher, 1973; Flynn and Wanke, 1974).

2. Active Surface Area

Laine _et al_. (1963) have discussed the importance of ASA on the carbon-oxygen gasification reaction. They oxidized Graphon, a highly graphitized non-porous carbon black devoid essentially of all impurities, to seven levels of burn-off varying between zero and 35%. The total surface area (TSA) of each sample was measured by the BET method using N_2 at =-196°C. The ASA was determined by chemisorption of oxygen at 300°C.

Reaction rate runs were then made at temperatures of 575, 625 and 675°C and an initial O_2 pressure of about 40 millitorr. It was ascertained that the reaction rates were solely controlled by the intrinsic chemical reactivity of the carbon samples. The concentrations of reactant and product gases during the reaction were followed continuously using a mass spectrometer. The amount of stable oxygen complex building up on the surface during reaction was followed by a continuous material balance at the end of a run by outgassing. From these data, the unoccupied active surface areas (UASA) were calculated.

From the reactivity results, Laine _et al_. (1963) calculated rate constants for the disappearance of O_2 and formation of CO and CO_2. On the basis of TSA, the rate constants were calculated by an equation of the form

$$-\frac{dP_{O_2}}{dt} = k'_{O_2}(P_{O_2})(TSA) \tag{4}$$

where $-dP_{O_2}/dt$ is the rate of decrease of O_2 pressure with time and (TSA) is the BET N_2 area for the particular Graphon sample. On the basis of ASA, the rate constants were calculated using an equation of the form

$$-\frac{dP_{O_2}}{dt} = k_{O_2}(P_{O_2})(ASA)(1-\theta) \qquad (5)$$

where (ASA) is the active surface area for the particular Graphon sample and (1-θ) is the fraction of the ASA which is unoccupied with complex under particular conditions of reaction time and temperature.

Laine et al. found that for a particular Graphon sample reacted with O_2 at 625°C, the rate constants based on TSA decreased sharply with time, only beginning to level off as the amount of stable oxygen complex formed tended to saturation. In contrast, the rate constants based on UASA were found to change relatively little with time. The rate constants as a function of prior Graphon burn-off for reaction at 625°C are listed in Table I. The rate constants, based on TSA, increased monotonically and sharply with prior burn-off given to the Graphon. In contrast, the rate constants, based on UASA, were essentially constant for Graphon samples with burn-offs between 3.3 and 34.9%. Laine et al. (1963) have offered a plausible explanation for the higher rate constants observed for the unactivated, that is, 0% burn-off Graphon sample.

It is instructive to emphasize that although the pioneering work of Laine et al. is of fundamental importance in understanding unambiguously the role of ASA in determining the kinetics of carbon gasification, their approach for expressing rate constants on the basis of UASA probably cannot be used in the case of chars. This is so because, as discussed earlier, during char gasification not only ASA but also diffusional effects and, hence, η, as well as the chemical form and degree of dispersion of the catalytic impurity can change significantly.

TABLE I

VARIATION OF RATE CONSTANTS WITH AMOUNT OF PRIOR GRAPHON BURN-OFF FOR REACTION WITH OXYGEN AT 625°C

(From Laine et al.,1963)

	$\times 10^6$, $sec^{-1}m^{-2}$(BET)				$\times 10^3$, $sec^{-1}m^{-2}$(UASA)			
Burn-off %	k'_{O_2}	k'_{CO_2}	k'_{CO}	k'_{C}	k_{O_2}	k_{CO_2}	k_{CO}	k_{C}
0	5.2	2.4	2.7	5.1	9.8	4.8	5.4	10.2
3.3	11.0	3.2	9.0	12.2	5.1	1.4	4.3	5.7
6.4	16.3	3.7	20.1	23.8	4.5	1.1	5.7	6.8
8.5	21.3	4.5	26.5	31.0	5.0	1.0	6.0	7.0
14.4	27.4	6.0	33.1	39.1	4.5	1.0	5.9	6.9
20.8	34.4	7.1	38.0	45.1	4.9	0.9	5.4	6.3
25.8	39.8	9.2	48.8	58.0	4.8	0.9	5.9	6.8
34.9	49.7	11.0	59.1	70.1	4.9	1.0	5.8	6.8

3. Rank of Parent Coal

Walker and his school have measured the reactivities of a number of chars (prepared at 1000°C from 40x100 mesh coals varying in rank from anthracite to lignite) in air (1 atm) at 405°C, CO_2 (1 atm) at 900°C, steam (0.022 atm)* at 910°C and H_2 (27.2 atm) at 980°C. Reactivity parameters R_T, as defined by equation (2), for various chars in different gasification atmospheres are listed in Table II. It is seen that reactivities in air, CO_2 and steam decrease, in general, with increase in rank of the parent coal. However, reactivities in H_2 show a random variation with rank. Furthermore, the spread in char reactivities in the oxidizing atmospheres

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*This steam pressure was generated by bubbling prepurified N_2 through deaerated distilled water maintained at 20°C.

TABLE II

REACTIVITIES OF CHARS IN DIFFERENT ATMOSPHERES

PSOC Sample No.	Parent Coal		Char ash %(dry)	Reactivity (R_T), gm $hr^{-1}gm^{-1}$			
	ASTM Rank	C(daf),%		Air[a]	CO_2[b]	Steam[c]	H_2[d]
91	Lignite	70.7	11	2.7	6.3	2.9	0.91
87	Lignite	71.2	13	1.1	-	2.8	2.2
140	Lignite	71.7	12	1.3	3.4	1.5	1.0
138	Lignite	74.3	16	0.53	1.9	1.2	1.1
98	Sbb-A	74.3	12	0.60	1.3	1.0	0.73
101	Sbb-C	74.8	8	1.8	4.6	2.5	1.1
26	HVB	77.3	20	0.30	0.18	0.25	0.63
22	HVC	78.8	23	0.34	0.59	0.45	1.3
24	HVB	80.1	14	0.46	1.3	0.52	1.2
67	HVB	80.4	5	0.27	0.15	0.22	1.1
171	HVA	82.3	11	0.08	0.08	0.15	0.43
4	HVA	83.8	2	0.26	0.20	0.30	0.86
137	MV	86.9	19	0.11	0.09	0.10	0.26
114	LV	88.2	12	0.13	0.07	0.07	0.37
127	LV	89.6	7	0.016	0.07	0.011	0.07
81	Anthracite	91.9	6	0.11	0.13	0.13	0.81
177	Anthracite	93.5	5	0.08	0.04	0.11	0.38

From: a, Soledade (1976a); b, Tomita (1976); c, Linares _et al_. (1977); d, Tomita _et al_. (1977).

is far greater than in H_2; the reactivities of various chars in air, CO_2, steam and H_2 show variations of about 170, 160, 260 and 30-fold, respectively.

For chars derived from sub-bituminous and bituminous coals, Daly and Budge (1974) found a much wider variation (15000-fold) in reactivities to CO_2 than that listed in Table II. These workers followed essentially the same experimental approach as that of Okstad and Hoy (1966) for measuring char reactivities. The reactant gas (CO_2) was passed at a known flow rate over the bed at temperatures between 750 and 1000°C. The reaction temperature was adjusted to give a conversion of approximately 10% under steady state conditions. The results were then re-calculated to a standard temperature of 950°C, assuming the activation energy for the C-CO_2 reaction to be 85 kcal/mole. The significance of a much wider variation in char reactivity observed by Daly and Budge should be considered in the context of two questionable points. First, these workers assumed, a priori, that the activation energy (E_a) for the C-CO_2 reaction for all cokes and chars was 85 kcal/mole. This is not necessarily true (Walker et al., 1959, 1968). Daly and Budge themselves emphasize that any errors resulting from incorrect values for E_a have a greater effect on reactivity the farther the reaction temperature is from the standard reaction temperature (950°C). Secondly, the chars were not prepared at the same temperature; the bituminous chars were prepared at 1050°C, whereas the more reactive sub-bituminous chars were prepared at 920°C. As will be discussed shortly, the temperature at which a char is prepared has a profound effect on subsequent char reactivity. Since the chars listed in Table II were all prepared at 1000°C, comparison of their reactivities is thought to be more meaningful.

4. Heat Treatment Conditions

a. Carbonization Temperature. Jenkins et al. (1973) have studied the effect of HTT of chars derived from PSOC-138 (lignite), PSOC-24 (HVB) and PSOC-171 (HVA) on subsequent reactivity in air at 500°C. The coal precursors (40x100 mesh) were heated in N_2 at temperatures between 600 and 1000°C. Results summarized in Figure 6 show that char reactivity decreases as HTT is increased. This was attributed to a combination of several factors, namely 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.

b. Heating Rate During Carbonization. Recently, Ashu (1976) has shown that the use of very high heating rates up to pyrolysis temperature can lead to substantial increases in subsequent char reactivity. He prepared chars from a North Dakota lignite (70x100 mesh) by heating in N_2 to maximum temperature either in a fluidized bed at 10°C/min or in a laminar flow unit at about 8×10^3°C/sec. In both cases, soak time at maximum temperature was under 1 sec. The chars were subsequently reacted with air (1 atm) at 500°C. Reactivity parameters (R_T) for various samples are listed in Table III. It is seen that rapid heating to 800°C yields a char having a subsequent reactivity almost twice that of the char produced by slow heating to 800°C. In the context of the work of Jenkins et al. (1973), referred to above, that char reactivity decreases with increase in HTT of the char, it is noteworthy that rapid heating to 800°C more than counterbalances the use of slow heating to only 500°C insofar as subsequent reactivity is concerned. Rapid heating to 800°C of a char which was previously slowly heated to 500°C also produced a substantial increase in reactivity. Even rapid heating to 800°C of a char which was previously slowly heated to 500°C results in some

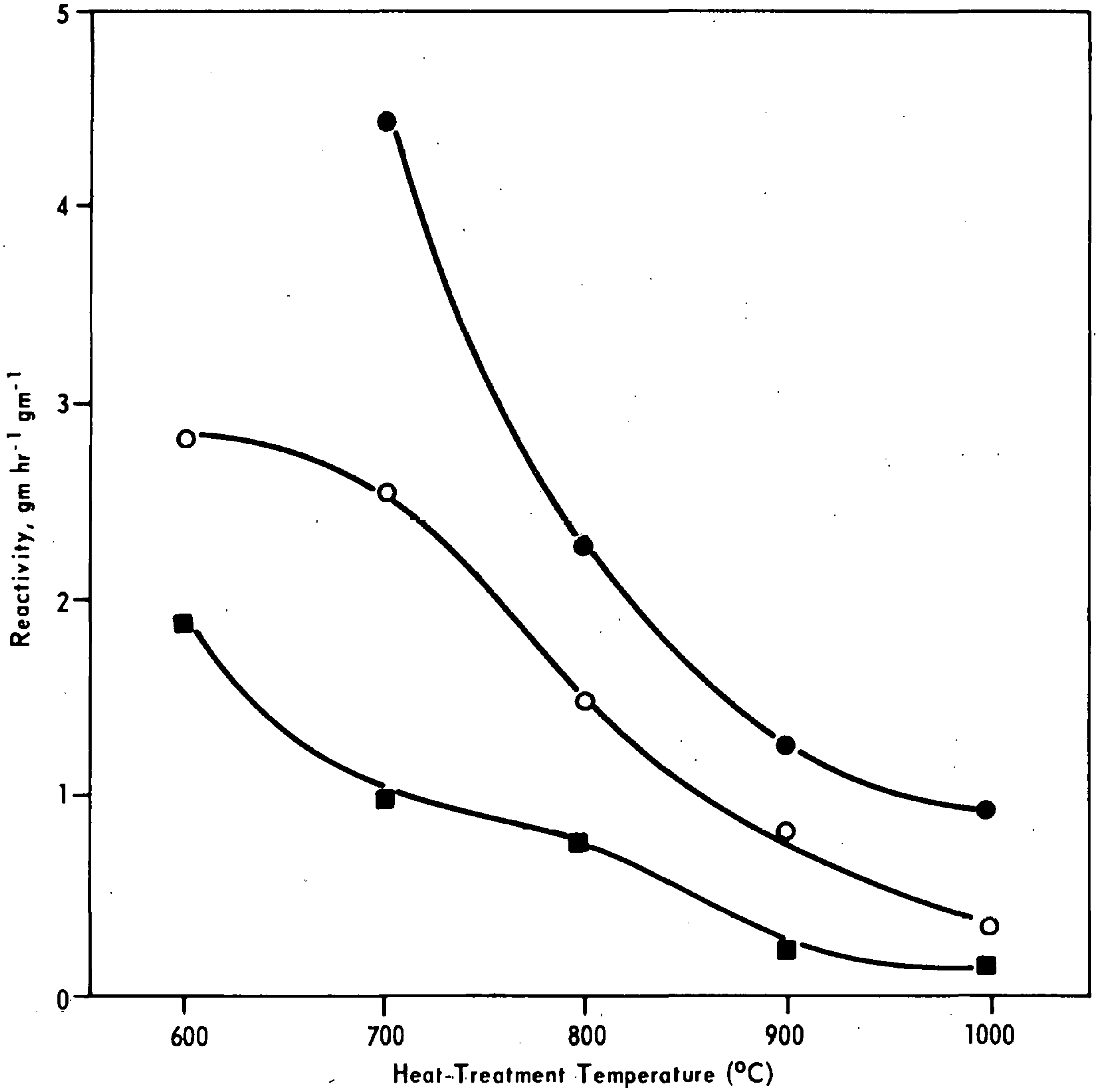

Figure 6. EFFECT OF TEMPERATURE OF HEAT TREATMENT OF CHARS ON THEIR REACTIVITY IN AIR AT 500°C
●, PSOC-138; ○, PSOC-24; ■, PSOC-171
From Jenkins et al. (1973)

enhancement of reactivity. These results show that in order to maximize char reactivity, it is desirable to maximize the heating rate during the carbonization of the precursor coal.

TABLE III

CHAR REACTIVITY FOLLOWING DIFFERENT HEAT TREATMENTS

(From Ashu, 1976)

Heat Treatments	Weight Loss on Heat Treatment, % (dry basis)	R_T, gm hr^{-1} gm^{-1}
10°C/min to 500°C	37.3	3.85
10°C/min to 800°C	43.8	2.79
8×10^3 °C/sec to 800°C	13.0,(22.8)*	5.17
10°C/min to 800°C followed by 8×10^3 °C/sec to 800°C	∿43.8	3.10
10°C/min to 500°C followed by 8×10^3 °C/sec to 800°C	∿37.3	4.89

*(22.8) is weight loss during heating up to reaction temperature in N_2 in the TGA unit at a rate of 10°C/min.

c. Concurrent Devolatilization and Gasification. When coals or low temperature chars are heated at higher temperatures, they lose volatile matter. The loss of volatile matter leaves behind nascent carbon sites which are highly reactive towards gasification (Walker et al., 1977b). In the absence of a reactant gas, the nascent sites are deactivated by rehybridization. Therefore, it is desirable to devolatilize coals in the presence of a reactant gas. The advantage of such an approach is illustrated by the hydrogasification results of Johnson (1974) for an HVA bituminous char (obtained from an air-pretreated caking coal) containing, on the dry basis, 28.4% volatile matter. He treated the char with H_2 in two different ways: i) the char was first devolatilized in N_2 (500 psi) at 927°C followed by reaction with H_2 (500 psi) at 927°C, and ii) the char was treated directly with H_2 (500 psi) at 927°C. From Figure 7, it is seen that the extent, as well as the rate of hydrogasification, are far greater when the char is hydrogenated directly. It is noteworthy that the weight loss, when hydrogasification is conducted following the devolatilization step, is only slightly higher than that involved during the devolatilization step itself.

5. Inorganic Impurities

Removal of inorganic impurities (mineral matter)*, either from precursors prior to their carbonization or from chars prepared from raw coals, has a marked effect on char reactivity in air (Jenkins et al., 1973), CO_2 (Hippo and Walker, 1975), steam (Linares et al., 1977), and H_2 (Tomita et al., 1977). In the case of chars derived from lower rank coals, removal of mineral matter decreases, in general, subsequent char reactivity. However, reactivity of chars prepared from higher rank coals increases upon removal of inorganic impurities. Removal of mineral matter from coals prior to their carbonization brings about profound changes in surface area and porosity of chars produced (Tomita et al., 1977). The changes in char reactivity and surface area are much less pronounced when the raw chars rather than the coal precursors are acid-washed or demineralized (Linares et al., 1977).

Recently, Hippo (1977) has shown that reactivity in steam of chars produced from a Texas lignite could be further enhanced by the addition of exchangeable potassium, sodium and calcium ions. At equivalent loading, the catalytic effect was most pronounced for potassium ions and about equal for sodium and calcium. Hippo prepared a number of chars containing

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*By acid-washing with HCl or by demineralizing with an HCl-HF mixture.

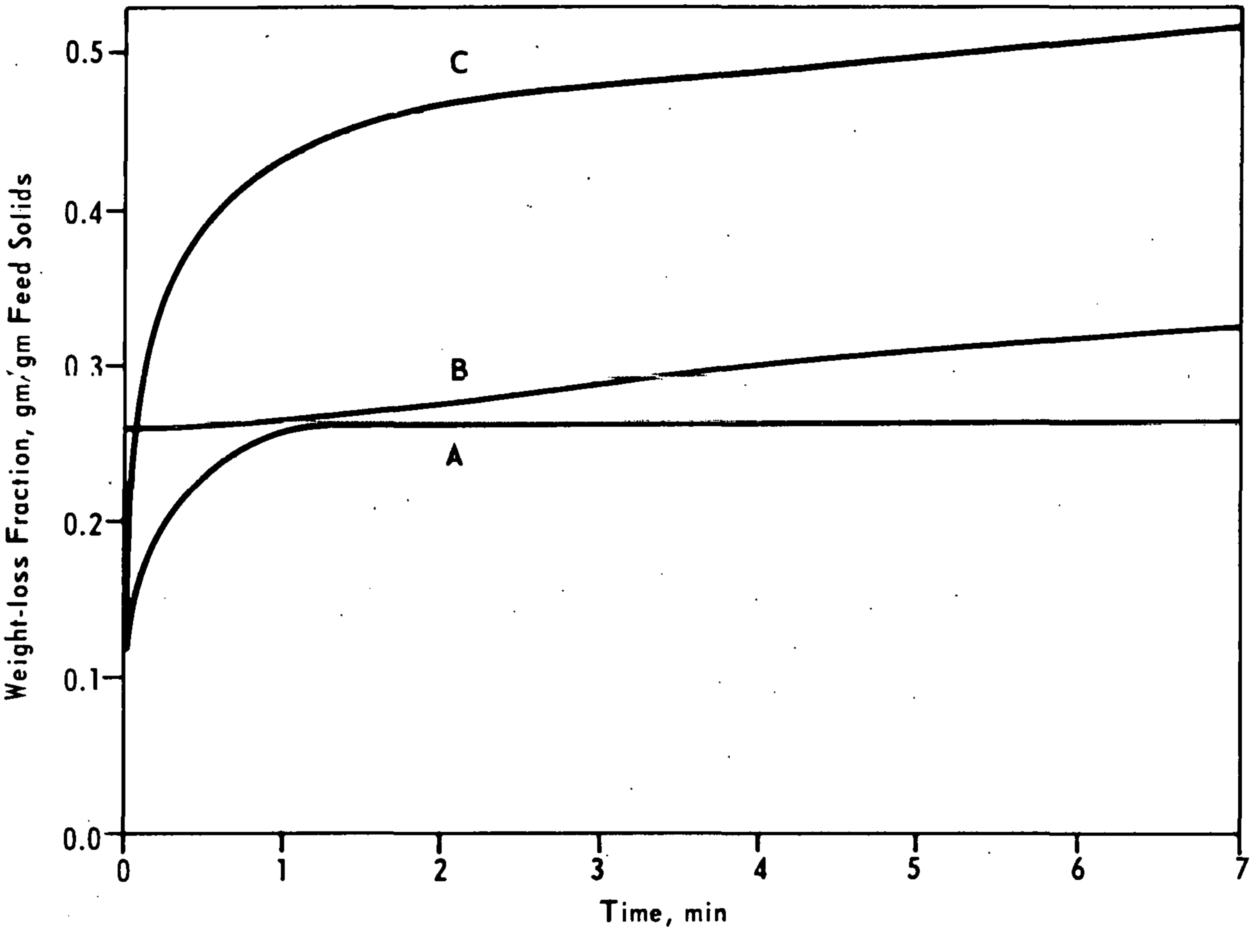

Figure 7. WEIGHT LOSS–TIME CURVES OBTAINED FOR A CHAR IN N_2 AND H_2 AT 500 psi AND 927 °C
A, char-N_2; B, char-N_2 followed by char-H_2; C, char-H_2
From Johnson (1974)

different amounts of calcium (up to a maximum of 12.9%, by weight) by heating calcium exchanged samples in N_2 at 800°C. Figure 8 summarizes results for reactivity of the various chars in 1 atm of steam at 650°C. It is seen that char reactivity increases linearly with increase in calcium content in the char and that the maximum reactivity achieved is about twelve times greater than that of the char prepared from the raw lignite.

Johnson (1975) also found a linear relationship between amounts of calcium and sodium added by ion exchange to North Dakota and Montana lignites and reactivity of product chars in H_2 at 35 atm and 927°C. For the same loading, sodium ions were found to be catalytically more active than calcium ions. Johnson also found that exchangeable sodium and calcium ions significantly enhanced char gasification in steam-H_2 mixtures, even more so than for gasification in H_2 alone. However, contrary to the behavior in pure H_2, the effect of the calcium concentration on reactivity in steam-H_2 mixtures was the same as that of sodium at corresponding loading.

6. Particle Size

Hippo and Walker (1975) studied the effect of particle size on reactivity in CO_2 (1 atm) at 900°C of a relatively unreactive low volatile bituminous char (PSOC-127) and a highly reactive lignite char (PSOC-87). Particle size fractions studied were 40x100, 100x150 and 200x325 mesh. It was found that a decrease in particle size invariably increased char reactivity, indicating that the gasification reaction was partly diffusion controlled. Whereas a reduction in particle size of PSOC-87 from 40x100 to 200x325 mesh resulted in a reactivity increase of only 2.7-fold, a similar particle size reduction of PSOC-127 resulted in a reactivity increase of 35-fold. These results show that the limitations

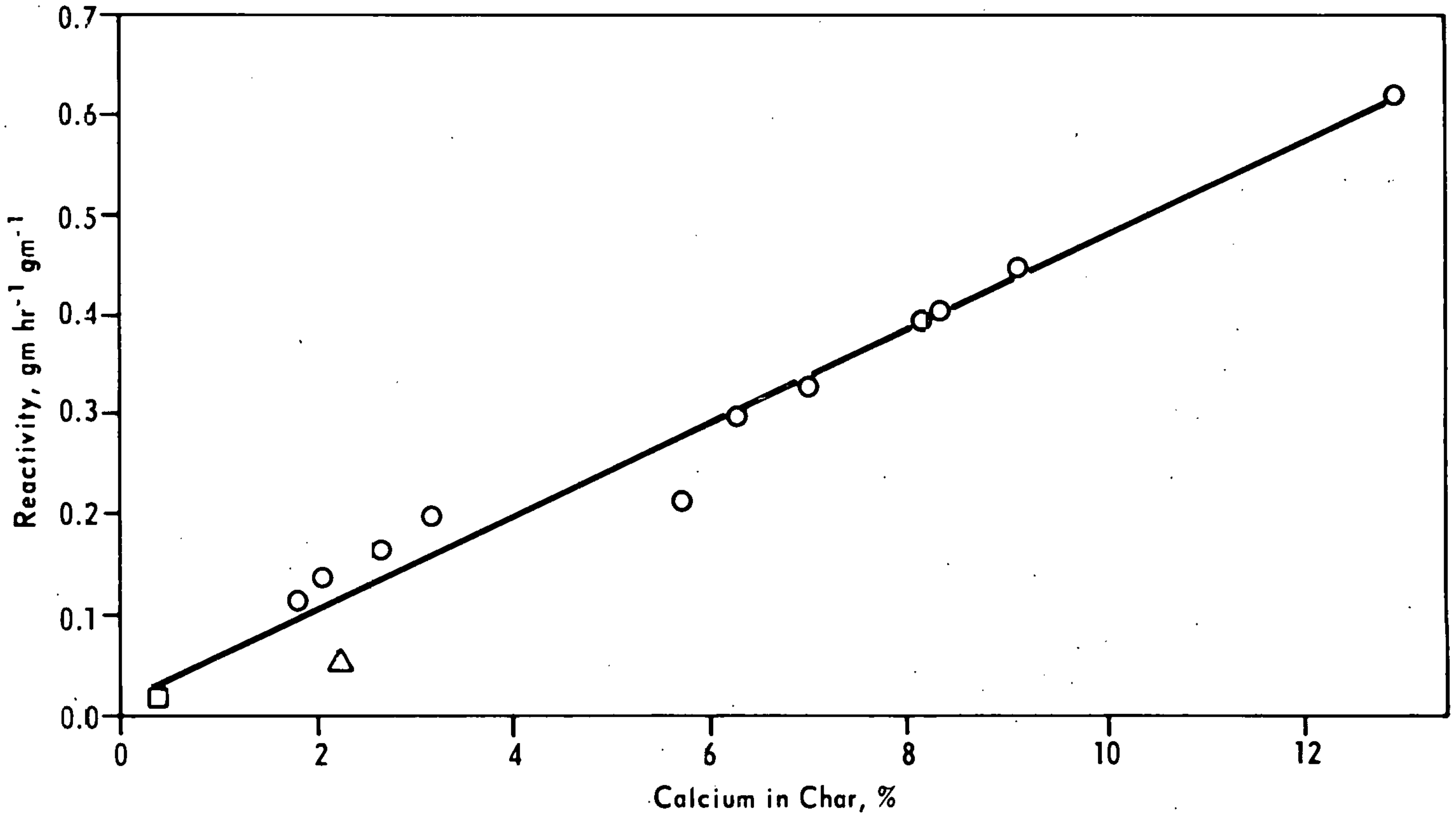

Figure 8. CHAR REACTIVITY IN STEAM AT 650°C IN RELATION TO CALCIUM CONTENT
△, raw; □, demineralized; ○, Ca-exchanged
From Hippo (1977)

which mass transport can impose on gasification rates of less reactive chars can be minimized by using increasingly smaller particle sizes in the reactor.

7. Reaction Temperature

Activation energies involved in the chemical step of char gasification are substantial (Walker et al., 1959). Therefore, an increase in reaction temperature enhances gasification rates so long as the reaction is not limited primarily by mass transport or equilibrium. However, even for a chemically controlled reaction, a given increase in reaction temperature may bring about different increases in reaction rates for different carbons. The reasons for this behavior have been discussed by Walker et al. (1959, 1968).

Tomita et al. (1977) determined reactivities of selected 40x100 mesh chars in H_2 (28.2 atm) at 875, 925 and 980°C. The reactivity of each char increased with temperature, as expected. The pseudo-activation energy for char gasification was found to increase with carbon burn-off and tended to level off towards an asymptotic value at higher burn-offs. This behavior, which was also observed by Zielke and Gorin (1955), was attributed by Tomita et al. (1977) to a reduction in diffusion control of gasification rates and/or a decrease in the extent to which gasification was catalyzed by impurities.

Linares et al. (1977) studies the reactivity of a Montana lignite char in steam (0.022 atm) in the temperature range 750-930°C. Below 890°C, the reaction was found to be chemically controlled, whereas above 890°C, it was diffusion controlled. Kayambe and Pulsifer (1976) also found that gasification rates of two chars with steam (1 atm) in the temperature range 600-850°C were controlled by chemical reaction at the carbon surface.

8. Pressure of Reactant Gas

Walker and his school have studied the effect of pressure of the reactant gas on the reactivity of a 1000°C Montana lignite char in different gasification atmospheres. Figure 9 shows burn-off versus time plots for the char reacted at 405°C in various partial pressures of O_2 at a total O_2-N_2 pressure of 1 atm. As expected, the gasification rate decreases sharply with decreasing O_2 pressure. Soledade (1976a) calculated that the reactivity parameter (R_T) for the lignite char was proportional to $p_{O_2}^{0.71}$. R_T values for the lignite char in different partial pressures of CO_2 (900°C) and of steam (910°C) at a total reactant gas-N_2 pressure of 1 atm were found to be proportional to the 0.55 and 0.60 powers of CO_2 (Linares, 1976) and steam (Linares et al., 1977) pressures, respectively. Tomita et al. (1977) found that in the hydrogen pressure range of 6.8-27.2 atm, the hydrogasification rate, when the kinetics followed a first order rate expression with respect to the unreacted char, was proportional to the first power of H_2 pressure.

9. Carbon Deposition

Recently, Kamishita et al. (1977) have studied the effect of carbon deposition (CD), resulting from the cracking of methane, on a lignite char on subsequent reactivity to air (1 atm) at 375°C. Different amounts of carbon were deposited at 855°C on raw and acid-washed chars prepared by the heat treatment in N_2 of a North Dakota lignite (40x100 mesh) at 855 and 1000°C. It was found that the reactivity decreased progressively with increasing amounts of CD. This was attributed to a decrease in ASA and deactivation of catalytic inorganic impurities due to coating with carbon. The results indicated that the deposited carbon was much less reactive to air than the lignite char. It was also found that surface area development in the char as a result of gasification was sharply reduced by prior CD. It was concluded that in order to maximize surface

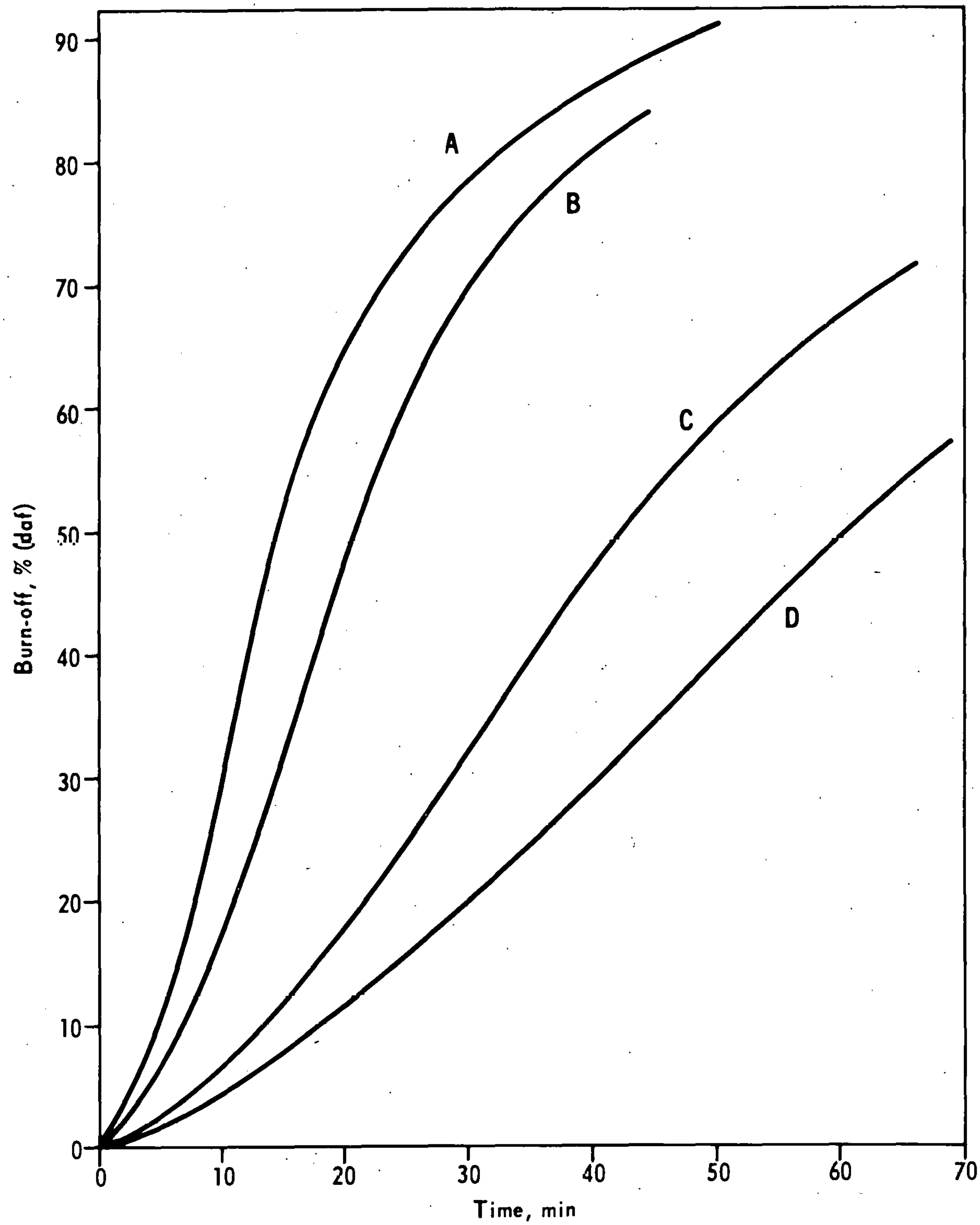

Figure 9. INFLUENCE OF OXYGEN CONCENTRATION ON REACTIVITY OF PSOC-91 CHAR AT 405°C
A, 21% O_2; B, 10% O_2; C, 4% O_2; D, 2% O_2
From Soledade (1976a)

area development and, hence, char reactivity to oxidizing gases carbon deposition from volatiles during the conversion of coal to char should be kept to a minimum.

C. Unification of Coal Char Gasification Reactions

In calculating char reactivities in different gasification atmospheres, we have so far used the simple expressions (2) and (3). As discussed earlier, even though there are major differences in char reactivity as the rank of the parent coal from which chars are derived is changed (Table II), the shapes of the burn-off versus reaction time plots are quite similar (cf. Figure 5). If this is so, all reactivity plots should be able to be normalized using an adjustable time parameter, τ, which can conveniently be used as a measure of differences in reactivity for a wide spectrum of chars. Walker et al. (1977a) have examined the feasibility of such a normalizing procedure. For this study, they considered burn-off plots for various chars in air (1 atm) at 405°C, CO_2 (1 atm) at 900°C, steam (0.022 atm) at 910°C, and H_2 (27.2 atm) at 980°C.

The principle of normalizing reactivity plots is shown in Figures 9 and 10. Figure 10 shows that individual reactivity plots corresponding to different partial pressures of O_2 (Figure 9) can be normalized using a dimensionless time scale such that $t/\tau_{0.5}$ equals one at a fractional burn-off of 0.5. Values of $\tau_{0.5}$, or the times to reach a fractional burn-off of 0.5, decrease from 61.0 min to 14.8 min as the percentage of O_2 in the reactant mixture is increased from 2 to 21%. Figure 10 is more or less typical of the shape of burn-off versus $t/\tau_{0.5}$ plots found for all chars reacted in all gases. The explanation that was offered earlier to account for the observed shape of the burn-off curve ignores the effect which catalysis by inorganic impurities can have on the shape of the burn-off curve. For example,

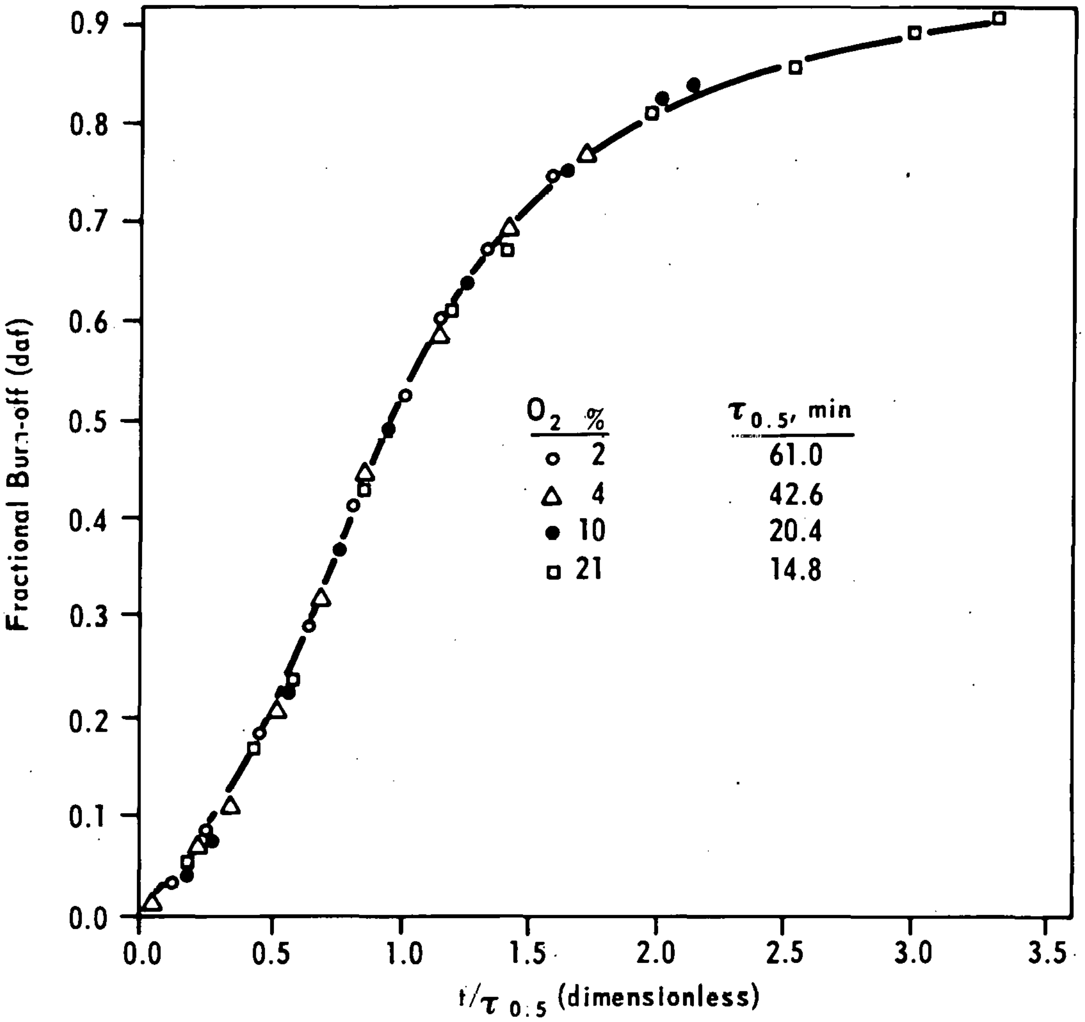

Figure 10. NORMALIZED PLOT FOR REACTIVITY OF PSOC-91 CHAR AT 405°C IN DIFFERENT CONCENTRATIONS OF O_2
From Walker *et al.*, (1977a)

if a catalyst is initially very active but, as burn-off proceeds, becomes less active because of sintering or change in chemical state, the $t/\tau_{0.5}$ region over which the gasification rate is increasing can be shortened or indeed removed completely. That is, the maximum rate can be observed immediately as gasification commences. In this case, the catalytic effect on gasification is obviously overshadowing the effect of increase in specific pore volume and specific surface area.

In order to find out if one equation, with $\tau_{0.5}$ being the only adjustable parameter, can unify all the char reactivity data, Walker et al. (1977a) conducted a computer correlation of data for each gasification medium, as well as a computer correlation of data for all gasification media. Burn-off versus time data for a fractional burn-off up to 0.7 were used in all cases. The suitability of the following equations to correlate the data was tested: a linear equation between burn-off and $t/\tau_{0.5}$, an equation involving first and second power terms in $t/\tau_{0.5}$, an equation involving first and third power terms in $t/\tau_{0.5}$, and an equation involving first, second and third power terms in $t/\tau_{0.5}$. The last equation was found to give the best correlation of the data.

Tables IV and V summarize the results. Table IV shows the wide variation of $\tau_{0.5}$ values for the chars in each reaction medium as the rank of coal from which the chars were produced changes. Generally, $\tau_{0.5}$ values for each reactant gas fall in the same order, but there are exceptions, as expected, which reflect the uniqueness of each reaction.

Table V presents the best values for coefficients in the cubic equations between fractional burn-off and $t/\tau_{0.5}$ for each reactant, as well as for all reactants. R^2 values give how much of the sum of variance, assuming no correlation between burn-off and $t/\tau_{0.5}$, can be removed by the particular cubic equation. It is obvious that for each individual reactant and also

TABLE IV

$\tau_{0.5}$ VALUES FOR GASIFICATION RUNS

(From Walker et al., 1977a)

PSOC	Parent Coal			$\tau_{0.5}$ for Different Reacting Gases, min			
Coal No.	ASTM Rank	Ash,% (dry)	C,% (daf)	Air	Steam	CO_2	H_2
89	Lignite	11.6	63.3	-	-	5.5	43.5
91	Lignite	7.7	70.7	14.8	10.6	5.0	36.5
87	Lignite	8.2	71.2	30.0	11.4	-	24.0
140	Lignite	9.4	71.7	29.6	19.6	10.3	34.0
138	Lignite	10.3	74.3	69.5	28.0	17.0	32.0
98	Sbb.A	8.4	74.3	66.4	-	26.0	50.0
101	Sbb.C	6.1	74.8	21.6	13.6	7.0	37.5
26	HVB	10.8	77.3	121	138	200	59.0
22	HVC	10.1	78.8	99.0	64.0	54.0	33.5
24	HVB	11.8	80.1	78.5	51.0	30.0	32.0
67	HVB	4.8	80.4	134	152	220	34.5
171	HVA	7.6	82.3	-	260	-	96.0
4	HVA	2.1	83.8	-	114	-	49.0
114	LV	9.8	88.2	-	-	-	126
81	Anthracite	7.8	91.9	-	255	270	51.5
177	Anthracite	4.3	93.5	-	330	-	110

TABLE V

UNIFICATION OF COAL CHAR GASIFICATION REACTIONS

(From Walker et al., 1977a)

Reactant	No. of Chars	Cubic Model				First Order	
		a	b	c	R^2,%	Slope	R^2,%
Air	10	0.317	0.367	-0.182	96.0	0.756	94.1
CO_2	11	0.436	0.189	-0.122	99.2	0.728	78.4
H_2O	13	0.375	0.276	-0.148	99.1	0.761	87.4
H_2	16	0.349	0.283	-0.144	96.6	0.693	88.6
All	50	0.368	0.277	-0.147	98.2	0.727	87.5

for all reactants the equations given yield a high correlation of results for burn-off versus $t/\tau_{0.5}$.

Since each char-reactant mixture shows some region of $t/\tau_{0.5}$ over which the reaction rate is first order in amount of char remaining, Walker et al. (1977a) made computer correlations with the first order model, $\ln[1/(1-BO)] = k(t/\tau)$, where BO is fractional burn-off. These results are also summarized in Table V. If the data perfectly obeyed the first order model, k must equal 0.69, since $t/\tau_{0.5} = 1.0$ at BO = 0.5. As seen in Table V, different reactions are seen to be more or less closely described, over a fractional burn-off range up to 0.7, by a first order equation. A reasonably good correlation is found for the C-air reaction, and a low correlation is found for the C-CO_2 reaction.

From these studies, Walker et al. (1977a) concluded that a good parameter to use to correlate char reactivity data is the time required to reach a fractional burn-off of 0.5. Furthermore, they suggested that since char reactivity runs also exhibit a $t/\tau_{0.5}$ region where the rate constant is first order in weight of char remaining, it probably is desirable to give first order rate constants for each run over this region in order to adhere to the more conventional treatment of kinetic data.

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