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EFFECTS OF HEAT TREATMENT CONDITIONS ON
REACTIVITY OF CHARs IN AIR

Technical Report 3

By
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1. INTRODUCTION

Extensive energy research is underway in the United States. This research is aimed at finding ways to meet the ever increasing energy demands. Energy is so important to this country's way of life that such research has become a national priority. It seeks to develop new and non-polluting energy alternatives to oil, which keeps the United States dangerously dependent on external sources of energy, as well as to develop new techniques of more efficient energy utilization. Energy alternatives include solar, geothermal, hydroelectric, wind and nuclear energies, and coal. Among these, coal is considered to be the most promising alternative. The United States has the largest known coal reserves in the world, which can be mined and processed with available technological know-how. Most coal research has centered around conversion to clean pipeline gas, production of low B.T.U. gas and conversion to oil.

A number of coal gasification and liquefaction processes are already in the developmental stage. These processes have been adequately reviewed elsewhere (1), but briefly they include:

- 1) hydrogasification process (or HYGAS process) developed by the Institute of Gas Technology (ITG), Chicago
- 2) CO₂-acceptor process (or CSG process) developed by the Consolidation Coal Company
- 3) FMC (COED) process developed by the Food Machinery Corporation, Char, Oil, Energy Development.

The HYGAS process uses coals varying in rank from lignite to high volatile bituminous. The caking properties of high volatile bituminous coals are eliminated by partial oxidation prior to gasification. It is a two-stage process in which: a) the coal feed passes through a fluidized bed hydrogasifier, countercurrent to a stream of hydrogen at 700-820°C and 70-100 atm pressure. Devolatilization and partial methanation occur, and b) in the second stage the resultant char moves into an electrothermal fluidized bed synthesis gas generator. Here, the char comes into contact with a mixed stream of steam and hydrogen at 930-980°C and 70-100 atm pressure. The end products are predominantly methane and carbon monoxide, and the residue is char, which is about 40% by weight of the starting coal feed.

In the CSG process the coal feed is mixed with calcined dolomite which reacts with carbon dioxide evolved in the gasifier. The heat required for the gasification reaction is supplied by the exothermic reaction between CaO and CO₂. Basically, carbon reacts with steam to form a mixture of carbon monoxide and methane. Residual char is used to regenerate used dolomite. A mixture of devolatilized char and methane is

carried in superheated steam into the gasifier where 60% of the carbon content of the char is gasified.

In the FMC (COED) process high volatile bituminous coal is fed into fluid bed reactors in which multistage pyrolysis takes place in the temperature range 320-870°C. Partial combustion of the resultant char produces hot gases which furnish the heat needed for the earlier pyrolysis reactions. Volatile products are recovered from the stage operating at 440°C; 99% of the volatile matter content of the original coal is removed. These products are then condensed to liquid products. Depending upon the nature of the coal used, the char residue is about 40-50% by weight of the starting coal feed.

Present coal conversion methods are wasteful to a certain extent. The residual chars must be utilized to produce more energy, if energy efficiency is the key note to current research activities. Generally, the chars can be used directly to fire electrical generating plants. However, this will necessitate the modification of existing conventional coal burners for more efficient combustion. But combustion characteristics of such chars are not yet completely understood. Such an understanding is absolutely essential for modification of existing commercial coal burners.

In order to understand the characteristics of coal chars, a number of facts governing their structure should be known. The structure of a char is dependent upon conditions used for its preparation such as: temperature, heating rate, and soak time at maximum temperature.

The purpose of this research was to study the reactivity of as-received pilot plant chars in air and to further examine the effect of heat treatment conditions on modifying their reactivity. Four chars, namely Exxon Wyodak, Exxon Illinois, U.S. Bureau of Mines and FMC (COED) have been used for the present study. In particular, the study is aimed at:

- 1) estimating the maximum temperature the chars 'saw' during their preparation by studying the effect of heat treatment temperature on subsequent char reactivity in air at 500°C,
- 2) studying the effect of soak time at the maximum heat treatment temperature 'seen' by the chars during their preparation on subsequent reactivity in air at 500°C,
- 3) studying the influence of heating rate on subsequent reactivity in air at 500°C,
- 4) studying the influence of gas atmosphere during heat treatment on subsequent reactivity, and
- 5) studying the effect of aging in air on subsequent reactivity.

2. LITERATURE REVIEW

2.1. Gas-Carbon Reactions

The literature contains numerous reports of studies on gas-carbon reactions. Studies have centered around evaluation of reaction rates of carbonaceous solids at various temperatures and pressures in reactant gases. These studies have been extensively reviewed by Walker et al. (2). It is now generally accepted that a heterogeneous reaction between a porous solid and a gas involves the following steps (3):

- i) transport of reactant from the main gas stream to the gas-solid interface,
- ii) intraparticle diffusion of the reactant,
- iii) adsorption of reactant gas at active sites located within the interior of the particle,
- iv) chemical reaction between the adsorbed species to form adsorbed products,
- v) desorption of adsorbed products,
- vi) transport of products from the interior of the solid particles to the outer surface of the particles,
- vii) diffusion of products from the surface of the particle to the bulk gas stream.

One or more of the above listed steps may control the kinetics of a heterogeneous gas-carbon reaction. In general, when reaction temperature is low, reaction rate is essentially chemically controlled, that is, by steps (iii) through (v). At higher temperatures, reaction is chemically and diffusion (intra-particle) controlled, that is, by steps (ii) through (vi). At very high temperatures, reaction is controlled by steps (i) and (vii).

Under ideal conditions, the variation of reaction rate with temperature can be divided into three zones (2). Reaction in Zone I is solely controlled by chemical reactivity in the solid, and the measured activation energy is equal to the true activation energy. In Zone II, reaction is both chemically and diffusion controlled, and the observed activation energy is one-half the true activation energy. Zone III is usually called the high temperature zone, where reaction is controlled by steps (i) and (vii) as discussed above, and the observed activation energy is very small.

2.2. Carbon-Oxygen Reaction

A considerable amount of work has been reported in the literature on the carbon-oxygen reaction. The primary emphasis has been on carbon dioxide, whether it is the primary product of the reaction or whether it is a secondary product resulting from the gas phase oxidation of carbon monoxide. Much of this work has been reviewed by Walker et al. (2). It is now generally accepted that both carbon monoxide and carbon dioxide are primary products of the oxidation of carbon. In these considerations the overall stoichiometric reactions and reaction mechanism have been established as follows:

2.2.1. Bulk Reactions

In the above reactions, carbon is taken to be stable graphite

2.2.2. Reaction Mechanism

The subscripts f and i represent carbon free site and intermediate product, respectively.

2.2.3. Diffusion

It has already been discussed in Section 2.1 that diffusion plays a major role in the gas-carbon reaction. In the gas-carbon reaction, the solid particle is surrounded by a gaseous environment in

which, closest to the solid surface, is a stagnant layer through which the reactant gas diffuses. Using this concept, Kuchta et al. (3) have formulated the following equation for the rate of diffusion through the stagnant layer:

$$R = DA \left(\frac{\Delta c}{\delta} \right) \quad (1)$$

where R = rate of diffusion (g-mol/sec)

D = diffusion coefficient (cm²)

A = external area (cm²)

Δc = concentration gradient (g-mol/cm³)

δ = thickness of stagnant layer (cm)

Diffusion of reactants into the pore system of the solid, or diffusion of products out of the system, can be explained in terms of (i) bulk diffusion, (ii) Knudsen diffusion, and (iii) activated diffusion. The relative magnitudes of the mean free path of the gas and the pore diameter through which diffusion occurs determine which type of diffusion is involved.

When pore diameter is larger than mean free path of the gas, collision between gas molecules is more frequent than between gas molecules and pore walls. In such a case bulk diffusion is involved. The bulk diffusion coefficient is proportional to the 1.5 power of temperature and to the -1 power of pressure. Where pore diameter is smaller than mean free path of the gas, collisions between gas molecules and pore walls are more frequent than collisions between gas molecules. Under such conditions, Knudsen diffusion is involved. The Knudsen diffusion coefficient is proportional to 0.5 power of temperature, but is independent of pressure. When pore radius is commensurate with the size of the diffusing gas, repulsive interactions between pore walls and gas molecules become dominant. In such a case, activated diffusion is involved. The activation energy is highly sensitive to small differences in pore size.

Due to a wide variation in pore sizes and pore lengths in coal chars it is difficult to calculate diffusion coefficients. All three modes of diffusion may be simultaneously involved. Smith (4) has described two models (the parallel pore and random pore models) for these calculations. In the first model, the pore volume and surface area of the solid are used to calculate the mean pore radius, which in turn is used to calculate bulk and Knudsen diffusion coefficients. The second model assumes a bi-modal distribution of pore volume consisting of macro- and micropores. The Knudsen and bulk diffusion coefficients are calculated from the mean pore radii of the two pore systems. When activated

diffusion is dominant, such as in microporous coals and chars, these calculations are not applicable. Steady-state diffusion coefficients can be measured for graphite. This is done by measuring the diffusion rates of N_2 and H_2 through a slab, when one side is exposed to N_2 and the other to H_2 . For coals and chars the diffusion coefficient is measured under unsteady-state conditions. Results of such measurements have been reported by Walker *et al.* (5). Argon, methane, nitrogen and carbon dioxide were utilized for measuring diffusion parameters, $D^{1/2}/r_0$. It is, however, impossible to calculate an accurate value of the diffusion path length, r_0 . Hence, absolute values of diffusion coefficients are, at best, good estimates.

2.3. Composition and Structure of Coal

It has been suggested that the basic structural units of coal are aromatic and hydroaromatic layers (5). These are joined together by sulfur and methylene cross-links, while hydroxyl, carbonyl oxygen and hydrogen groups are attached to the periphery of the layer planes. Therefore coal can be considered to be a polymer. The polymer units are poorly packed in three dimensions, resulting in a highly porous structure. The nature of the porous structure and surface area of coals have been the subject of many studies (5-14).

In the study of porosity and surface area of porous solids, physical adsorption of gases is regarded as one of the most important tools. Zwietering and Van Krevelen (6) studied surface areas of coals using adsorption, density and mercury penetration techniques. It was found that some coals have a macropore system with a surface area of 1-2 m^2/g and a micropore system with an area of about 100 m^2/g .

Both N_2 and CO_2 surface areas show a dependence on coal rank (15). Gan *et al.* (15) have shown that for coals with carbon contents greater than 80% or less than 70%, even though total surface area as measured by CO_2 adsorption is high (150-400 m^2/g), N_2 surface area is usually less than 1 m^2/g . N_2 surface area is appreciable only for coals with carbon contents between 75 and 80%.

Nitrogen adsorption is usually carried out at 77°K while carbon dioxide adsorption is carried out at 298°K. At 77°K some of the micropore system in coals is inaccessible to nitrogen molecules. Nandi and Walker (7), in their activated diffusion studies of CO_2 and N_2 in coals of various ranks, found that N_2 has a higher activation energy for diffusion than CO_2 . The inaccessibility of some of the micropores to N_2 may be explained in terms of either actual pore shrinkage at 77°K or an activation diffusion process (8,9). Walker and Nandi (7) have suggested that the very low N_2 areas can be accounted for primarily by the low

diffusion rate of N_2 at 77°K. The N_2 area at this temperature represents mainly the sum of the macropore and transitional pore surface areas, physical shrinkage of pores being of insignificant consequence. In a later study, Walker and Kini (10) concluded that surface area of coals, obtained from carbon dioxide adsorption at 298°K, very closely represents the total surface area.

2.4. Structure of Coal Chars

There is a general agreement (11-14) that the structure of coal chars depends on a number of variables, among which are: the nature of the starting coal, heating rate, gaseous atmosphere used during carbonization, pressure, maximum temperature and soak time. Depending upon their behavior during heat treatment, coals can be classified into thermosetting and thermoplastic (11). A thermosetting coal yields a char upon heat treatment, while a thermoplastic coal undergoes softening and yields a coke.

Many of the characteristics of the coal precursors are carried over to the resultant chars. During heating, volatile matter is first released from the skeleton framework, creating additional surface area. Further heating destroys some of the cross-links, permitting aromatic units to align. This results in reduced surface area (11,12,14). Thus, over a given temperature range the surface area goes through a maximum. The exact temperature at which the maximum occurs depends upon the starting coal (11,12,14).

Donald (16) pyrolyzed an anthracite coal in N_2 from room temperature to 925°C and determined its surface area. It was found that the surface area decreased at heat treatment temperatures above 770°C.

2.5. Inorganic Impurities in Coals and Coal Chars

Coals and their char derivatives contain varying amounts of inorganic impurities (17,18). These inorganic impurities are broadly divided into two categories: i) discrete mineral matter, and ii) minor and trace elements. The principal minerals found in coals include kaolite, pyrite, illite, calcite and quartz. They are usually present as particles greater than about 1 μ . Upon heat treatment of the coal to elevated temperatures, the minerals are changed chemically as described by O'Gorman and Walker (19). Associated with the organic phase of coal are trace elements, which are more uniformly dispersed on a much finer scale than discrete mineral matter. They too can undergo some change upon heat treatment. For example, cation nuclei associated with carboxyl groups in lignites probably diffuse across the coal surface following decomposition of the carboxyl groups, and form agglomerates.

2.6. Factors Influencing Char Reactivity

So far we have been primarily concerned with structure and composition of coals and chars. We have emphasized the structural changes that take place during heat treatment of coals under different conditions. At this stage, it is desirable to examine the factors influencing char reactivity. It has been reported that upon heating in an inert atmosphere, the surface area of coal chars goes through a maximum (11,12,14). Jenkins *et al.* (17) have reported that coals of different rank undergo significant changes in N_2 and CO_2 areas upon heat treatment up to $1000^\circ C$ and that the rank of the parent coal determined the pore structure developed in the char. It is desirable to have large specific surface areas for higher gasification rates. It is also important to have micropores adequately connected to large voids so that reactant molecules can diffuse rapidly into the internal area and active sites. It is known that if a coal char lacks macro- or transitional pores, gasification rates in air and carbon dioxide are low (17,18). Char reactivity has also been shown to be dependent on the rank of the parent coal (17,18,20,21). Chars derived from low rank coals usually have higher reactivities than those derived from higher rank coals.

The presence of inorganic impurities in chars has been known to catalyze gasification rates (17,18,22,23). Two approaches have been used to study such effects, namely: i) addition of inorganic 'impurities' to chars and ii) removal of mineral matter from chars by extraction with HCl and HF. The addition of potassium and sodium as carbonates has been shown to increase char reactivity (22,24-27). It has been suggested that the silica content of ash of the char can react with sodium carbonate to form catalytically inert silicate (25,26). Walker and co-workers (17,18) have found no correlation between reactivity and alkali content of chars. Char reactivity in CO_2 and steam has been reported to increase upon addition of iron to chars (22,23), but the presence of silica initially present in the chars can deactivate the iron. The addition of calcium oxide to chars has been reported to increase char reactivity (21,24). Walker *et al.* (17,18) observed that char reactivity in air and CO_2 increases as the calcium and magnesium contents of chars increase. The effect of mineral matter removal has been reported in the literature (17,18,28,29). Reactivity of chars produced from lower rank coals decreases upon mineral matter removal. It has been suggested that in such cases mineral matter catalyzes the gasification rates (17,18). However, in the case of chars derived from higher rank coals, reactivity increases upon demineralization (17,18,28,29). This has been attributed to opening up of previously blocked feeder pores; the increase in porosity facilitates the transport of the reactant gas into the internal pore structure of the chars. It has been suggested that in such cases, the increase in porosity more than offsets the decrease in reactivity which might result from the loss of catalytically active mineral matter.

3. EXPERIMENTAL AND PROCEDURES

3.1. Sample Selection

Four chars were used for the major part of this study. They were: Exxon Wyodak, Exxon Illinois, Bureau of Mines and FMC (COED) chars. The Exxon chars were produced at the Exxon Baytown Research and Development Division. One char was derived from a Wyodak coal (Wyodak Resources Development Company Mine) and the other from an Illinois coal (Monterey Coal Company No. 1 Mine). The preparative methods for the two Exxon chars are proprietary. The Bureau of Mines char was prepared from a high volatile bituminous coal, Utah King Mine, in an entrained carbonizer at the Grand Forks Station. The FMC (COED) char was derived from Illinois No. 6 (Peabody Mine No. 10). As stated in the introduction part of the report, the (COED) process involves multistage pyrolysis in fluid reactors in the temperature range 320-870°C and a slight partial combustion (about 10% by weight combustion loss) to heat the pyrolysis stages. Proximate and ultimate analyses of the various parent coals and chars derived from them are given in Table 1. The as-received Bureau of Mines and FMC (COED) chars were of 40x100 mesh size. The Exxon chars were ungraded. These chars were sieved and 40x100 mesh fractions were used for reactivity measurements. In a few studies, chars prepared from a lignite coal, PSOC-246, were also used.

3.2. Gases

Purified N₂, air, H₂ and CO₂ supplied by the Linde-Harvey Company were used in this study. Nitrogen gas had a minimum purity of 99.997%. It contained moisture and oxygen estimated to be about 3 ppm and 1 ppm, respectively. The dry air had a maximum moisture content of about 3 ppm. Both H₂ and CO₂ used were of high purity grade.

3.3. Thermogravimetric Studies

3.3.1. The Thermogravimetric Analyzer

The Fisher Thermogravimetric Analyzer (TGA) was used in the present study. It is made up of modular components which are specifically designed to perform automatically programmed thermogravimetric analyses. During operation, weight change of a material can be recorded as a function of time or temperature. Figure 1 shows a block diagram of the system. The TGA assembly incorporates a stainless steel weighing chamber

Table 1

Analyses of Parent Coals and Chars

Identification	Proximate Analysis, % Dry			Ultimate Analysis, % daf				
	Ash	VM	Fixed C	C	H	N	S	O (by Diff.)
<u>Parent Coals</u>								
Exxon Wyodak	7.9	44.0	48.1	73.8	5.4	0.98	0.76	19.2
Exxon Illinois	9.4	42.0	48.6	75.1	5.3	1.3	5.1	13.2
Bureau of Mines	5.4	46.3	48.3	76.3	6.1	1.4	0.5	15.7
FMC (COED)	13.5	38.0	48.5	77.5	5.5	1.5	4.4	11.1
<u>Chars</u>								
Exxon Wyodak	40.2	8.0	51.8	98.7	0.94	0.55	2.8	- 3.1
Exxon Illinois	24.3	13.8	61.9	95.8	1.10	0.64	2.7	- 0.36
Bureau of Mines	13.3	5.1	81.6	94.0	1.10	1.60	0.58	2.6
FMC (COED)	21.3	2.5	76.2	93.6	1.00	1.20	4.00	Nil

Figure 1. FLOW SHEET OF FISHER TGA APPARATUS

and an adjustable furnace platform within an open metal cabinet. It is a self-contained module and permits processing of samples in static and vacuum environments as well as under gas flow conditions.

In the present work, it was operated under gas flow conditions. The Cahn Electrobalance is mounted in the weighing chamber and equipped with stirrups. A small platinum pan is suspended by a steel wire from the left stirrup and balanced with tare weights on the right hand side. Then a thermocouple is placed in close proximity to the pan and a quartz concentric flow tube is inserted around the sample and thermocouple. The furnace is placed on the adjustable furnace platform,

To perform a TGA analysis, the sample is placed in the weighing pan and a quartz hang-down tube is placed around the concentric flow tube. The furnace is raised into position and a programmed heating rate is selected on the temperature programmer. Sample weight changes and temperatures are recorded continuously and simultaneously on the two-pen recorder. A more detailed description of the equipment covering scientific and engineering principles and weighing procedures is listed elsewhere (30).

During a few preliminary runs, it was observed that it was not possible to obtain good weight measurements consistently at higher temperatures because the sample pan and hang-down wire stuck to the side of the concentric flow tube. This behavior was thought to be due to electrostatic effect. To remove this effect, a thin nickel wire was wound around the tube and grounded to the weighing chamber.

3.3.2. Reactivity Measurements

3.3.2.1. Procedure

About 5-9 mg of sample were weighed in the sample pan in the TGA unit as described previously. Jenkins *et al.* (16) have previously shown that in the coal char-air reactivity experiments, diffusion through the sample bed was minimized when the bed height (or weight) was kept below 10 mg. A stream of N₂ at a flow rate of 300 cc/min was passed for 30 minutes through the system to displace the air present. A heating rate was selected on the temperature programmer and heating started. In those cases where the desired temperature was 500°C, as soon as the sample attained a temperature of 500°C, heating-up was terminated. A period of 15 min was allowed for thermal equilibrium between the sample and furnace. At this stage, N₂ was replaced by air at the same flow rate (300 cc/min). Weight changes were then recorded continuously as a function of time. When the desired final temperature was above 500°C, heating was stopped as soon as the sample attained the desired maximum temperature. The sample then was cooled to 500°C. The temperature (500°C) was kept isothermal for 15 min to allow thermal equilibrium to be attained. At this stage, N₂ was replaced by air. The extent of burn-off was monitored as a function of time.

3.3.2.2. Calculations

For each char, burn-off versus time plots indicated a region of maximum rate of reaction which was discernible in the 10-50% carbon burn-off range. Following the suggestion of Jenkins *et al.* (17), the reactivity parameter was calculated by the following equation:

$$R_T = \frac{1}{w} \cdot \frac{dw}{dt}$$

where R_T = reactivity ($\text{mg hr}^{-1} \text{ mg}^{-1}$)

w = starting weight of char on a dry-ash-free basis (mg)

$\frac{dw}{dt}$ = maximum rate of reaction (mg hr^{-1})

Triplicate reactivity runs on the as-received Exxon Wyodak char heat treated to 500°C at a rate of $10^\circ\text{C}/\text{min}$ prior to reaction with air show (Appendix A) that reactivity values are reproduced within an error limit of ± 0.14 . Error bars are not included in Figures 5 and 6, because the size of data points is about equal to the experimental error limit (± 0.14).

3.4. Rapid Heating in the Isothermal Reactor

3.4.1. The Isothermal Reactor

The isothermal reactor is so-called because it operates at a constant temperature. In the present study, this temperature was 800°C . The reactor is also called the laminar flow reactor because the Reynold number is about 450 (31). Figure 2 shows a block diagram of the system. It is composed of a preheater, water-cooled coal feeder probe, furnace, water-cooled char collector probe, cyclone, and char collector. It is connected to two gas tanks via the coal feeder probe and the preheater. The isothermal reactor has three major functions:

- 1) It is designed to feed coal at a known rate into the reaction zone, usually $0.5 \text{ g}/\text{min}$.
- 2) It allows the sample to be heated to a predetermined temperature at a very fast rate. In this case the predetermined temperature was 800°C and the heating rate was about $8000^\circ\text{C}/\text{sec}$. The total residence time of a particle in the reaction zone can be valued at about 300 milliseconds.

Figure 2. ISOTHERMAL REACTOR

- 3) Finally, the sample is rapidly quenched in a water-cooled collector probe. This prevents occurrence of secondary reactions outside the reactor zone.

A more detailed description of the equipment has been reported by Nsakala (31).

3.4.2. Procedure

The system was heated to 800°C and allowed to stabilize for at least 30 min, N₂ was introduced through the feeder probe at a flow rate of 160 cc/min and through the preheater at a flow rate of 2380 cc/min. The sample was placed in a hopper regulated to feed it into the feeder probe in a stream of N₂. The char was rapidly heated as it moved into the reaction zone. After a residence time of up to 300 milliseconds in the reaction zone, it entered the water-cooled char collector probe where the devolatilization reaction was quenched. Finally, it was sucked through a cyclone and collected in the char collector.

3.5. Surface Area Measurements

3.5.1. Adsorption Apparatus

A conventional volumetric adsorption apparatus was used for the surface area measurements. A diagram of the apparatus is shown in Figure 3. It consists of a glass sample holder, a calibrated burette placed in a water jacket maintained at a constant temperature, a high vacuum oil pump, a mercury diffusion pump and a McLeod gauge. The components are connected as shown in the diagram.

The adsorption apparatus was used to obtain surface areas by nitrogen and carbon dioxide adsorption at 77°K and 298°K, respectively. It works on the same principles as described by Emmett (32). If the volume and number of molecules of a gas corresponding to the formation of a monomolecular layer can be estimated, then multiplication of the number of molecules corresponding to monolayer coverage by cross-sectional area of the adsorbed molecule will give the surface area of the adsorbent.

3.5.2. Procedure

Nitrogen surface areas were measured at 77°C, using liquid nitrogen in a Dewar flask as a cooling jacket outside the sample holder. Depending upon the adsorption capacity of the sample, a known weight of

Figure 3. VOLUMETRIC ADSORPTION APPARATUS FOR SURFACE AREA MEASUREMENTS

sample (usually 0.5-1.0 g) was placed in the glass sample holder. A small amount of glass wool was placed in the neck of the sample holder to ensure that the sample was not sucked out of the holder during evacuation. The sample holder was attached to the system and evacuated overnight. Heating was stopped and the sample holder cooled to room temperature. The sample holder was then surrounded by a Dewar flask containing liquid nitrogen. The system was allowed to attain thermal equilibrium for at least 30 min. Free volume of the system was measured using high purity helium gas.

Following free volume determination, the system was evacuated for at least 30 min to remove helium. Following this, a dose of N₂ was introduced into the system with the stopneck controlling passage into the sample holder being closed. The pressure of the gas was recorded. Then the stopneck was opened to allow the gas to come into contact with the sample. An arbitrary time of 30 min was allowed for each adsorption point. At the end of this period, the equilibrium pressure was measured. At least four adsorption points in the relative pressure range 0.05-0.35 were obtained.

The procedure for measuring CO₂ surface areas was the same as that for N₂ areas, except that adsorption measurements were made at 298°K.

3.5.3. Calculation of Surface Area

3.5.3.1. Volume of Free Space

Volume of free space was calculated using the following pressure-volume relationship:

$$PV_d = P_i(V_c + V_{fs}) \frac{T_s}{T_r} \quad (2)$$

where P = pressure of gas in dead space

V_d = volume of dead space

P_i = equilibrium pressure

V_c = cumulative volume of system at P_i

V_{fs} = volume of free space

T_s = temperature of sample

T_r = room temperature

3.5.3.2. Nitrogen Surface Area

The BET equation given below was used for N₂ surface area calculations:

$$\frac{P_i}{\Sigma V_a (P_o - P_i)} = \frac{1}{V_m C} + \left(\frac{C-1}{V_m C}\right) \cdot \frac{P_i}{P_o} \quad (3)$$

where P_i = equilibrium pressure (torr)

P_o = saturation vapor pressure of N₂ (760 torr)

V_m = monolayer volume (cm³)

C = constant

ΣV_a = cumulative volume of gas adsorbed (cm³)

A plot of $\frac{P_i}{\Sigma V_a (P_o - P_i)}$ against $\frac{P_i}{P_o}$ gave a straight line whose slope was $\frac{C-1}{V_m C}$ and intercept $\frac{1}{V_m C}$. The sum of the slope and intercept equals $\frac{1}{V_m}$. The specific surface area was calculated from the following equation:

$$\text{Surface area} = V_m \left(\frac{\sigma N}{V_o} \right) \quad (4)$$

where σ = cross-sectional area of a N₂ molecule (16.2 Å²)

N = Avogadro's number

V_o = volume of one mole of gas at STP (22.4lit)

3.5.3.3. Carbon Dioxide Surface Area

The Dubinin-Polanyi equation given below was used to calculate the CO₂ areas:

$$\text{Log } V_a = \text{Log } V_o - 0.43 \frac{4B}{\beta^2} T_s^2 \left[\log \left(\frac{P_i}{P_o} \right) \right]^2 \quad (5)$$

where V_a = volume of CO₂ adsorbed (cm³/g)

V_o = micropore capacity (cm^3)

B = constant which is a measure of average size of micropores

T_s = sample temperature ($^{\circ}\text{K}$)

equilibrium pressure of adsorbed gas (torr)

P_o = saturation vapor pressure of CO_2 (4830 torr)

β = affinity coefficient of CO_2 relative to N_2

From a plot of $\log V_a$ versus $\log^2 \left(\frac{P_i}{P_o} \right)$ the intercept, $\log V_o$, could be determined. This value was then converted to a micropore surface area, taking the cross-sectional area of the CO_2 molecule as $25.3 \text{ \AA}^2$.

3.6. Determination of Particle Size Distribution

3.6.1. Procedure

A number of standard sieves were arranged in series between 420μ (40 mesh) and 149μ (100 mesh). The sample was placed in the top sieve. The top and bottom sieves were closed and the set was shaken in a Rotap machine for 30 min. Following this, the set was removed from the machine and the sieves separated. The weight of sample retained by each sieve was determined and added to the weight of the sample retained by the sieve(s) above it. In this way, cumulative weights of sample retained on each sieve were obtained.

3.6.2. Calculations

Particle size distribution was calculated according to the Rosin-Rammler equation:

$$R = 100 \exp \left[- \left(\frac{x}{x'} \right)^n \right] \quad (6)$$

where R = weight percent of particles greater than x

x = particle size (μ)

x' = measure of fineness of particles

n = measure of size dispersion

Equation (6) can be rewritten in the form:

$$\text{Log} \left(\log \frac{100}{R} \right) = n \log x + K \quad (7)$$

where $K = \text{constant}$.

In order that a size distribution obeys the Rosin-Rammler equation, a plot of $\log \left(\log \frac{100}{R} \right)$ against $\log x$ should give a straight line. For these calculations, the Rosin-Rammler graph paper was used. In each case, a linear relationship was observed. At $R = \frac{100}{e} = 36.79$, $x' = x$. In this way x' was read directly from the graph paper. The slope, n , was read from the plot. The mean size by weight, $\bar{x}$, was calculated from the following equation:

$$\bar{x} = \int_0^{\infty} x \, dR \quad (8)$$

where $dR = \text{change in } R \text{ as the function goes from } 0 \text{ to } \infty$. From equations (6) and (8), the following relation is obtained:

$$\bar{x} = x' \phi(n) \quad (9)$$

where $\phi(n) = \Gamma\left(\frac{1}{n} + 1\right)$. The gamma function was read from standard tables.

3.7. Determination of Volatile Matter Content of Chars

3.7.1. Procedure

The char was dried in a weighed sample cup with cover on. Drying was done in an oven at 115°C for 90 min. The sample, cup and cover were weighed before being placed in the oven, maintained at 950°C . The sample was kept at 950°C for 7 min. After this, the sample holder was removed and cooled in the atmosphere for 14 min and then reweighed. The decrease in weight was taken as a measure of volatile matter content of the char.

4. RESULTS

4.1. Burn-Off Curves

Burn-off vs. time curves for the four chars heated at a rate of $10^{\circ}\text{C}/\text{min}$ to 500°C prior to reaction in air at 500°C are given in Figure 4. A close look at these curves reveals the presence of three distinct regions: (i) in the first region, reaction rate increases slowly. During this increase in reaction rate three processes seem to take place: (a) the system is purged of N_2 as air flows in, (b) oxygen gradually chemisorbs on the char surface, forming complexes on it, and (c) the char is activated, resulting in an increase in surface area, and, hence, an increase in reaction rate. (ii) In the intermediate region, reaction rate is a maximum. This suggests that active surface area, that is concentration of edge carbon atoms, increases with burn-off, and is maximum in this region. (iii) In the third region, reaction rate decreases continuously. In this region, gasification removes walls between pores, resulting in a decrease in surface area and, hence, a decrease in reaction rate.

4.2. Effect of Heat Treatment Temperature on Reactivity

Char reactivities measured at 500°C in air following heat treatment at a rate of $10^{\circ}\text{C}/\text{min}$ to different temperatures are listed in Table 2 and are plotted in Figure 5. It is seen that for each char the reactivity remains essentially constant up to a certain heat treatment temperature (HTT) and decreases thereafter. For the four chars this temperature is between 725 and 750°C . Since reactivity of a char is expected to remain constant up to the maximum HTT "seen" by the char during its preparation and decrease thereafter, it can be concluded that the four chars saw a temperature of about 750°C during their preparation.

4.3. Effect of Soak Time at Maximum HTT on Char Reactivity

The effect of soak time at maximum HTT, that is the temperature above which reactivity starts decreasing, on reactivity was studied for all the chars. Each char was heated in a N_2 flow ($300\text{ cc}/\text{min}$) from room temperature to the maximum HTT at a rate of $10^{\circ}\text{C}/\text{min}$. As soon as the maximum HTT was attained, the temperature was kept constant for various time intervals up to 120 min. The char was then cooled to 500°C at a rate of $10^{\circ}\text{C}/\text{min}$ and its reactivity to air determined at 500°C . A fresh sample was used for each run.

The results are listed in Table 3 and illustrated in Figure 6. It is seen that for each char reactivity remains constant up to 15 min

Figure 4. BURN-OFF CURVES IN AIR AT 500°C FOR AS-RECEIVED CHARS

Table 2

Effect of Heat Treatment Temperature on Subsequent
Reactivity of Chars to Air at 500°C

HTT, °C	Char Reactivity, $\text{mg hr}^{-1} \text{mg}^{-1}$			
	Exxon Wyodak	Exxon Illinois	Bureau of Mines	FMC (COED)
500	4.06	3.43	2.96	2.25
600	3.95	3.39	2.97	2.20
650	--	--	2.96	--
675	--	--	2.96	--
700	3.90	3.38	2.91	2.21
725	3.90	3.37	2.80	2.20
735	3.72	3.30	--	2.20
750	3.69	3.13	2.71	2.20
800	3.12	3.00	2.50	1.90
870	2.46	--	--	--
900	2.06	2.70	2.42	1.80
1000	1.92	2.50	2.16	1.60

Figure 5. EFFECT OF HEAT TREATMENT TEMPERATURE ON SUBSEQUENT REACTIVITY TO AIR AT 500°C

Figure 6. EFFECT OF SOAK TIME AT THE MAXIMUM HTT ON REACTIVITY

soak time, and decreases thereafter. For Exxon Wyodak, Exxon Illinois and FMC (COED) chars, decrease in reactivity continues up to 30 min soak time and remains constant thereafter. In the case of the Bureau of Mines char, the decrease in reactivity continues up to 60 min.

Table 3
Effect of Soak Time at Maximum HTT on Char
Reactivity to Air at 500°C

Soak Time (min)	Char Reactivity, $\text{mg hr}^{-1}\text{mg}^{-1}$			
	Exxon Wyodak	Exxon Illinois	Bureau of Mines	FMC (COED)
0	3.90	3.39	2.96	2.20
15	3.85	3.37	2.91	2.20
30	3.02	3.00	2.90	1.55
60	3.00	3.00	2.04	1.53
90	3.00	--	--	--
120	3.04	3.00	2.02	1.53

4.4. Effect of Aging on Reactivity

Following heat treatment up to 800°C at a rate of 10°C/min, Exxon Wyodak char was stored in a desiccator. Portions of it were withdrawn at intervals of 1 and 4 days and its reactivity measured in air at 500°C. The results are presented in Table 4. It can be seen that aging has little or no effect on char reactivity.

4.5. Effect of Heating Rate on Reactivity

The effect of heating rate on char reactivity was studied next. The char samples were heated at different rates (5, 10, 20, and 25°C/min) to their maximum HTT's. The results are listed in Table 5 and illustrated in Figure 7. It is seen that in each case reactivity increases slightly with increase in heating rate between 5°C/min and 25°C/min.

Table 4

Effect of Aging in Air at Room Temperature on
Reactivity of Exxon Wyodak Char to Air
at 500°C

Exposure Time in Air (days)	Reactivity, $\text{mg hr}^{-1} \text{ mg}^{-1}$
0	3.12
1	3.12
4	3.10

Table 5

Effect of Heating Rate on Char Reactivity

Heating Rate (°C/min)	Reactivity, $\text{mg hr}^{-1} \text{ mg}^{-1}$			
	Exxon Wyodak	Exxon Illinois	Bureau of Mines	FMC (COED)
5	3.68	3.25	2.65	2.11
10	3.90	3.43	2.96	2.20
20	4.12	3.50	3.10	2.30
25	4.21	3.54	3.21	2.35

Figure 7. BURN-OFF CURVES IN AIR AT 500 °C FOR EXXON WYODAK CHAR HEAT TREATED AT DIFFERENT HEATING RATES

4.6. Influence of Rapid Heating on Reactivity

It was decided to preheat the chars at higher rates to study the effect of rapid heating on reactivity. Samples were heated at a rate of about 8000°C/sec in the Isothermal Reactor to 300°C. Following rapid heating, reactivity measurements were made in air at 500°C. Table 6 lists a comparison of reactivity of chars heated at 10°C/min to 800°C and those rapidly heated. The ratios of reactivities of rapidly and slowly heated chars are also listed in Table 6. Burn-off vs. time curves for the rapidly heated chars are plotted in Figure 8. Burn-off curves for the rapidly and slowly heated Bureau of Mines char are shown in Figure 9. It is seen (Table 6) that in each case reactivity of the rapidly heated char is appreciably higher than that of the char heated at a rate of 10°C/min. Ratios of reactivities of the rapidly and slowly heated chars are 1.63, 1.37, 1.47 and 1.62 for the Exxon Wyodak, Exxon Illinois, Bureau of Mines and FMC (COED) chars, respectively. The corresponding ratio for the PSOC-246 char is 1.11. This char was prepared by heating the raw coal to 800°C in a N₂ atmosphere in a fluidized bed reactor at the rate of 10°C/min. As soon as the sample attained a temperature of 800°C, heating was stopped and the sample cooled in N₂ to room temperature. A portion of this char was subsequently rapidly heated to 800°C in the Isothermal Reactor. It is noteworthy that when the raw coal is rapidly heated in the Isothermal Reactor, its reactivity is almost twice as much as that of the char prepared at a heating rate of 10°C/min. It is thought pertinent to point out that the reactivity of PSOC-246 coal, heat treated to 500°C at the rate of 10°C/min, was 3.85 mg hr⁻¹ mg⁻¹. This is much less than the reactivity for the coal rapidly heated to 800°C. It has hitherto been believed that HTT prior to reactivity measurement has a more pronounced effect on the subsequent reactivity of the char than the heating rate used during the heat treatment. The present results show conclusively that even though the temperature "seen" by the coal during rapid heating is about 300°C higher than that "seen" during slow heating, the gasification rate is much faster in the former case.

The maximum HTT "seen" by the Exxon Wyodak char during rapid heating was also determined in the manner described in Section 4.2 of the report. The rapidly heated char was subsequently heated in the TGA unit in N₂ at a rate of 10°C/min to different temperatures in the range 500°-800°C. Following each heat treatment, reactivity to air at 500°C was measured as in Section 4.2 of the report. The results are shown in Table 7. It is seen that reactivity remains essentially constant up to a HTT of about 780°C. Following the same logic as in Section 4.2, it can be concluded that the char saw a maximum HTT of about 780°C during rapid heating. The point is, though, that slow heating of the rapidly heated char even up to 800°C resulted in a relatively minor decrease in its subsequent reactivity.

Table 6

Effect of Rapid Heating of Chars or Coal
to 800°C on Char Reactivity
to Air at 500°C

Sample	Reactivity ($\text{mg hr}^{-1}\text{mg}^{-1}$)		R_T (Rapid Heating)
	Heating Rate 10°C/min	Rapid Heating	R_T (10°C/min)
<u>Chars</u>			
Exxon Wyodak	3.12	5.08	1.63
Exxon Illinois	3.00	4.11	1.37
Bureau of Mines	2.50	3.67	1.47
FMC (COED)	1.90	3.08	1.62
PSOC-246	2.79	3.10	1.11
<u>Coal</u>			
PSOC-246	2.79	5.17	1.86
PSOC-246 (500°C)*	3.85	--	--

*In this case the coal was heated at 10°C/min to reaction temperature (500°C) and subsequently reacted with air.

Figure 8. BURN-OFF CURVES IN AIR AT 500°C FOR CHARS RAPIDLY HEATED TO 800°C

Figure 9. BURN-OFF CURVES IN AIR AT 500°C FOR RAPIDLY AND SLOWLY HEATED BUREAU OF MINES CHAR

Table 7

Effect of Heat Treatment Temperature on Reactivity
of Rapidly Heated Exxon Wyodak Char

HTT, °C	R_T (mg hr ⁻¹ mg ⁻¹)
500	5.00
600	5.00
700	4.98
750	4.98
775	4.94
780	4.93
790	4.83
800	4.80

4.7. Effect of Rapid Heating on Particle Size Distribution

The effect of rapid heating on particle size distribution was studied as well. The as-received chars were sized in a series of standard sieves arranged in order: 420, 297, 250, 177 and 149 μ . Separated fractions were weighed. In the same manner, the rapidly heated chars were sized. Size distributions were calculated according to the Rosin-Rammler equation. The results are listed in Table 8. It is seen that $\bar{x}$, the mean particle size by weight, decreases after rapid heating. The decrease is more pronounced for the Exxon Wyodak and Exxon Illinois chars.

4.8. Volatile Matter Content

Volatile matter content of as-received and rapidly heated chars was determined using the ASTM technique. The results are listed in Table 9. The results show that the chars lose considerable amounts of volatile matter upon rapid heating.

Table 8
Particle Size Distribution for the As-Received
and Rapidly Heated Chars

Char	Mean Particle Size by Weight, $\bar{x}$ (μ)	
	As-Received Char	Rapidly Heated Char
Exxon Wyodak	264	233
Exxon Illinois	277	225
Bureau of Mines	273	270
FMC (COED)	287	278

Table 9
Volatile Matter Content of Chars

	Volatile Matter, % (daf)	
	As-Received	Rapidly Heated
Exxon Wyodak	10.9	7.3
Exxon Illinois	15.1	10.7
Bureau of Mines	4.8	2.7
FMC (COED)	4.1	3.2

4.9. Surface Areas

The N₂ and CO₂ surface areas of chars heated at a rate of 10°C/min to 800°C and those rapidly heated up to 800°C are listed in Table 10. Both N₂ and CO₂ areas are consistently higher for the rapidly heated chars.

4.10. Effect of Gaseous Atmosphere During Heat Treatment on Char Reactivity

Exxon Wyodak char was preheated in three different gas atmospheres (N₂, H₂, CO₂) to 725°C at a rate of 10°C/min. It was then cooled to

Table 10

Surface Area of Chars

Char	N ₂ Surface Area (m ² /g)				CO ₂ Surface Area (m ² /g)			
	Slow HT		Rapid HT		Slow HT		Rapid HT	
	dry basis	daf basis	dry basis	daf basis	dry basis	daf basis	dry basis	daf basis
Exxon Wyodak	133	186	143	200	449	630	553	775
Exxon Illinois	305	379	382	474	213	264	419	521
Bureau of Mines	313	355	363	411	357	404	552	626
FMC (COED)	262	318	281	340	365	443	540	655
PSOC-246	93	106	139	157	449	511	569	646

500°C and its reactivity to air measured at 500°C. The results are listed in Table 11. It is seen that gaseous atmosphere used during heat treatment has little or no effect on subsequent char reactivity.

Table 11

Effect of Gas Atmosphere During Heat Treatment on
Subsequent Reactivity of Exxon Wyodak Char
to Air at 500°C

HT Atmosphere	R_T (mg hr ⁻¹ mg ⁻¹)
N ₂	3.90
H ₂	4.00
CO ₂	3.84

5. DISCUSSION

Coal is a complex organic precursor for the production of cokes and chars. It contains aromatic and hydroaromatic material, heteroatom functional groups at the edges of the planar regions, and crosslinks between molecules. As the rank of coal changes from anthracite to lignite, important changes occur in (i) the average size of the aromatic and hydroaromatic groups, (ii) the ratio of aromatic to hydroaromatic material, (iii) the amount and chemical composition of the functional groups, and (iv) the density and chemical composition of the crosslinks. Although this presents a complex situation, at the same time this complexity gives great flexibility in the structure of cokes and chars which can be produced from coals.

As microporous coals are thermally treated, they lose volatile matter, planar regions grow in size and crosslinks are broken. The nature of porosity in the coal is expected to change as a function of such variables as: heating rate, maximum temperature, soak time at maximum temperature, atmosphere under which heating occurred, particle size, inorganic impurities present and their distribution in coal, maceral composition and whether the coal behaves as a thermoplastic or thermosetting material.

The first step in the overall gasification of relatively pure carbons is the dissociative chemisorption of reactant gas molecules at the active sites, that is, carbon atoms located at the edges of layer planes. Diamond (33) has made a detailed study of changes in crystallite diameter (L_a) of coals of different rank heat treated to different temperatures. He found that for a given HTT, chars derived from higher rank coals have larger L_a . In other words, the concentration of active sites in chars decreases with increase in rank of the parent coal.

Since coal chars are highly nonporous materials, most of the area and active sites will be located within the micropores. Obviously, gasification rates will be determined by the ease with which the reactant molecules can diffuse into the internal pore structure. Thus, it is desirable to have the micropores adequately connected to the feeder pores, that is, transitional and macropores.

Coals and, hence, chars derived from them, are invariably associated with varying amounts and types of mineral (inorganic) impurities. It is well known that impurities catalyze various gas-carbon reactions (12, 34). The specific activity of a catalyst depends upon its amount, chemical form and degree of dispersion. Relative activity of the same impurity changes depending upon which gasification reaction is being catalyzed. For example, iron is a more active catalyst than nickel for catalyzing the carbon-oxygen or carbon-steam reaction whereas nickel is more active than iron for catalyzing the gasification of carbon by hydrogen.

From the above discussion, it is obvious that char gasification rates will be governed primarily by three factors: (i) concentration of active sites, (ii) presence of catalytic inorganic impurities, and (iii) diffusional limitations on how rapidly the reactant gas molecules can reach the active sites. The mechanism of char gasification is complicated further by the fact that gasification involves dynamic changes in char properties. For example, the concentration of active sites can change as a result of opening up of closed pores and enlargement of existing pores. The extent to which concentration of active sites will change with carbon burn-off will depend upon such variables as the starting structure of char, gasification temperature, reactive gas, nature and dispersion of inorganic impurities as well as the level of carbon burn-off.

With increasing carbon burn-off, rates of diffusion of reactant gas molecules to active sites and product molecules away from active sites increase. This results in a progressive decrease in mass transport control of gasification. Since most of the micropores in coal chars (prior to their gasification) are very small or of a size commensurate with that of the reactant gas molecule, diffusion is activated. Therefore, diffusion rates increase very sharply with small amounts of carbon burn-off.

The specific catalytic activity of inorganic impurities can also change during gasification due to changes in their chemical form and degree of dispersion. For example, iron is a good oxidation catalyst but is soon deactivated due to the formation of oxides. The removal of carbon atoms by gasification would reduce the pinning of small inorganic species at the surface, thereby increasing their mobility and, hence, accelerating a decrease in their dispersion as they coalesce.

It is in the light of the above discussion that the results of the present investigation have to be interpreted.

Reactivities of the four chars used in the present study follow the order: Exxon Wyodak >Exxon Illinois >Bureau of Mines >FMC (COED). This order is valid up to a HTT (prior to reactivity measurements) of 800°C (Table 2). At HTT's above 800°C, reactivity of Exxon Wyodak char decreases sharply. Reactivities of the 1000°C heat treated chars follow the order: Exxon Illinois >Bureau of Mines >Exxon Wyodak >FMC (COED).

The extensive work done in this laboratory shows that reactivity of chars to air (17), CO₂ (18), steam (35), and H₂ (36) decreases, in general, with increase in rank of the parent coal. The results of the present investigation also show that the reactivities of the chars heat treated up to a maximum temperature of 800°C also decrease with increase in rank, that is, carbon content, of the parent coals. This emphasizes the importance of rank of the parent coal in determining the reactivity of the chars even in those cases where the chars experienced different thermal histories and carbon burn-off during their preparation. Essenhugh et al. (37) have calculated the fixed carbon conversion percentages

for the four chars. These calculations indicate that the two Exxon chars, during their preparation, received quite heavy gasification treatment, the Bureau of Mines char an intermediate treatment and the COED char only very slight treatment.

Essenhig et al. (37) have investigated the combustion characteristics of the four chars, used in the present study, using a plane-flame furnace. For each char, they measured the distance between the flame front and a water-cooled tube bank. This distance was used as a qualitative measure of char reactivity. The distance for the four chars follows the order: Exxon Illinois >Exxon Wyodak >Bureau of Mines >FMC (COED). Using the principle that a shorter distance between the flame front and the water-cooled tube bank is indicative of a higher char reactivity, the combustion characteristics of the four chars indicate that their 'reactivities' vary in the order: Exxon Illinois >Exxon Wyodak >Bureau of Mines >FMC (COED). This reactivity order is different from that observed in the present study. There may be several reasons for this discrepancy. These are discussed below: (i) in the present study, the particle size for each char varied from 149 to 420 μ . Essenhig et al. (37) used chars containing at least 45% by weight 44 μ fractions. It is known that a decrease in particle size can enhance char reactivity due to a decrease in diffusion path length. (ii) The maximum HTT used in the present study prior to reactivity measurements at 500°C was 1000°C whereas in the study of Essenhig et al. (37) the flames were stabilized at much higher temperatures (up to 1400°C). It is known that the higher HTT used during the preparation of a char, the lower is the subsequent char reactivity. Because of the inherent differences in the nature of coal precursors, the magnitude of the decrease in char reactivity under similar heat treatment conditions is expected to be different for different chars. In this context, it is noteworthy that an increase in HTT from 800° to 1000°C has the most pronounced adverse effect on the reactivity of Exxon Wyodak char (Table 2 and Figure 5). (iii) As indicated by the proximate analysis, the Exxon Wyodak char used by Essenhig and Cogoli (37) seems to be different from that used in the present study (Table 1). The sample used by Essenhig and Cogoli had an ash content of 21.25% whereas the ash content of the char used in the present study was 40.20%. Since impurities catalyze gasification rates, a higher concentration of impurities may enhance the gasification rates but may adversely affect the combustion characteristics because a part of the heat released during combustion will be used to heat the 'inert' impurities.

The thermal history of a char, that is, heating rate, maximum HTT, soak time at maximum HTT, gaseous atmosphere used during charring, affects the structure, porosity and surface area of the char. These changes, in turn, are expected to affect reactivity of chars. It is logical to conclude that the reactivity of a char will remain constant up to the maximum HTT seen by the char during its preparation and to decrease thereafter. This decrease could be due to loss of surface area and porosity as well as to a change in the chemical form of the catalytic impurities and/or to a decrease in the degree of dispersion of the impurities.

When the data listed in Table 2 are considered in the light of the above discussion, it may be concluded that during their production the four chars saw a maximum HTT of about 750°C. The fact that the reactivity of each char decreases above the maximum HTT seen by the char during its production indicates that any increase in surface area resulting from the loss of volatile matter at higher temperatures is more than offset by a decrease in surface area and porosity resulting from the breakage of cross links and alignment of crystallites and/or to a decrease in specific activity of catalytic impurities.

When a coal or a low-temperature char reaches the predetermined maximum HTT, it still undergoes dynamic changes in its structure at this temperature. These changes include release of volatile matter, breakage of cross links and realignment of crystallites as well as composition and degree of dispersion of catalytic impurities. When the maximum HTT is kept isothermal, the system tends to stabilize and after a certain period of soak time the char properties become invariant with respect to time. This time may not be the same in each case due to the inherent difference in the properties of the starting coals or chars. The results listed in Table 3 confirm this.

Following HTT of chars at higher temperatures, the resultant chars are expected to chemisorb oxygen upon subsequent exposure to air at room temperature. Puri (39) carbonized cane sugar and coconut shells at various temperatures between 350° and 600°C. The resultant chars were then exposed to three different atmospheres at room temperature: a) dry air, b) humid air, and c) pure oxygen. It was observed that the chars picked up oxygen slowly from dry air but rapidly from the pure oxygen atmosphere. It took 12 hours to reach equilibrium in pure oxygen and 3 months in dry air. There was no significant adsorption in humid air after 3 months. It was also noted that the amount of oxygen absorbed in (a) and (b) decreased as the carbonization temperature increased.

In the case of microporous chars, chemisorption of oxygen is expected to result in narrowing down of micropores or effective blockage of some of the pores resulting in a decrease in surface areas. Decrease in pore size can increase the mass transport control of gasification. The results listed in Table 5 show that exposure to air (at room temperature) of chars heated to 800°C has little or no effect on subsequent reactivity in air. In the present study, the exposure of the char to air was of much shorter duration than that in the study of Puri (39). However, it has been reported by Walker *et al.* (40) that when a clean carbon surface is exposed to oxygen at room temperature, it picks up, in the first few minutes, a major proportion of oxygen that can ultimately be chemisorbed on the surface. A substantial portion of oxygen chemisorbed at room temperature on the char surface is expected to be desorbed upon subsequent heat treatment (HT) up to 500°C prior to reactivity measurement.

In the 'literature survey' section of this report, it was mentioned that the gas atmosphere used during the preparation of a char influences its subsequent reactivity. However, the results of the present investigation show (Table 11) that char reactivity is essentially the same when preheat treatment at 725°C is done in N₂ or CO₂ or H₂. This is presumably due to the fact that gasification rates in one atmosphere of CO₂ and H₂ at 725°C are reasonably low. That is, any increase in surface area and porosity arising out of gasification will be minimal. However, the treatment with H₂ can result in chemisorption of hydrogen at the active sites. Puri (39) has reported that elimination of surface oxygen groups on microcrystalline carbons occurs at lower temperatures in a H₂ atmosphere than in vacuum or an inert atmosphere. Furthermore, Bansal *et al.* (41) have shown that essentially the same active sites are involved in the chemisorption of oxygen and hydrogen. Taken in the context of the present study, this means that following treatment with H₂ at 725°C, essentially all the active sites in the char will be covered with chemisorbed oxygen. Since dissociative chemisorption of the reactant molecules is the first step in the gasification process, it may be argued that following HT in H₂, subsequent reactivity in air should be relatively low compared to that when the sample is heated in a N₂ atmosphere. The fact that such is not the case (Table 11) indicates that gasification is a dynamic process. At 500°C, oxygen (present in air) can react with chemisorbed hydrogen giving water. This will create active sites which subsequently can take part in gasification. In this context, Snow *et al.* (42) have reported that during gasification of carbon blacks, the C/H ratio of the residue increased sharply with increasing burn-off, indicating that hydrogen was being preferentially oxidized relative to carbon.

The extent of sintering of supported metal catalysts is reported to be affected by the gaseous atmosphere used during the HT(43). Inorganic impurities associated with the chars invariably catalyze their gasification rates. Since reactivity of the char heat treated in the three atmospheres is the same, it may be concluded that neither the chemical form of the catalytic impurities nor their degree of dispersion undergo any noticeable change during HT in the three atmospheres.

Perhaps the most salient feature of this study is the effect of rapid heating on reactivity (Table 6) and surface area (Table 10). Reactivity and surface area (both N₂ and CO₂) of the rapidly heated samples are appreciably higher than those of the slowly heated samples. Except in the case of the slowly heated Exxon Illinois char, CO₂ area for the remainder of the samples is larger than the N₂ area. This indicates that at 77°K ultrafine micropores in these chars are inaccessible to N₂ molecules due to an activated diffusion process or actual shrinkage of pores (6,9). The higher N₂ area for the Exxon Illinois char relative to the CO₂ area indicates that in this char pores are of such dimensions that reversible filling of the pores may be occurring. It has been suggested that such N₂ areas are often meaningless (44).

Perusal of the literature shows that the effect of rapid heating upon subsequent char reactivity has not been studied. However, the effect on other char properties has been reported. Okada *et al.* (45) studied the effect of rapid heat treatment on the properties of pitch-bonded carbon made from petroleum coke and coal tar pitch. They baked the samples to 1200°C. The resultant chars were then further heated to 1500, 1800, 2100, 2300, 2500 and 2800°C and soaked at each HTT for 15 min. In each case, two heating rates were used: 100°C/hr and 1000°C/min. It was found that the properties of samples heated at the faster heating rate differed from those heated at the slower rate. Rapid heating was found to cause pore closure and thermal expansion of the samples. It has been suggested that rapid heat treatment may cause either pore opening or decrepitation depending upon whether the coal is thermoplastic or thermosetting (11).

The higher reactivities and surface areas of the rapidly heated chars relative to those of the slowly heated chars have to be explained in terms of the changes occurring, during the HT, in the three factors, referred to earlier in this report; governing the gasification rates.

Even though the four chars used in the present study are by-products of gasification processes, they still retain significant amounts of volatile matter (Table 9). Each char loses significant amounts of volatile matter upon rapid heating up to 800°C. Methane is a component of the volatile matter released during the HT (pyrolysis). Because of the highly microporous nature of chars, the rate of diffusion of methane out of the pores is expected to be relatively low. That is, methane will take a finite time to diffuse out of the micropores. During this time, methane molecules will collide many times with the pore walls. Since surfaces are known to catalyze the cracking of hydrocarbons (46-48), it is possible that methane diffusing out of the micropores may crack on the carbon surface resulting in carbon deposition (CD). Hoffman (49) has shown that cracking of propylene on a graphitized carbon sample associated with inorganic impurities occurs first on the inorganic impurities, then on the edge carbon sites and finally on the basal planes of the carbon crystallites. Kamishita (50) has recently studied the cracking of methane on a lignite char. He found that inorganic impurities strongly catalyze the cracking and that CD appreciably decreases surface area and porosity and subsequent reactivity of the char to air. Taken in the context of the present study, the work of Hoffman (49) and Kamishita (50) suggests that CD resulting from the cracking of methane will adversely affect the reactivity of chars. Because of the small residence time during rapid heating, there is a sudden build-up of released volatile matter (including methane) within the char particle. Because of the large concentration (pressure) gradient of the volatile matter between the surface and center of the particle, the flow of products out of the pores is expected to be fairly rapid. This means that the released methane will have relatively less time to deposit carbon on the active sites and the catalytic inorganic impurities than when the char particles are heated at slower rates. In the latter case,

the volatile matter is released slowly and continuously over the entire temperature range of HT and at no stage is there any significant accumulation of released volatile matter within the char particles. Therefore it is suggested that methane released during slower heating will have a greater tendency to crack, that is, to deposit carbon, on the active sites and the catalytic inorganic impurities than when the sample is rapidly heated.

The deposited carbon is likely to have a smaller concentration of active sites than the turbostratic chars. This is so because pyrolytic carbons usually show reasonable crystallite alignment with their basal planes parallel to the substrate surface on which CD has occurred. The rapid build-up of pressure due to the release of volatile matter within the char particles during rapid heating can also result in particle breakage, that is, reduction in particle size. This is supported by the data listed in Table 8. The decrease in particle size is expected to increase the gasification rates due to a decrease in the diffusion path length.

The higher surface areas of the rapidly heated samples relative to slowly heated samples (Table 10) may be due to two reasons. First, it is known that the structure and, hence, porosity of a char is determined not only by the maximum HT used during its preparation but also by the heating rate. The heating rate can affect the rate of volatile matter release as well as the breakage of cross links and, hence, realignment of crystallites.

Second, CD can also affect surface area and pore size distribution of the char. Since methane is expected to be released more rapidly during rapid heating than during slow heating, the extent of CD is likely to be more pronounced when the chars are heated at lower heating rates. Since most of the area of the microporous chars is located within the pores, it is reasonable to assume that most of the CD will occur within the pores. Therefore, the greater the extent of CD, the greater will be the possibility of a decrease in surface area due to closure or narrowing down of the capillary pores. In the light of the above discussion, it is expected that the rapidly heated chars will have larger surface areas than the chars prepared by using slower heating rates. This is experimentally observed (Table 10).

The higher surface areas of the rapidly heated chars may be due to another reason. It is not known if the substrate, that is the char, and the carbon deposited from the decomposition of methane have the same coefficient of thermal expansion. If the coefficient is different in the two cases, it is possible that upon sudden quenching of the rapidly heated char, the char and the deposited carbon will shrink (contract) at different rates. Thus, the thermal shock can bring about additional fissures and cracks thus resulting in an increase in surface area.

Finally, the decrease in catalytic activity due to sintering of the catalytic impurities is expected to be less for the rapidly heated chars.

This is so because during slow heating of the chars, the catalytic impurity particles or crystallites migrate across the surface for a much longer time and thus have a greater tendency to collide with each other resulting in crystallite growth than when the char is rapidly heated. For instance, when a heating rate of $10^{\circ}\text{C}/\text{min}$ is used, it will take about 80 min to heat the char from ambient temperature to 800°C . The residence time during rapid heating is only 300 millisecc. Furthermore, following HT at 800°C , the slowly heated char also cools down slowly whereas the rapidly devolatilized char is quenched almost instantaneously. The extent of catalyst sintering will be determined not only by the maximum HT temperature but also by the duration of the HT cycle. In light of the above discussion, it appears that the decrease in char reactivity due to sintering (particle growth) of catalytic impurities will be less pronounced in the case of the rapidly heated chars.

No significant increase in the char reactivity is observed when the char is preheated to 800°C at the rate of 5, 10, 20 and 25°C per min (Table 5). This indicates that these relatively slow heating rates are not sufficient to cause significant changes in the rates of diffusion of methane out of the micropores.

6. CONCLUSIONS

The major conclusions drawn from this study are as follows:

1. Reactivities of chars are maximized by keeping heat treatment temperatures as low as possible, minimizing soak time at maximum HTT and maximizing heating rates.
2. It is feasible to use reactivity parameters as a tool for the study of thermal history of carbonaceous materials. The correlation between reactivity and HTT on the one hand, and reactivity and soak time on the other, has been utilized to determine maximum temperature "seen" by the chars during preparation, as well as the maximum soak time at maximum HTT. This technique has been used to determine the temperature seen by rapidly heated Exxon Wyodak char and there is an excellent agreement between the temperature determined experimentally and that predicted theoretically.
3. Maximum HTT as well as the heating rate used for char preparation seem to be more important parameters in influencing char reactivity than the atmosphere used during preparation.
4. Aging of chars in air following heat treatment at 800°C has little or no effect on subsequent char reactivity.
5. The most significant conclusion of this investigation is that rapid heating results in significant increase in char reactivity to air.
6. Surface areas of rapidly heated samples are significantly higher than those prepared at the same temperature using slower heating rates.

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A P P E N D I X

Reproducibility of Results of Reactivity Measurements

Sample and HTT Conditions Prior to Reactivity Measurements in Air at 500°C	Run No.	R_T	Mean, $\bar{x}$	Error, $\bar{x}_c$, a 95% Confidence Level
		mg hr ⁻¹ mg ⁻¹ , $\bar{x}$		
Exxon Wyodak: HTT = 500°C at heat- ing rate of 10°C/min	1	4.06		
	2	3.95	3.97	± 0.14
	3	3.90		
Exxon Wyodak: Rapidly heated to 800°C	1	5.08		
	2	5.10	5.09	-----
Bureau of Mines: HTT = 500°C at heating rate of 10°C/min	1	2.96		
	2	3.08	3.02	-----
PSOC-246 Coal: Rapidly heated at 800°C	1	5.22		
	2	5.12	5.17	-----