

ROLES OF CATALYSIS AND CARBON ACTIVE SITES IN  
THE GASIFICATION OF LIGNITE CHARs

L. R. Radovic

Department of Chemical Engineering  
The Pennsylvania State University, USAP. L. Walker, Jr. and R. G. Jenkins  
Fuel Science Program, Department of Materials Science  
and Engineering, The Pennsylvania State University, USA

## SUMMARY

A fundamental gasification study has been made on a North Dakota Lignite. A very wide range of char reactivities was obtained by varying pyrolysis conditions and pretreatment of the lignite. For the predominantly uncatalyzed gasification reaction, carbon active site concentration was shown to be a meaningful reactivity index for demineralized chars and for carbons of varying crystallinity. For raw lignite chars, it was shown that CaO is the predominant catalytic species responsible for their high gasification reactivities. Lignite char gasification should be regarded as a catalyzed gas-solid reaction with the catalyst dispersion being the relevant reactivity parameter. When rates are expressed as turnover frequencies, observed reactivity differences of as much as 200-fold are reduced to within one order of magnitude. The commonly observed phenomenon of coal char deactivation with increasing pyrolysis severity was correlated with decreases in carbon active surface area and catalyst dispersion. This fundamental approach was confirmed for chars obtained from potential coal conversion processes.

## INTRODUCTION

Successful modeling and design of coal gasifiers and gasification processes is critically dependent on the availability of reliable kinetic parameters for the heterogeneous reactions between the devolatilized coal (coke or char) and the reactive gases ( $H_2O$ ,  $O_2$ ,  $CO_2$ ,  $H_2$ ). In spite of (or, perhaps and paradoxically so, due to) the existence of a voluminous literature on the kinetics of char gasification (1-4), the task of selecting the appropriate reactivity parameters, for the purpose of design of a particular process for a particular coal, can be a difficult exercise. Predictive capabilities of the available correlations (1-6) are limited to the structural

and compositional differences between coals of varying rank which are generally subjected to widely varying pyrolysis conditions.

From a fundamental point of view, higher rates of gasification of certain coal chars (and carbons in general), compared to others, may be due to some or all of the following factors: higher concentration of active sites, i.e., carbon atoms located at the edges of graphite-like planar regions (crystallites); higher catalytic activity and/or dispersion of the inorganic constituents; higher accessibility of reactive gases to the active sites. Much work has been done to elucidate the last effect, that of mass transport. Its quantitative treatment has evolved from the pioneering works of Thiele (7) and Wheeler (8), and has reached an advanced level of development for the case of a porous solid catalyst (9). However, in porous carbons such as coal chars, the situation is more complicated due to the dynamic nature of the porous structure. The surface area of the char and the effective diffusivity of the reactive gas in the pores of the char are not constant parameters during gasification. Realistic models of pore structure should take into account the complicated development of porosity during reaction. In recent years, various such models have been proposed (10-18).

Smith (5) has recently reviewed the application of the classical reaction-diffusion theory (19) to the studies of reactivity of carbons ranging in crystallinity (and purity) all the way from natural graphite to lignite chars. He compared the experimental results on an Arrhenius plot in terms of rates per unit total (BET) surface area at 0.1 MPa O<sub>2</sub>. The result of this comparison was that there exists a very wide range of rates, even when corrected for mass transport (up to four orders of magnitude), found by the different investigators at presumably identical conditions of temperature and pressure. Figure 1 shows the best-fit line through the experimental points. Its validity is, nevertheless, very limited due to the great scatter of data.

In recognition of the dynamic nature of the porous structure of chars, Simons and co-workers (6,12, 13,20) have developed a "tree (or river)-system" model of pore structure, branching and combination. When applied to char gasification, this model predicts a change in reactivity of no more than one order of magnitude with conversion. Their correlation is also shown in Figure 1.

These studies suggest that the use of more sophisticated reaction-diffusion models does not seem to provide a solid basis for explaining or predicting the sometimes dramatic differences (see, for example, Figure 3) in observed char reactivities. If one hopes to understand the reactivity behavior of carbons in general, and coal chars in particular, one must attempt to quantify the effects of catalysis and carbon active sites. The present study was undertaken with the objective to make a contribution in this field. It is a part of an extensive report (21) on the gasification characteristics of coal chars (lignite in particular), whose major findings have already been published (22-26). The purpose of this paper is to present an integral summary of this work.

## EXPERIMENTAL

Figure 2 summarizes the experimental approach taken in this study. The solid lines represent the flow of material (coal or char), and the broken lines represent the feedback loops of ideas. Coal pretreatment consisted of essentially complete demineralization, selective removal of exchangeable cations and a selective cation loading. Chars were prepared from raw and pretreated lignite under widely varying conditions of pyrolysis heating rate, temperature and residence time. Rapid pyrolysis ( $\sim 10^4$  K/s) was performed

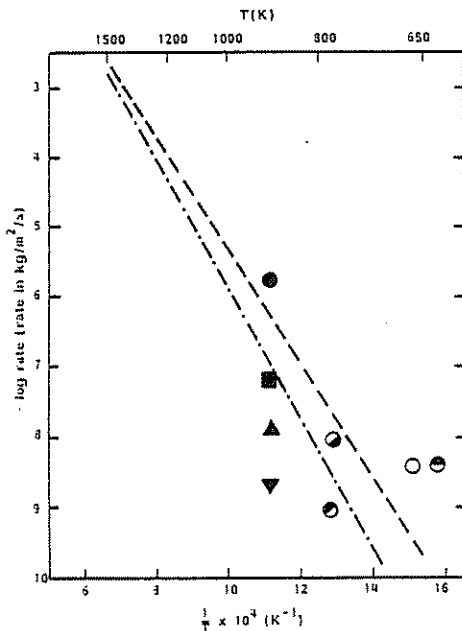


FIGURE 1. Correlations and Experimental Data for the Carbon-Oxygen Reaction Kinetics at 0.1 MPa O<sub>2</sub>. — Smith (Ref. 5); — Lewis and Simons (Ref. 5); ● brown coal char (Ref. 28); ■ graphitized carbon black (Ref. 29); ▲ nuclear graphite (Ref. 30); ▼ SP-1 graphite (Ref. 31); ○ raw lignite char - slow pyrolysis (Ref. 32); ○ demineralized lignite char - slow pyrolysis (Ref. 32); ○ Na-loaded lignite char - slow pyrolysis (Ref. 32); ○ raw lignite char - rapid pyrolysis (this study).

in an entrained flow reactor at temperatures between 975 and 1275 K for residence times between 0.15 s and 30 min in an inert atmosphere. Slow pyrolysis (10 K/min) experiments were conducted in a horizontal-tube furnace up to final temperatures of 975-1475 K with a maximum soak time at final temperature of 1 h. The gasification reactivity of the chars was determined by isothermal thermogravimetric analysis (TGA), mostly in 0.1 MPa air. Some runs were also conducted in 0.1 MPa CO<sub>2</sub> and 3.1 kPa H<sub>2</sub>O. Conditions of the reactions were carefully selected in order to eliminate interparticle and intraparticle heat and mass transfer limitations. Detailed analyses of the structural and surface properties of the chars were performed. The total surface area (TSA) was determined in conventional manner from CO<sub>2</sub> physical adsorption data collected at 298 K. The carbon active surface area (ASA) of the chars was estimated from O<sub>2</sub> chemisorption data obtained at 375 K and 0.1 MPa air. The catalyst (CaO) dispersion (surface area) was estimated from x-ray diffraction data.

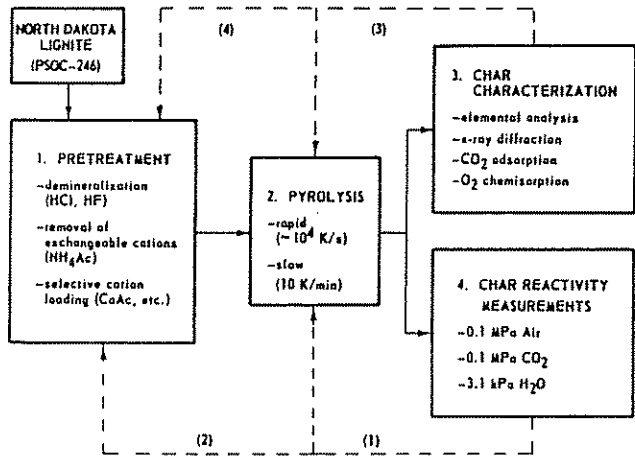


FIGURE 1. Block Diagram Representation of the Overall Experimental Approach

gasification behavior and some of the fundamental, yet measurable, properties of the chars.

The details of the experimental procedures have already been published (22-26).

## THEORETICAL

Due to the presence of more or less active and more or less highly dispersed inherent inorganic constituents in coal, the gasification reactivity of a coal char should be regarded in general as a potential catalytic gas-solid reaction. The overall reactivity, at constant concentration of the reactive gas (pseudo-zero order), expressed in Arrhenius form is then (27)

$$R = S_c A_c \exp\left(-\frac{E_c}{RT}\right) + S_u A_u \exp\left(-\frac{E_u}{RT}\right), \quad 1)$$

where  $S_c$  and  $S_u$  represent, respectively, the specific surfaces on which the catalyzed and the uncatalyzed reaction occur. The relative importance of these two parallel reactions depends on the inherent activity and concentration of the catalyst and carbon active sites.

A convenient definition of reactivity ( $R$ ) in terms of unit mass of char ( $M_c$ ) is

$$R \equiv -\frac{1}{M_c} \frac{dM_c}{dt}. \quad 2)$$

Defining conversion of carbon (dry, ash-free char),  $X_c$  in conventional terms, i.e.,

$$X_c \equiv \frac{M_{c,o} - M_c}{M_{c,o}},$$

where  $M_{c,o}$  is the initial mass, Equation 2 becomes

$$R \equiv \frac{1}{1-X_c} \frac{dX_c}{dt}. \quad 3)$$

Combination of Equations 1 and 3 gives

$$\frac{dX_c}{dt} = S_c A_c \exp\left(-\frac{E_c}{RT}\right) (1-X_c) + S_u A_u \exp\left(-\frac{E_u}{RT}\right) (1-X_c). \quad 4)$$

The term  $dX_c/dt$  represents the slope of the TGA plot of conversion vs time. It is seen that it depends on conversion and on the way the catalyst and carbon active surface area vary with conversion. In the absence of knowledge of these functional relationships at the present time, two extreme and simplifying cases are considered in this study.

Demineralized lignite chars (Dem-chars) were taken as "model compounds" for studying the predominantly uncatalyzed carbon gasification (23). It was assumed that the high concentration of carbon active sites in these highly disordered carbonaceous materials masks the minor contribution of the catalyzed reaction to the overall rate. In this case, Equation 4 reduces to

$$\frac{dX_c}{dt} = k_u S_u (1-X_c),$$

where  $k_u$  is the rate constant for the uncatalyzed reaction. The carbon ASA was measured in the absence of gasification (23) and the rate constant was determined from the initial slope of the TGA plot, i.e., at  $X_c=0$ :

$$k_u = \frac{(dX_c/dt)_0}{S_{u,0}}$$

5)

Lignite chars which were demineralized and subsequently loaded with  $Ca^{++}$  by ion exchange prior to pyrolysis (Dem+Ca-chars) were taken as "model compounds" for the predominantly catalyzed reaction. In the presence of relatively highly dispersed CaO, the relative contribution of the uncatalyzed gasification was shown to be negligible (22,24). Thus

$$\frac{dX_c}{dt} = k_c S_c (1 - X_c)$$

The dispersion of the catalyst was measured prior to gasification, i.e., at  $X_c=0$ , and by analogy with Equation 5, the rate constant is determined as

$$k_c = \frac{(dX_c/dt)_0}{S_{c,0}}$$

6)

RESULTS AND DISCUSSION

Figure 3 illustrates the major effects of coal pretreatment and pyrolysis conditions on subsequent char reactivity. Short-residence

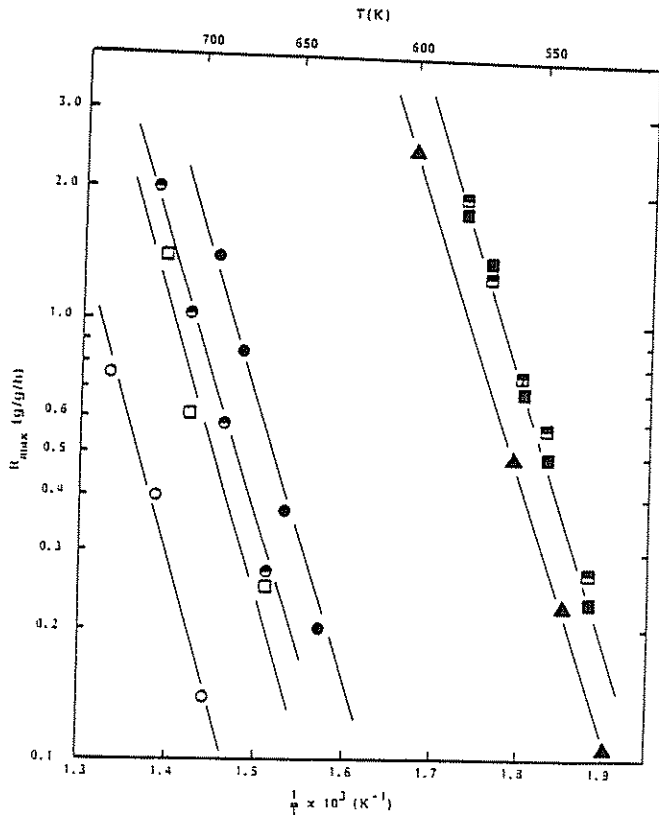


FIGURE 3. Effect of Coal Pretreatment and Pyrolysis Conditions on Char Reactivity in 0.1 MPa Air: ○ Dem (1 h, 1475 K), ● Dem (0.3 s, 1275 K), ◐ Dem (1.3 s, 1275 K), ◑ Dem+Ca (1 h, 1475 K), ◒ Dem+Ca (0.3 s, 1275 K), ◓ Dem+Ca (1.3 s, 1275 K), ▲ Raw (0.3 s, 1275 K)

time raw and Ca-loaded chars react in air at rates which are 2-4 orders of magnitude greater than the ones predicted for the various carbonaceous materials by the correlations of Smith (5) and Lewis and Simons (6). (See also Figure 1.) A very wide range of reactivities (up to three orders of magnitude) exists even when the same carbonaceous precursor, in this case a lignite, is used. In all cases, however, the observed activation energy was about the same (125-135 kJ/mol), suggesting that the variations in rate are due to changes in the concentration of active sites.

It is seen in Figure 3 that Dem-char is about 30 times less reactive than the raw lignite char. When only  $Ca^{++}$  (principal cation in lignites) was added back to the demineralized coal,

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the original reactivity was more than completely restored. It was concluded (22,24) that Dem+Ca-chars behave essentially in the same way as raw lignite chars. It is also seen that the extent of char deactivation (i.e., decrease in reactivity with increasing severity of pyrolysis) is significantly reduced in the absence of Ca. However, deactivation of Dem-char is initially faster. These and other results (26) suggested that the observed deactivation of Dem- and raw or Dem+Ca-chars was governed by two fundamentally different processes, i.e., a decrease in carbon ASA and catalyst crystallite growth (sintering), respectively.

The effect of not considering the carbon ASA when determining kinetic parameters is illustrated in Figure 1. Reactivities of four different carbons, ranging from brown-coal char to spectroscopically pure natural graphite, were calculated at 900 K and 0.1 MPa O<sub>2</sub> using the original data (28-31). It is seen that the reactivity per unit TSA decreases in the following order:

brown-coal char > graphitized carbon black > nuclear graphite > SP-1 graphite

From knowledge of the structure of these carbons, it is expected that the ASA would follow the same trend. A quantitative confirmation of this expectation was obtained in the present study (23). Table 1 gives the values of surface area and reactivity for selected

TABLE 1. SURFACE AREAS AND REACTIVITIES OF DEM-CHARS AND CARBONS OF INCREASING PURITY AND CRYSTALLINITY

Sample <sup>a</sup>	TSA (m <sup>2</sup> /g)	ASA (m <sup>2</sup> /g)	R <sub>700</sub> (g/g/h)	R <sub>700</sub> (g/m <sup>2</sup> TSA/h) x10 <sup>3</sup>	k <sub>700</sub> (g/m <sup>2</sup> ASA/h) x10 <sup>3</sup>
R-0.3 s	630	225	1.8	2.9	8.0
R-1.8 s	730	133	0.94	1.3	7.1
R-5 min	710	73	0.30	0.42	4.1
S-30 min	665	n.d. <sup>b</sup>	0.28	0.42	n.d.
S-1 h	n.d.	50	0.25	n.d.	5.0
S-1 h (975 K)	n.d.	108	1.2	n.d.	11
S-1 h (1475 K)	n.d.	25	0.15	n.d.	6.0
Saran Char	1,224 <sup>c</sup>	50 <sup>c</sup>	0.15	0.12	3.0
CB-Monarch 700	206 <sup>d</sup>	n.d.	0.05	0.24	n.d.
GCB, V3G	63 <sup>c</sup>	<1 <sup>c</sup>	~2x10 <sup>-4e</sup>	0.0032	>0.2
SP-1 Graphite	1.8 <sup>f</sup>	<0.1 <sup>f</sup>	~2x10 <sup>-5e</sup>	0.011	>0.2

<sup>a</sup>R, rapid pyrolysis, S, slow pyrolysis; <sup>b</sup>n.d., not determined;

<sup>c</sup>Data taken from Ref. 35; <sup>d</sup>Data taken from Ref. 36; <sup>e</sup>Extrapolated value; <sup>f</sup>Data taken from Ref. 37

Dem-chars prepared under a wide range of pyrolysis conditions. Total surface areas were estimated by the Dubinin-Polanyi approach, assuming that the micropore volume is approximately equal to the BET monolayer capacity (26,34). Values of ASA, i.e., surface area occupied by dissociatively chemisorbed oxygen atoms were calculated assuming a value of 0.08 nm<sup>2</sup> for the area occupied by each oxygen atom (29). The reactivity values at 700 K were obtained by interpolation of data on the experimental Arrhenius plots. Also shown are the corresponding values of surface area and reactivity for carbons of increasing purity and crystallinity, including a Saran (Dow Chemical Corp.) char, a carbon black (CB, Monarch 700, Cabot Corp.), a graphitized carbon black (GCB, V3G, Cabot Corp.), and a spectroscopically pure natural graphite (SP-1, Union Carbide Corp.).

It is seen in Table 1, in agreement with the analysis of Smith (5), that the TSA is not a relevant reactivity normalization

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parameter. For example, at 1275 K the observed char gasification rate decreased by a factor of six between 0.3 s and 5 min. However, TSA increases in this range of pyrolysis residence time. This conclusion is confirmed in the case of carbons of higher crystallinity: a difference in observed rates of four orders of TSA is taken into account. On the other hand, it is seen that a difference in observed reactivities of Dem-chars of a factor of 12 is reduced to within a factor of three when the rate constants are obtained per unit ASA according to Equation 5. Extending the analysis to other carbons it is seen that despite the differences in observed reactivity of about five orders of magnitude, the rate constant expressed per unit ASA seems to be dependent solely on temperature (as it should be) and not also on the char (carbon) precursor and its pyrolysis history.

It is well known (32,38-41), yet too often ignored, that catalysis plays a major role in the gasification reactivity of lignite chars in oxidizing gases (see Figures 1 and 3). The presence of exchangeable cations (mainly Ca<sup>++</sup>) associated with the carboxyl groups in the lignites makes possible their very high initial dispersion upon pyrolysis. Table 2 summarizes the information on reactivities and CaO dispersion for a series of Dem-Ca-chars with widely varying

TABLE 2. EFFECT OF PYROLYSIS CONDITIONS ON THE REACTIVITY OF DEM+Ca-CHAR AND CaO DISPERSION

Sample <sup>a</sup>	CaO (wt%)	D (nm)	d (%)	S <sub>CaO</sub> (m <sup>2</sup> /gCaO)	R <sub>625</sub> (g/gC/h)	R <sub>625</sub> (g/m <sup>2</sup> CaO/h)	TOF (s <sup>-1</sup> )
R-0.3 s	8.0	-- <sup>b</sup>	>25 <sup>c</sup>	>300	-10 <sup>d</sup>	<0.42 (>0.10)	<0.67 (>0.16)
R-1.8 s	9.3	-- <sup>b</sup>	>25 <sup>c</sup>	>300	-10 <sup>d</sup>	<0.36 (>0.09)	<0.58 (>0.14)
R-30 s	9.5	21.5	5.8	72	1.3	0.19	0.30
R-1 min	9.5	23.5	5.3	65	1.1	0.18	0.29
R-3 min	8.9	23.5	5.3	65	1.1	0.19	0.30
R-5 min	10.4	24.5	5.1	63	1.0	0.15	0.24
S-0 h	7.6	25.0	5.0	62	0.90	0.19	0.30
S-1 h	7.5	28.0	4.4	55	0.40	0.10	0.16
S-1 h (975 K)	7.2	-- <sup>b</sup>	>25 <sup>c</sup>	>300	- 5.0 <sup>d</sup>	<0.23 (>0.03)	<0.37 (>0.05)
S-1 h (1475 K)	5.6	47.0	2.6	33	0.05	0.03	0.05

<sup>a</sup>R, rapid pyrolysis; S, slow pyrolysis; <sup>b</sup>Not detectable by XRD;

<sup>c</sup>Assuming D < 5 nm; and <sup>d</sup>Extrapolated value

pyrolysis temperature-time histories (24). The average crystallite diameter (D) of CaO was calculated from x-ray diffraction using the line broadening concept and the Scherrer equation. Dispersion (percentage exposed) was then calculated as  $d=1.24/D$ , with D in nm. In terms of catalyst surface area this is  $S=1538/D$ , with D in nm. It is seen that when the reactivities of the various chars are normalized with respect to the initial char weight, they differ by as much as 200 times. On the other hand, when they are normalized with respect to the catalyst surface area, according to Equation 6, or when the rates are expressed as turnover frequencies (TOF), these differences are reduced to within one order of magnitude.

The results summarized and presented succinctly here, and discussed in detail elsewhere (22-26), have shown that the application of the concept of active sites leads to a fundamental understanding of char gasification reactivity. On the other hand, predictions of behavior on the basis of development of porosity and TSA are likely to be of limited success. Further development of this concept is necessary, though. In particular, measurements by independent techniques would be highly desirable. The reactivities reported

throughout this investigation were always initial (and maximum) steady-state values. No attempt was made to investigate the entire range of conversion. In the case of predominantly uncatalyzed gasification, prior knowledge of the variation of ASA with conversion is necessary. For the catalyzed reaction, a knowledge of the change on catalyst dispersion and contact with the char support would be necessary. The relative importance of the catalyzed and uncatalyzed reactions also needs to be assessed in every particular case. It is thought, though, that the present study has demonstrated that these fundamental concepts, developed in the field of catalysis and carbon gasification, can be successfully used to quantify in a meaningful manner and explain the complex gasification behavior of coal chars.

The usefulness of the proposed fundamental approach was tested in analyzing the gasification behavior of chars obtained as residues in several commercial or developing coal conversion processes (25). The information on their origin and production conditions is summarized in Table 3 (42). Their reactivities in 0.1 MPa air are presented in Figure 4. It is seen that they differ by as much as 200 times,

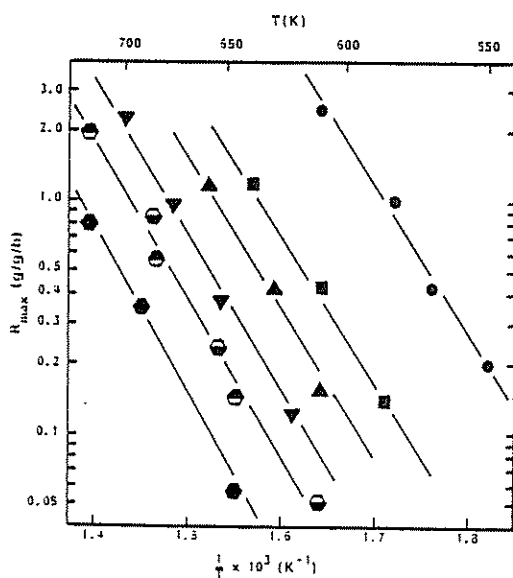


FIGURE 4. Reactivities in 0.1 MPa Air of Chars Obtained as Residues in Selected Coal Conversion Processes: ● Occidental, ■ TOSCOAL, ▲ BIGAS, ▼ COED, ◆ Rockwell (Hydrogasification), ● Rockwell (Hydroliquefaction, residence time = 60 ms), ● Rockwell (Hydroliquefaction, residence time = 600 ms) - (after Ref. 25)

the Occidental Char being the most reactive and the Rockwell Hydroliquefaction Char (residence time, 600 ms) being the least reactive. However, the activation energy is the same in all cases, about 130 kJ/mol, essentially identical to those obtained for various pretreated lignite chars in Figure 3. Interpretation and meaningful comparison of these reactivities would require a better knowledge of the exact pyrolysis history of the chars and a thorough study of their physical properties, both of which are unavailable at the present time. However, the existing general knowledge about these chars does allow a qualitative discussion about their reactivities. The gasification behavior of the Rockwell bituminous coal char is seen to be very similar to that of the reactivity and the dependence on pyrolysis conditions. Thus, its observed deactivation is expected to be due to a decrease in its concentration of carbon active sites. Indeed, from the general knowledge of the composition and dispersion of the inorganic constituents in bituminous coals, catalysis is not expected to play a major role during gasification in oxidizing media. At the other extreme, the reactivity of the Occidental subbituminous coal char is seen to be comparable to that of the short-residence-time raw and Ca-exchanged lignite chars. This is, indeed, what one would predict on the basis of the expected similarity in the composition and dispersion of their inorganic constituents.

These results show a striking similarity in the gasification behavior of coals of different rank when compared on the basis of their expected and measured ASA and catalyst activity and dispersion. They confirm that the fundamental approach taken in this study seems to be a very promising avenue of research which will eventually lead to



TABLE 3. REPRESENTATIVE OPERATING CONDITIONS FOR SELECTED COAL CONVERSION PROCESSES WITH HIGH YIELDS OF RESIDUAL CHAR (AFTER REF. 25)

<u>Process</u>	<u>Heating Rate (K/s)</u>	<u>Temperature (K)</u>	<u>Residence Time</u>	<u>Pressure (MPa)</u>	<u>Atmosphere</u>	<u>Parent Coal</u>	<u>Reactor Type</u>
Occidental (Flash pyrolysis)	$10^4$	875-1075	1-2 s	0.1	Recycled combustion gases	Wyoming Monarch subbituminous	Entrained flow
TOSCOAL (pyrolysis)	$10^2$	800	15-30 min	0.1	Pyrolysis products	Utah bituminous	Externally heated moving bed
BIGAS (Gasification)	$10^5$	1375	3 s	5	Char combustion gases	Montana Rosebud subbituminous	Two-stage entrained flow
COED (Pyrolysis)	$10^3$	610-1175	2 h	0.1	Combustion gases and steam	Pittsburgh bituminous	Four-stage fluidized bed
Rockwell (Hydrogasification)	$3 \times 10^5$	1175-1275	0.5-2.5 s	0.7	$H_2, O_2, H_2O$	Kentucky #9 bituminous	Entrained flow
Rockwell (Hydroliquefaction)	$3 \times 10^5$	1175-1275	60 ms 600 ms	0.7	$H_2, H_2O$	Kentucky #9 bituminous	Entrained flow

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the possibility of designing reactors and processes on the basis of rate parameters obtained in the laboratory.

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