

## COMBINED EFFECTS OF INORGANIC CONSTITUENTS AND PYROLYSIS CONDITIONS ON THE GASIFICATION REACTIVITY OF COAL CHARs

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### ABSTRACT

A detailed phenomenological study of the gasification behavior of a North Dakota lignite was undertaken and the fundamental parameters that determine char reactivity were investigated. Differences in reactivity of up to three orders of magnitude were obtained by varying the conditions of coal pretreatment and pyrolysis. Pretreatment included demineralization with HCl and HF, ion exchange with ammonium acetate and back exchange with calcium acetate. Pyrolysis temperature, residence time and heating rate were varied in the range 975–1475 K, 0.3 s–1 h and 10 K/min– $10^4$  K/s, respectively. The observed reactivity differences were rationalized in terms of variations in the concentration of carbon and catalyst active sites.

### INTRODUCTION

Coal chars in general, and lignite chars in particular, are heterogenous and complex materials and a complete fundamental understanding of their gasification behavior is an ambitious goal. It is not a trivial matter to design experiments that will allow a systematic study of the individual parameters that may affect char reactivity. Any kind of treatment of a coal (e.g., drying, acid washing, pyrolysis) usually results in changes in more than one of its properties. One of the key issues in coal gasification is to identify and measure the surface(s) on which this heterogeneous gas–solid reaction occurs. The present study was undertaken in an attempt to make a contribution in this field. Its major findings have already been reported [1–5]. The purpose of this paper is to report some important additional and complementary findings and to present a synthesis of this work.

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## EXPERIMENTAL

Figure 1 depicts a block-diagram scheme of the overall experimental approach. The solid lines represent the flow of material and the broken lines the flow of ideas. The goal of the coal pretreatment and pyrolysis steps was to obtain major reactivity differences among the resulting chars. This was accomplished by selectively altering the composition of the coal's inorganic constituents (block 1) and by varying over a wide range the pyrolysis temperature-time history of the chars (block 2), as indicated by feedback loops (1) and (2). Ultimately, the observed reactivity differences (block 4) were to be related to the relevant physical characteristics of the chars (block 3), as indicated by the dotted line between blocks 3 and 4. Feedback loops (3) and (4) indicate that the pretreatment and pyrolysis conditions were also adjusted in some cases so as to produce major differences in some of these characteristics. The objective was to establish quantitative correlations between the observed reactivity behavior and some of the fundamental, yet measurable, properties of the chars.

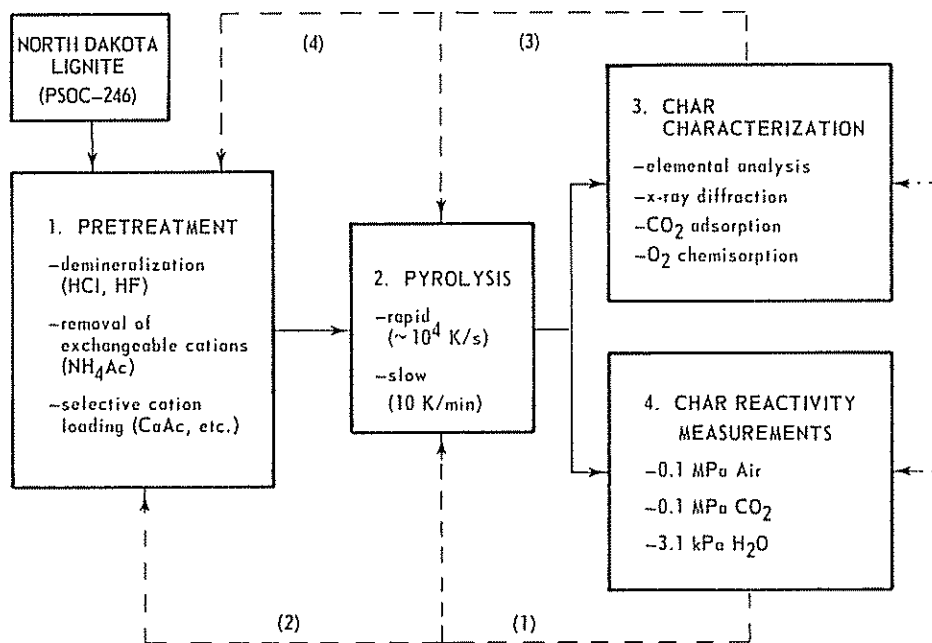


Fig. 1. Block diagram representation of the overall experimental approach.

### Coal pretreatment

The raw (as received), size-graded lignite (PSOC-246; 70 × 100 mesh, mean particle size ~170 μm; 200 × 270 mesh, mean size ~60 μm) was

subjected to acid washing and ion exchange. Demineralization with HCl and HF removed essentially all the inorganics, both the discrete minerals and the exchangeable cations [2]. Ion exchange with 0.5 N ammonium acetate ( $\text{NH}_4\text{Ac}$ ) removed selectively only the cations (principally  $\text{Ca}^{2+}$ ), and left essentially intact the discrete minerals. About 10 g of coal was mixed with 300 ml  $\text{NH}_4\text{Ac}$  and stirred at room temperature for 1 h. The coal was filtered, washed repeatedly with 50 ml of fresh solution, and subjected again to a 2 h ion exchange with 200 ml of fresh solution, followed by the washing procedure. Five additional ion exchange cycles were used. The total exchange time was about 30 h. The filtrates were collected after each cycle in order to follow the kinetics of ion exchange. The final washing was performed using a dilute solution of  $\text{NH}_4\text{Ac}$  (0.1 N). The coal was dried overnight at  $\leq 383$  K in a vacuum oven and resieved. Portions of demineralized (dem) and  $\text{NH}_4\text{Ac}$ -exchanged lignite were subsequently back-exchanged with 1.5 N calcium acetate ( $\text{CaAc}$ ) in order to selectively load only  $\text{Ca}^{2+}$  onto the carboxyl groups. About 70 g of coal were mixed with 500 ml of solution and magnetically stirred on a hot-plate apparatus. The exchange was effected at 335 K in a period of about 8 h, after which the solution was filtered and the coal washed thoroughly with distilled water. The coal was subsequently dried overnight in a vacuum oven and resieved. The amount of exchange was determined by atomic absorption spectroscopy (AAS). The cation-exchanged coal ( $\sim 0.1$  g) was mixed with 50 ml of 0.1 N HCl, shaken for 24 h and the filtrate was analyzed by AAS.

#### *Coal pyrolysis*

Raw and pretreated lignite were devolatilized in  $\text{N}_2$  (99.99% purity) under widely varying conditions of pyrolysis temperature (975–1475 K), residence time (0.3 s–1 h) and heating rate. Slow pyrolysis (10 K/min) was carried out in a conventional horizontal-tube furnace. Rapid pyrolysis ( $\sim 10^4$  K/s) was carried out in an entrained-flow furnace (reactor) described in detail elsewhere [6]. The residence time in one pass through the 66-cm isothermal zone was estimated to be about 0.3 s for  $70 \times 100$  mesh particles and about 0.5 s for  $200 \times 270$  mesh particles. Coal was fed continuously through a water-cooled injector. The char particles were received into a water-cooled collector and separated in a cyclone for subsequent analysis and reactivity studies. Char recycling up to five times through the reactor gave pyrolysis residence times of as much as about 3 s. In order to obtain longer-residence-time chars, a different collector was used. A ceramic crucible was fixed on top of a cylindrical mullite tube with high-temperature cement. The bottom of the tube was sealed with a rubber stopper provided with two holes, one for the cooling gas ( $\text{N}_2$ ) connection and the other for a temperature-controlling thermocouple. The sheathed thermocouple (Pt vs. Pt/10% Rh) was directly contacted with the ceramic crucible. The top part of the tube had slit-shaped holes drilled into it in

order to permit the cooling gas to flow around the crucible (thus enhancing sample cooling) and out of the tube. In this mode of operation, about 2 g of coal were injected as a batch. The char particles were received in the crucible at the bottom of the isothermal reaction zone and allowed to devolatilize further for up to 30 min. The collector was then lowered to a nonheated zone within the furnace, less exposed to radiation from the walls but still not accessible to O<sub>2</sub> from the surroundings. Simultaneously, the flow of N<sub>2</sub> through the collector tube was turned on to enhance the cooling of the sample. When the temperature had dropped below 375 K, the collector was removed from the furnace.

#### *Char reactivity measurements*

Intrinsic, chemically controlled reactivities [2] of the various chars were determined by isothermal thermogravimetric analysis (TGA) mostly in 0.1 MPa air (dry grade), but also in 0.1 MPa CO<sub>2</sub> (99.5% minimum purity) and in H<sub>2</sub>O. Steam was introduced by bubbling N<sub>2</sub> (99.999% purity) through the fritted disk of a sealed wash bottle filled with distilled, de-aerated water maintained at a constant temperature of 298 K. Its saturation pressure at this temperature is 3.1 kPa. A Fisher TGA unit (Model 360) was used [1,2].

#### *Char characterization*

The extent of lignite devolatilization was measured using the ash-tracer technique. Elemental analyses of selected chars were also performed. Micropore volumes were measured and surface areas were estimated from CO<sub>2</sub> adsorption isotherms at 298 K. A conventional volumetric apparatus was used. X-ray diffraction and O<sub>2</sub> chemisorption measurements are described elsewhere [2,3].

### RESULTS AND DISCUSSION

#### *Coal pretreatment and pyrolysis*

The efficiency of pretreatment was determined by monitoring both the ASTM ash and the calcium content of the coal. The latter, being the most abundant cation present in the lignite, decreased from about 1.5 wt. % (dry) in the raw coal to about 0.011% in the dem-coal and 0.08% in the NH<sub>4</sub>Ac-treated coal. (Ninety percent of ion exchange occurred in the first 6 h). The respective ash yields were 9.7, 0.2 and 2.4%. Selective ion exchange with CaAc resulted in a loading of about 2.9% Ca.

Figure 2 shows that after about 1 s of entrained-flow pyrolysis of raw lignite at 1275 K, the yield of volatiles becomes essentially constant at 50 ± 3% daf coal. However, the ASTM volatile matter (VM) of the char

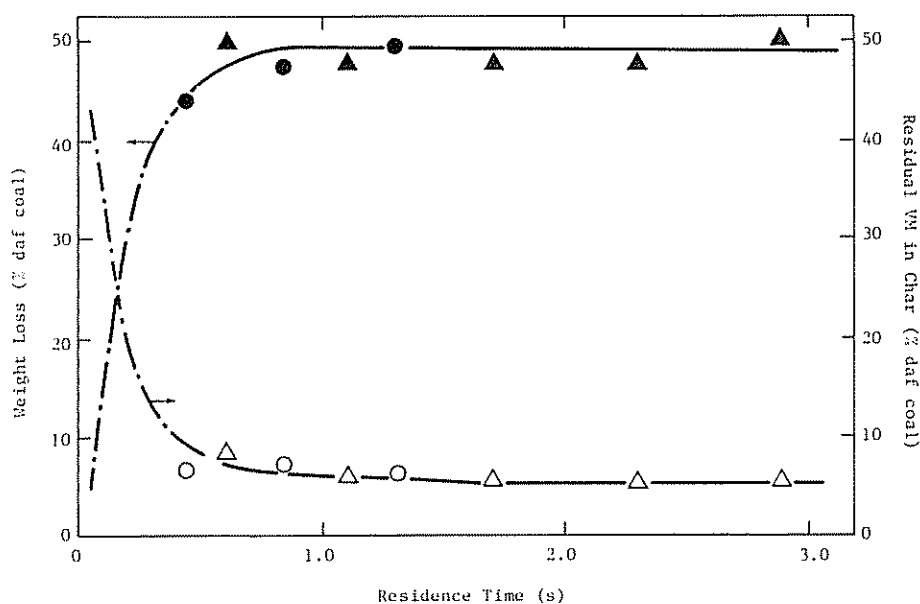


Fig. 2. Variation of weight loss and residual volatile matter as a function of pyrolysis residence time at 1275 K: ● — weight loss, 70 × 100 mesh; ○ — residual VM, 70 × 100 mesh; ▲ — weight loss, 200 × 270 mesh; △ — residual VM, 200 × 270 mesh.

does not decrease to zero even after 3 s. This apparent residual VM is probably due to  $O_2$  chemisorption upon char exposure to air at near room temperature after pyrolysis (and before the residual VM test). In fixed-bed pyrolysis, the yield of volatiles (~45% daf) is consistently lower than the maximum yield of about 58% observed in entrained-flow conditions or the ASTM VM yield of about 53% daf. This is attributed to the secondary reactions of cracking and/or repolymerization of the volatiles [7,8]. The yield enhancement, due to entrainment and dilute-phase pyrolysis ( $Q$ -factor [9]), for this lignite (which releases a relatively small amount of tars, compared to bituminous coals) and under coal loading conditions of 4–5 wt. %, is relatively small and considerably less than predicted by Nsakala et al. [10] for the same coal under similar conditions.

A limited kinetic study of rapid pyrolysis of the raw lignite in the range 975–1275 K [11] suggested that a better fit through the data points on a first-order isothermal plot could be obtained by curves of constantly decreasing slope (rate constant) rather than by one [6,9] or even two [10] straight lines. This trend of changing (increasing) apparent activation energy with conversion [12], also observed in coal liquefaction (partly a thermal decomposition process) by Szladow and Given [13], is in agreement with the intuitive expectation that reactions with relatively low activation energies (rupture of weak bonds [14]) are predominant in the early stages of pyrolysis. When sufficient time was allowed for pyrolysis

TABLE 1

Elemental analysis of raw,  $\text{NH}_4\text{Ac}$ -,  $\text{NH}_4\text{Ac}+\text{Ca}$ - and dem+Ca-coal and selected chars prepared at 1275 K

Sample	Content (wt. %, dry)					Atomic H/C (daf)
	C	H	N	Ash	O+S <sup>a</sup>	
<i>Coal</i>						
Raw	64.1	4.4	1.4	9.7	20.4	0.91
$\text{NH}_4\text{Ac}$	64.6	4.5	2.7	2.4	25.8	0.86
$\text{NH}_4\text{Ac}+\text{Ca}$	61.0	4.6	1.6	7.7	25.1	0.98
<i>Char<sup>b</sup> (raw)</i>						
R — 0.3 s	76.9	2.0	1.2	11.5	8.4	0.35
R — 5 min	79.2	0.5	1.0	14.7	4.6	0.09
S — 30 min	84.2	0.4	1.4	13.0	1.0	0.07
<i>Char (<math>\text{NH}_4\text{Ac}</math>)</i>						
R — 0.3 s	81.9	2.0	2.2	3.3	10.6	0.30
R — 5 min	86.9	0.7	1.6	4.2	6.6	0.10
S — 30 min	89.1	0.5	2.5	4.3	3.6	0.07
<i>Char (<math>\text{NH}_4\text{Ac}+\text{Ca}</math>)</i>						
R — 0.3 s	71.9	2.0	1.8	11.1	13.2	0.38
R — 5 min	72.4	0.5	1.2	14.1	11.8	0.10
S — 30 min	81.4	0.3	1.1	13.0	4.2	0.05

<sup>a</sup>By difference.

<sup>b</sup>R, rapid pyrolysis; S, slow pyrolysis.

(of the order of minutes at 975 K vs. seconds at 1275 K), the ultimate yield of volatiles was independent of temperature. Coal pretreatment had no effect on yield in fixed-bed pyrolysis, in agreement with the recent results of Hengel and Walker [15]. (In entrained-flow, short-contact-time pyrolysis, Morgan and Jenkins [16] recently showed that the exchangeable cations affect both the kinetics of evolution and the yield of volatiles, for residence times up to 0.3 s at 1175 K.) Table 1 gives the elemental analyses of the raw and variously pretreated coal and selected chars.

#### *Effect of pyrolysis conditions on char reactivity*

Figures 3–5 show a significant decrease in raw char reactivity, both in air and  $\text{CO}_2$ , with increasing severity of pyrolysis conditions. The same effect was observed in steam. Short-residence-time chars react in air at rates which are 2–4 orders of magnitude greater than the ones predicted by the correlations of Smith [17] and Lewis and Simons [18]. The value of activation energy of about 130 kJ/mol agrees very well with that found by Smith and co-workers [19,20] for a brown-coal char and by Dutta and Wen [21] for a series of chars produced from bituminous coals in the Synthane, Hydrane and Hygas processes.

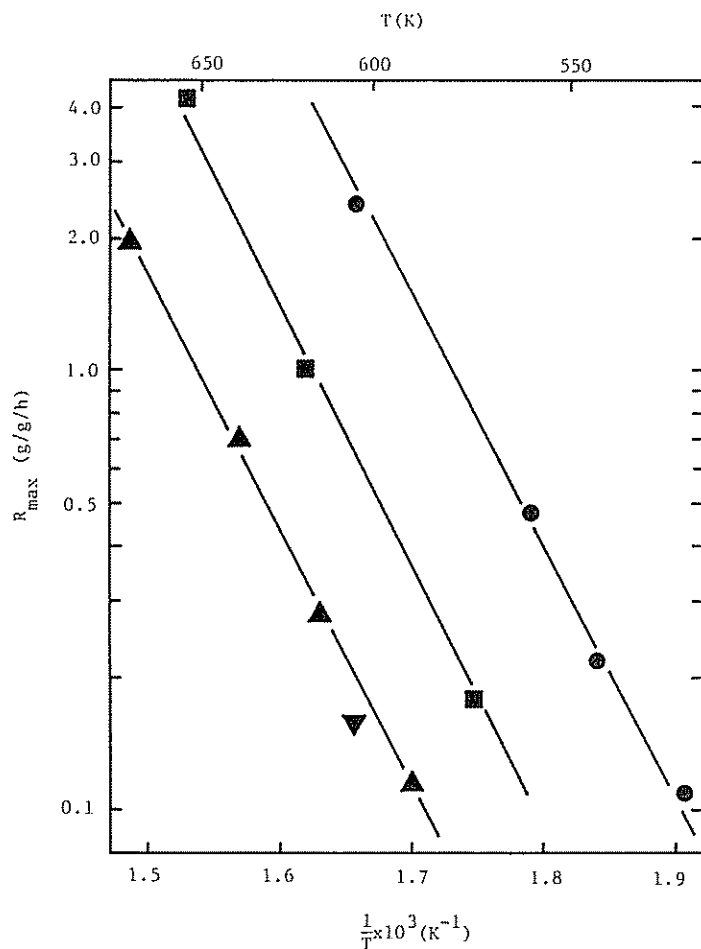


Fig. 3. Effect of pyrolysis residence time (at 1275 K) between 0.3 s and 30 min on the reactivity of raw char in 0.1 MPa air: ● — 0.3 s (1.8 s); ■ — 0 h (slow pyrolysis); ▼ — 5 min; ▲ — 30 min.

The activation energy in  $\text{CO}_2$  and  $\text{H}_2\text{O}$  was greater than in air: about 220 and 170 kJ/mol, respectively. Dutta et al. [22] found, for a series of chars gasified in  $\text{CO}_2$  at 1100–1375 K, an activation energy of about 250 kJ/mol. However, at 950 K the rate for the short-residence-time (0.3 s) lignite char prepared at 1275 K is again about three orders of magnitude higher than that obtained by extrapolation of their data for a Pittsburgh HVab coal char (pyrolyzed *in situ* in a TGA apparatus). For the reaction in 2.3 kPa  $\text{H}_2\text{O}$  of a Montana lignite char, prepared by slow pyrolysis (1275 K, 2 h), Linares-Solano et al. [23] found essentially the same activation energy, about 176 kJ/mol. However, the short-residence-time char produced in this study reacted at the same rate in 3.1 kPa  $\text{H}_2\text{O}$  at a temperature 150 K lower.

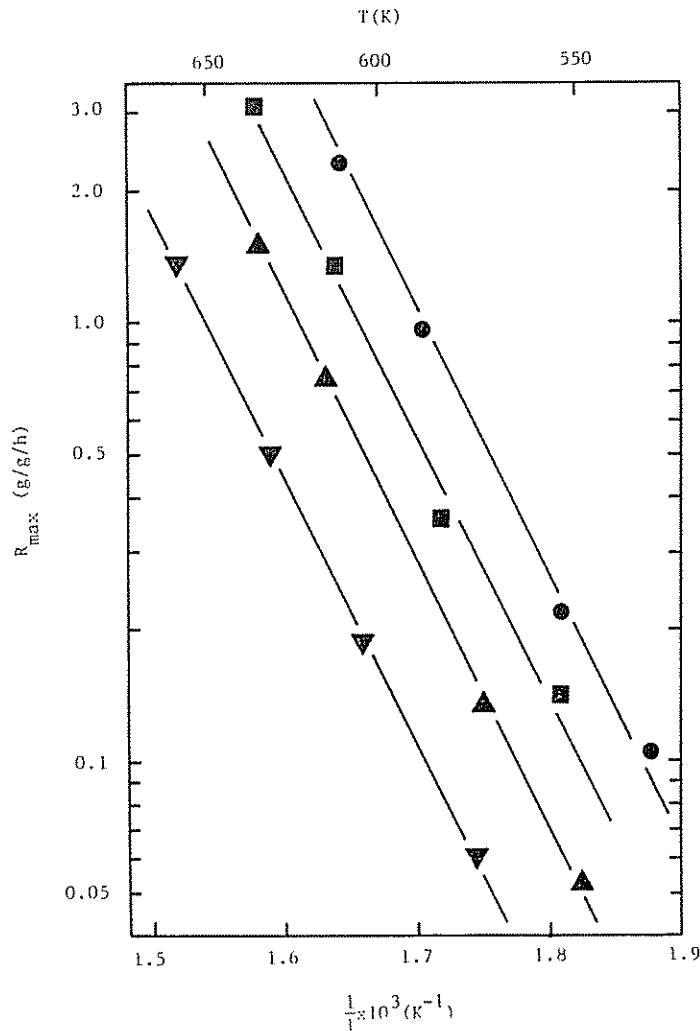


Fig. 4. Effect of pyrolysis temperature on the reactivity of raw char in 0.1 MPa air. Residence time, 5 min: ● — 975 K; ■ — 1075 K; ▲ — 1175 K; ▼ — 1275 K.

Pyrolysis temperature—time history thus has a decisive (and sometimes dramatic) effect on subsequent char reactivity.

Attempts to explain the commonly observed differences in gasification reactivities of coal chars (and carbons in general) on the basis of their total surface area (TSA) have not been successful [17]. Traditionally, the surface area of both porous and nonporous carbons is determined by gas adsorption in conjunction with a suitable isotherm equation. In the case of coal chars, the most extensively used ones are the BET and the Dubinin—Radushkevich (D—R) equation [24]. Their applicability in specific cases has been a subject of controversy and still seems to be misunderstood.



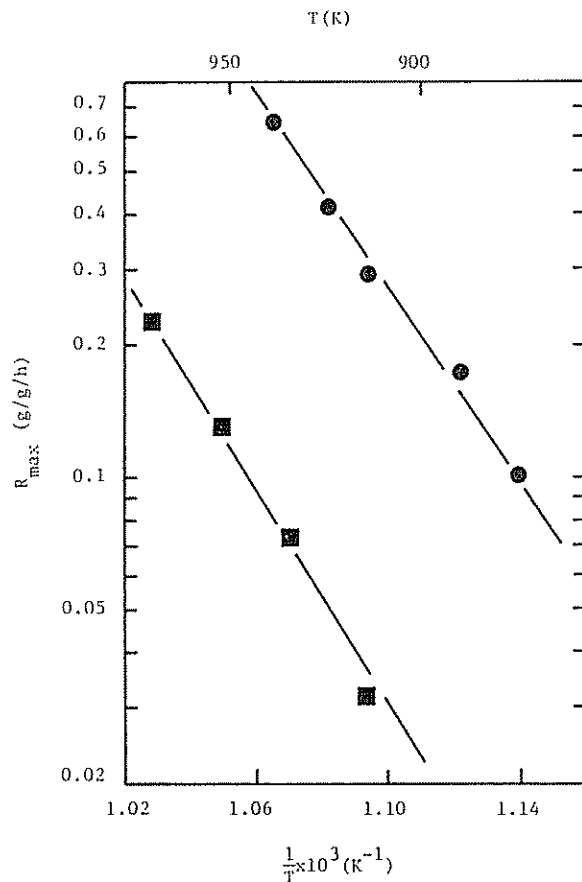


Fig. 5. Effect of pyrolysis residence time (at 1275 K) between 0.3 s and 5 min on the reactivity of raw char in 0.1 MPa  $\text{CO}_2$ ;  $\bullet$  — 0.3 s;  $\blacksquare$  — 5 min.

The crucial issue is the dependence of the mechanism of adsorption on pore size. It is now generally accepted that if the pores are very fine (close to molecular dimensions), the proximity of the pore walls gives rise to volume filling at low relative pressures. Many coal chars, and especially those derived from lignites, possess a wide pore-size distribution and two mechanisms of adsorption are expected to be operative: layer-by-layer adsorption in the wider pores (as envisaged by the BET theory) and volume filling in the very narrow pores (as hypothesized by the D-R theory). Thus, the strict applicability of either one of these two isotherms alone for calculating the true TSA of chars is subject to some uncertainty.

Figure 6 shows the effect of pyrolysis residence time at 1275 K on the calculated TSA of the resulting chars. The D-R equation was used to obtain the limiting volume of adsorption in the micropores [25]. Assuming that the micropore volume is approximately equal to the monolayer ca-

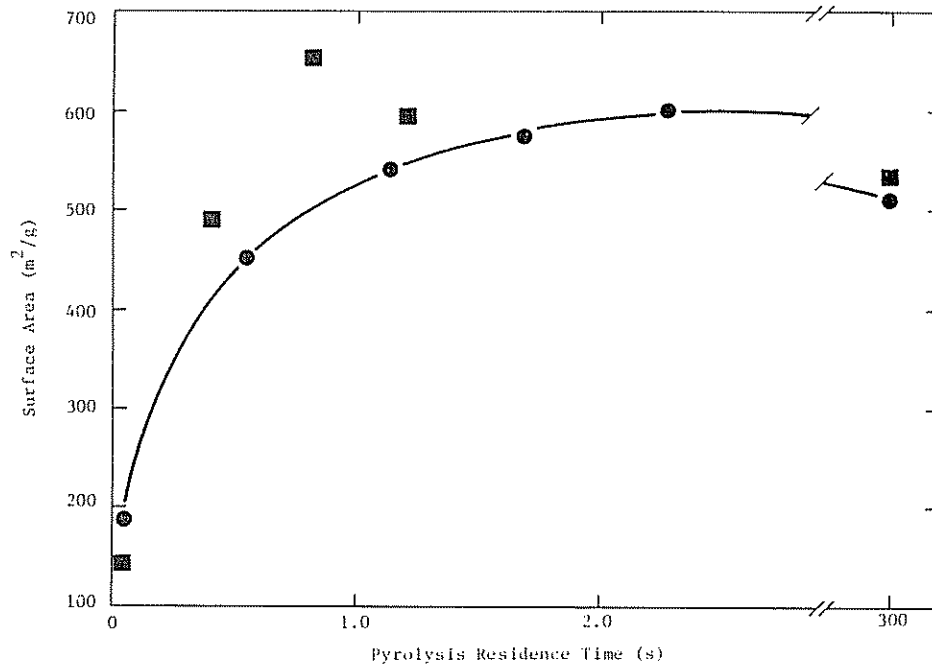


Fig. 6. Variation of total surface area of raw chars with pyrolysis residence time at 1275 K: ● — 200 × 270 mesh; ■ — 70 × 100 mesh.

capacity, TSA was then obtained using the classical BET approach. This assumption is valid if the contribution of feeder pores to TSA is small compared to the micropores. It is seen that the calculated TSAs cannot explain the reactivity differences observed in Figs. 3 and 5. The reactivity differences for chars with residence times of 0.3 s and 5 min are an order of magnitude greater than the TSA differences, even after allowing for up to 100% uncertainty in the calculation of relative TSAs. The same conclusion was reached in the case of dem-chars and carbons of varying crystallinity and purity from Saran char to natural graphite [2]. McKee et al. [26] have come to the same conclusion in their study of gasification behavior (in  $\text{CO}_2$  and  $\text{H}_2\text{O}$ ) of chars prepared from variously pretreated samples of Illinois No. 6 bituminous coal.

Owing to the presence of inorganic impurities in coal chars, their gasification should be regarded as a potentially catalytic gas—solid reaction. The overall reactivity expressed in Arrhenius form is then [27]

$$R = sA_c \exp\left(-\frac{E_c}{RT}\right) + (1-s)A_u \exp\left(-\frac{E_u}{RT}\right)$$

where  $s$  represents the fraction of the surface on which catalysis occurs and the subscripts  $c$  and  $u$  denote reaction at catalyst and carbon sites, respectively. The relative importance of these two parallel reactions

depends on the inherent activity and concentration of these sites. Activity depends only on the composition of mineral matter in the coal; site concentration depends also on the conditions of pyrolysis. We have shown recently that with increasing severity of pyrolysis (higher temperature and/or longer residence time) both the concentration of carbon active sites (carbon active surface area) [2] and the concentration of catalyst sites (catalyst dispersion) [3] decrease. In the case of dem-chars and relatively pure carbons, the former was shown to be a good index of gasification reactivity [2] suggesting the predominance of the uncatalyzed reaction. For raw and Ca-exchanged lignite chars, the latter was shown to be a good index of reactivity [3], suggesting the predominance of the presumably structure-insensitive catalyzed reaction [28]. The gasification behavior of chars produced in several coal conversion processes of commercial interest was also recently rationalized on the basis of differences in their active surface area (either carbon or catalyst) caused by differences in process conditions [4].

It is concluded that the fundamental concept of active sites, developed in the field of catalysis and carbon gasification, can be successfully used to quantify and explain the complex gasification behavior of coal chars.

#### *Effect of coal pretreatment on char reactivity*

Figure 7 shows the effect of lignite pretreatment on char reactivity [1]. Dem-char was taken as a "model compound" for the predominantly uncatalyzed carbon gasification [2]. It was assumed that the high concentration of carbon active sites in this highly disordered carbonaceous material masks the minor contribution of the catalyzed reaction to the overall rate. Similarly, dem+Ca-char was taken as a "model compound" for the predominantly catalyzed reaction of raw lignite chars [3]. Table 2 shows the effect of pretreatment on char deactivation with increasing severity of pyrolysis. It is seen that the extent of deactivation is significantly reduced in the absence of Ca. However, deactivation of dem-char is initially faster. These were the initial results that suggested the later confirmed possibility that the observed deactivation of dem- and dem+Ca-chars was governed by two fundamentally different processes, i.e., a decrease in carbon active surface area and catalyst crystallite growth (sintering), respectively. It is interesting to note that a very wide range of carbon gasification reactivities [17] can be obtained using the *same* carbonaceous precursor, in this case a lignite, by varying the conditions of its pyrolysis and pretreatment. For example, a dem+Ca-char heated to 1275 K with a residence time of 0.3 s had a reactivity which is about three orders of magnitude higher than that of a dem-char heated to and soaked for 1 h at 1475 K. However, in all cases 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.

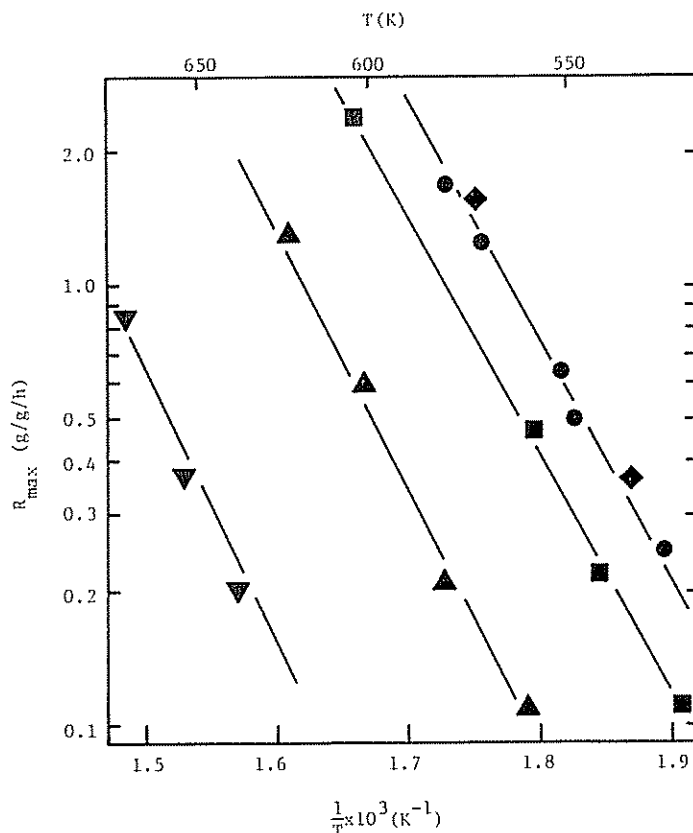


Fig. 7. Effect of coal pretreatment on char reactivity in 0.1 MPa air. Pyrolysis temperature, 1275 K; residence time, 0.3 s: ● — dem+Ca; ◆ — NH<sub>4</sub>Ac+Ca; ■ — raw, ▲ — NH<sub>4</sub>Ac, ▼ — dem.

The insensitivity of activation energy of char gasification to the pretreatment of coal, i.e., to the relative absence or abundance of catalytic species, was further investigated. The graphitized carbon black V3G, whose reactivity is reported elsewhere [2], was treated with concentrated HNO<sub>3</sub> in order to introduce some carboxyl groups on its surface [29]. Subsequently, the protons on the carboxyl groups were exchanged by Ca<sup>2+</sup> and Ba<sup>2+</sup> using a 0.5 M solution of CaAc and BaAc, respectively. This treatment resulted in a loading of less than 1 wt. % cation. The pretreated carbons were then heat-treated at 10 K/min to final temperatures of 975 and 1275 K. The reactivities of the carbons obtained are reported in Fig. 8. It is seen that the catalytic effect of Ca- and Ba-species (CaO and, presumably, BaO) is manifested again in the increase of the pre-exponential factor. The activation energy of about 190 kJ/mol remained unchanged. Otto et al. [30] observed the same behavior in the case of alkaline-earth-catalyzed steam gasification of SP-1 graphite.

TABLE 2

Effect of coal pretreatment on char reactivity in air

Pyrolysis conditions <sup>a</sup>	Ratio of reactivities <sup>b</sup>	
	In presence of Ca (dem+Ca)	In absence of Ca (dem)
$t_p = 1$ h $T_p = 1275 - 1475$ K	~ 6	~ 1.6
$t_p = 1$ h $T_p = 975 - 1475$ K	~ 100	~ 5
$T_p = 1275$ K $t_p = 0.3$ s - 1 h	~ 20	~ 8
$T_p = 1275$ K $t_p = 0.3 - 1.8$ s	~ 1	~ 2

<sup>a</sup> $t_p$  = pyrolysis residence time. $T_p$  = pyrolysis temperature.<sup>b</sup>Reactivity at minimum temperature (time)/reactivity at maximum temperature (time)

It is seen from data presented in Table 1 and elsewhere (Table 1, Ref. [1]; Table 2, Ref. [2]) that char deactivation in all cases is accompanied by a decrease in the H/C ratio of the chars, suggesting a qualitative relationship between active site concentration and H content. This is in agreement with the fact that the presence of H prevents alignment of carbon crystallites and thus the formation of a less disordered char.

The possible effect of interaction of Ca with the discrete mineral matter (e.g., clays), as a mechanism of catalyst deactivation was also investigated. As shown in Fig. 9, contrary to the case of K-catalysis [5,26,31], it does not seem to be important. In the  $\text{NH}_4\text{Ac}+\text{Ca}$ -chars this interaction would have resulted, for example, in the formation of inactive Ca-aluminosilicates and, therefore, in a decrease in reactivity compared to dem+Ca-chars, where no such interaction is possible.

Two additional factors need to be considered when assessing the validity of using dem+Ca-char as a model compound for raw lignite char: the possible effects of other cations, especially Mg [32], and the effect of demineralization. The former has been recently addressed by Hengel and Walker [15], who concluded that Ca activity was not affected by the presence of Mg in the lignite. The latter is related to the possible inhibiting effect of Cl if retained in the coal and char after acid (HCl) washing. Hengel and Walker [15] report for a Montana lignite (PSOC-833) a higher reactivity of raw char compared to dem+Ca-char, even though the latter contains more Ca (4 vs. 4–7%). They also report a higher reactivity of  $\text{NH}_4\text{Ac}+\text{Ca}$ -char vs. dem+Ca-char at similar Ca loadings and attribute this behavior to Cl retention during acid washing (0.42 vs. 0.04% in the raw lignite)

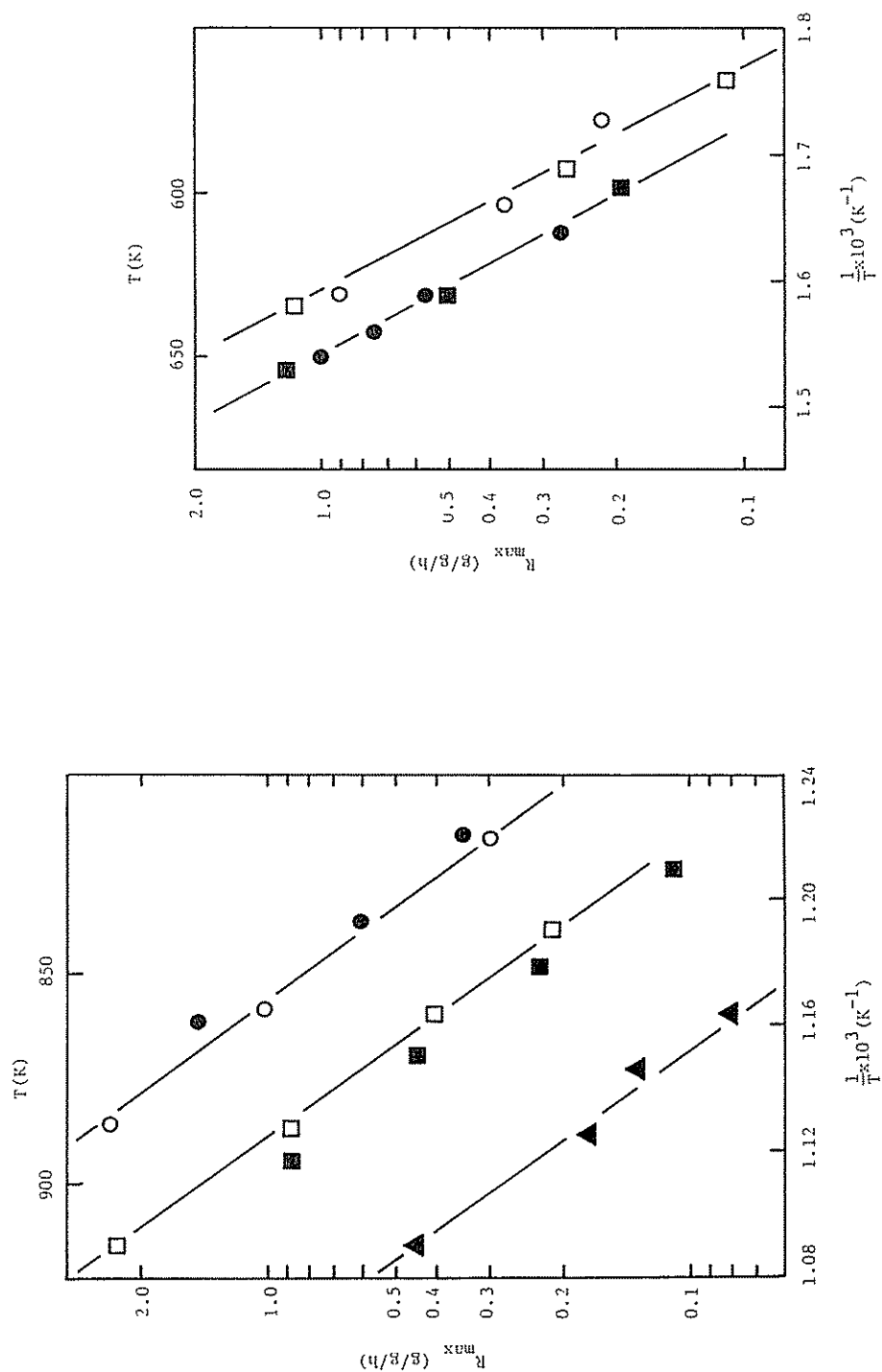


Fig. 8. Effect of catalysis by Ca and Ba on the reactivity of graphitized carbon black (V3G): ● — V3G + Ba (975 K); ○ — V3G + Ca (975 K); ■ — V3G + Ba (1275 K); □ — V3G + Ca (1275 K); ▲ — V3G.

Fig. 9. Comparison of reactivities of dem+Ca-chars and NH<sub>4</sub>Ac+Ca-chars obtained by slow pyrolysis at 1275 K (Ca exchange effected using 0.1 M acetate). Pyrolysis residence time, 0–1 h; ○ — dem+Ca, 0 h; □ — NH<sub>4</sub>Ac+Ca, 0 h; ● — dem+Ca, 1 h; ■ — NH<sub>4</sub>Ac+Ca, 1 h.

and subsequent catalyst poisoning. In the present study, performed on a North Dakota lignite, dem+Ca-chars were generally slightly more reactive than raw and NH<sub>4</sub>Ac+Ca-chars, as expected on the basis of their higher Ca content. No chlorine retention was detected, which is consistent with the apparent absence of catalyst poisoning.

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#### REFERENCES

- 1 Radovic, L.R., Walker, P.L., Jr. and Jenkins, R.G., 1983. *Fuel*, 62: 209.
- 2 Radovic, L.R., Walker, P.L., Jr. and Jenkins, R.G., 1983. *Fuel*, 62: 849.
- 3 Radovic, L.R., Walker, P.L., Jr. and Jenkins, R.G., 1983. *J. Catal.*, 82: 382.
- 4 Radovic, L.R., and Walker, P.L., Jr., 1984. *Fuel Processing Technology*, 8: 149.
- 5 Radovic, L.R., Walker, P.L., Jr. and Jenkins, R.G., 1984. *Fuel*, 63: 1028.
- 6 Scaroni, A.W., Walker, P.L., Jr. and Essenhigh, R.H., 1981. *Fuel*, 60: 71.
- 7 Scaroni, A.W., Walker, P.L., Jr. and Jenkins, R.G., 1981. *Fuel*, 60: 558.
- 8 Gray, D., Cogoli, J.G. and Essenhigh, R.H., 1974. In: Massey, L.G. (Ed.), *Coal Gasification, Advances in Chemistry Series, No. 131*, Amer. Chem. Soc., Washington, D.C., p. 72.
- 9 Badzioch, S. and Hawksley, P.G.W., 1970. *Ind. Eng. Chem., Process Des. Dev.*, 9: 521.
- 10 Nsakala, N.Y., Essenhigh, R.H. and Walker, P.L., Jr., 1977. *Combust. Sci. Technol.*, 16: 153.
- 11 Radovic, L.R., 1982. Ph.D. Thesis, The Pennsylvania State University.
- 12 Golikeri, S.V. and Luss, D., 1972. *AIChE J.*, 18: 277.
- 13 Szladow, A.J. and Given, P.H., 1981. *Ind. Eng. Chem., Process Des. Dev.*, 20: 27.
- 14 Boudart, M., 1968. *Kinetics of Chemical Processes*, Prentice-Hall, Englewood Cliffs, NJ, Chap., 2, p. 8.
- 15 Hengel, T.D. and Walker, P.L., Jr., 1984. *Fuel*, 63: 1214.
- 16 Morgan, M.E. and Jenkins, R.G., 1983. *Amer. Chem. Soc., Div. Fuel Chem., Prepr.*, 28(4): 138.
- 17 Smith, I.W., 1978. *Fuel*, 57: 409.
- 18 Lewis, P.F. and Simons, G.A., 1979. *Combust. Sci. Technol.*, 20: 117.
- 19 Hamor, R.J., Smith, I.W. and Tyler, R.J., 1973. *Combust. Flame*, 21: 153.
- 20 Smith, I.W. and Tyler, R.J., 1974. *Combust. Sci. Technol.*, 9: 87.
- 21 Dutta, S. and Wen, C.Y., 1977. *Ind. Eng. Chem., Process Des. Dev.*, 16: 31.
- 22 Dutta, S., Wen, C.Y. and Belt, R.J., 1977. *Ind. Eng. Chem., Process Des. Dev.*, 16: 20.
- 23 Linares Solano, A., Mahajan, O.P. and Walker, P.L., Jr., 1979. *Fuel*, 58: 327.

- 24 Gregg, S.J. and Sing, K.S.W., 1982. Adsorption, Surface Area and Porosity, 2nd edn., Academic Press, London.
- 25 Dubinin, M.M., 1983. Carbon, 21: 359.
- 26 McKee, D.W., Spiro, C.L., Kosky, P.G. and Lomby, E.J., 1982. Amer. Chem. Soc., Div. Fuel Chem., Prepr., 27(1): 74.
- 27 Feates, F.S., Harris, P.S. and Reuben, B.G., 1974. J. Chem. Soc., Faraday Trans. I, 70: 2011.
- 28 Boudart, M., 1969. Adv. Catal., 20: 153.
- 29 Mahajan, O.P., Youssef, A. and Walker, P.L., Jr., 1978. Sep. Sci. Technol., 13: 487.
- 30 Otto, K., Bartosiewicz, L. and Shelef, M., 1979. Carbon, 17: 351.
- 31 Mims, C.A. and Pabst, J.K., 1980. Amer. Chem. Soc., Div. Fuel Chem., Prepr., 25(3): 258.
- 32 Morgan, M.E., Jenkins, R.G. and Walker, P.L., Jr., 1981. Fuel, 60: 189.