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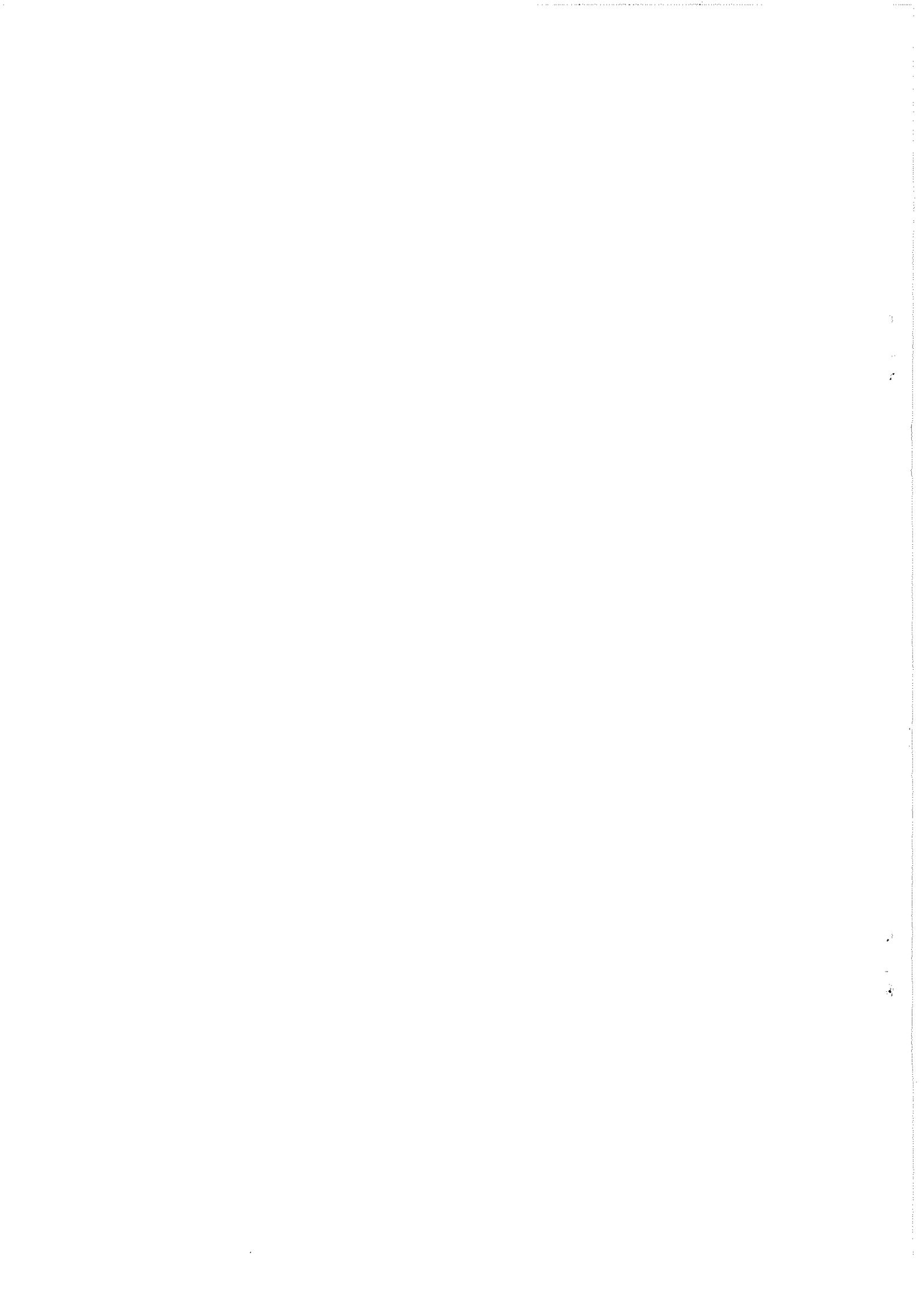
Effect of lignite pyrolysis conditions on calcium oxide dispersion and subsequent char reactivity*

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A demineralized North Dakota lignite was loaded with 2.9 wt% Ca by ion exchange. Chars were prepared by pyrolysis in N_2 at 1275 K and residence times between 0.3 s and 1 h. Major differences were observed in their subsequent reactivities in 0.1 MPa air. X-ray diffraction analysis was carried out to obtain information on the state and dispersion of the Ca species on the various chars. The results clearly indicate that CaO is the predominant species responsible for catalysis of lignite char gasification. It is concluded that pyrolysis residence time also has a profound effect on CaO dispersion. Thus, a correlation was established between a fundamental physical property (catalyst dispersion) and the observed gasification behaviour of lignite chars prepared under different pyrolysis conditions.

(Keywords: lignite; pyrolysis; catalysis; calcium salts; gasification)

It is well known that the gasification reactivity of chars is strongly dependent on the rank of the precursor coal.[1] When obtained under identical pyrolysis conditions, lignite chars are more reactive than anthracite chars by a factor of about 20–40.[1-3] Their relatively high reactivity has been attributed primarily to the high activity or dispersion, or both, of the inherent catalyst derived from the abundant inorganic elements (principally Ca^{++}) associated with the carboxyl groups in the lignite. However, even though there have been many studies of the importance of catalysis in lignite char gasification,[4-7] the catalyst has not been clearly identified nor has its dispersion been measured.

It has been shown (see, for example, references 1 and 8) that chars obtained from the same coal under different pyrolysis conditions have different reactivities. Thus, for example, McCarthy[8] used the energy of thermal deactivation as an additional parameter in the Arrhenius rate expression to relate the decrease in reactivity to the increase in pyrolysis temperature. The problem with this and similar concepts, from a fundamental standpoint, is that they lump all the factors responsible for deactivation into an overall parameter that cannot be easily related to measurable physical properties of the char.

The commonly reported decrease in char gasification reactivity with increasing pyrolysis temperature (or residence time) can be explained by a decrease in the concentration of carbon active sites or a decrease in catalyst activity, or both.[9] This study was designed to investigate the second of these two factors. The former is discussed in a future publication.[10]

EXPERIMENTAL

Coal pretreatment

A lignite from North Dakota (PSOC-246), the organic and inorganic fractions of which had previously been thoroughly characterized,[11,12] was used in this study. It contains ≈ 1.5 wt% Ca^{++} (dry). A 70 × 100 US mesh fraction of the raw coal, mean particle size $\sim 170\,\mu m$, was demineralized with HCl and HF. The demineralized coal (Dem-coal) was subsequently ion-exchanged with Ca^{++}, using a 1.5 M solution of Ca acetate. Detailed experimental procedures are given elsewhere.[13]

Coal pyrolysis

The demineralized and Ca-exchanged coal (Dem + Ca-coal) was devolatilized in N_2 by both slow and rapid pyrolysis. Slow pyrolysis (10 K min⁻¹) was carried out in a 50 mm diameter horizontal-tube furnace with ≈ 2 g of size-graded coal placed in a quartz boat. The flow rate was 500 cm³ (s.t.p.) min⁻¹. The temperature was monitored with a chromel-alumel thermocouple.

Rapid pyrolysis was carried out in an isothermal entrained-flow furnace, described previously by Scaroni et al.,[14] in which the particle heating rate is estimated to be of the order of 10^4 K s⁻¹. The gas temperature was measured by suction pyrometry. Maximum residence time of the coal (char) particles in one pass through the reactor is nominally estimated to be 0.3 s for the 70 × 100 US mesh fraction at 1275 K. By using a newly designed char collector,[13] in which the char particles are collected in a ceramic crucible within the hot zone of the furnace, the pyrolysis residence time could be extended indefinitely.

Table 1 Elemental analysis of raw and Dem+Ca-coal and selected Dem+Ca-chars prepared at 1275 K

| Sample | Analysis (wt% dry coal) | | | | | Atomic C/H (daf) |
	C	H	N	Ash	O+S[a]	
Coal						
Raw	64.1	4.4	1.4	9.7	20.4	1.1
Dem+Ca	63.8	4.6	1.0	5.4	25.2	1.1
Char (Dem+Ca)						
R-0.3 s[b]	75.0	2.2	1.2	7.6	14.0	2.8
R-1.5 s	75.9	1.5	1.4	9.4	11.8	4.1
S-30 min[c]	87.9	0.5	1.5	9.5	0.6	15
S-1 h	90.9	0.4	1.3	9.6	~0	19

[a] By difference
[b] R = rapid pyrolysis
[c] S = slow pyrolysis

Char reactivity measurements

Reactivities of the chars were determined by isothermal thermogravimetric analysis (t.g.a.) in 0.1 MPa air. Air was chosen as the reactant gas because the high reactivity of carbon in oxygen allows operation at low temperatures, between 525 and 700 K, at which the highly disordered structure of the short-residence-time chars is essentially preserved. The equipment was operated under gas flow conditions of 300 cm^3 (s.t.p.) min^{-1}. It has been shown previously,[1] and confirmed in this study, that interparticle diffusional limitations are eliminated when the sample weight (related to the bed height) was kept below 10 mg. The very high reactivity of short-residence-time chars and the accompanying strong heat transfer effects dictated the use of 1–2 mg samples, in some cases, to prevent ignition and non-isothermal behaviour. For the reactor system used, it was found in a series of preliminary experiments that no measurable temperature increase occurs if the reaction rates are kept below 5 mg h^{-1}. The reactivities are thus determined under essentially isothermal conditions. Conditions were also selected to ensure, in the maximum possible measure, the absence of intraparticle mass transfer limitations.[10]

The experiments were carried out with a constant thermal equilibration time. The furnace was pre-heated to the reaction temperature and raised to surround the hangdown tube (with the sample holder) in which a flow of dry, O$_2$-free N$_2$ was maintained. After a period of 15 min, in which the recorded sample temperature and weight reached equilibrium values, the flow of N$_2$ was switched to air. Weight changes were recorded continuously as a function of time.

Char characterization

Elemental analyses (C,H,N) were performed on selected chars to verify the extent of their devolatilization. X-ray diffraction (XRD) patterns were also obtained for selected Dem + Ca-chars in order to determine the state and dispersion of the Ca species on their surface. A Rigaku diffractometer (Geigerflex D/max; 40 kV, 20 mA, CuKα radiation) was used. The samples were mounted into a hollow aluminium holder (20 × 17 × 2 mm) provided with a glass slide on the bottom.

RESULTS AND DISCUSSION

The demineralization of the lignite resulted in the removal of essentially all the inorganic constituents. The ASTM ash content was thus reduced from 9.7 wt% (dry) in the

raw coal to about 0.2 wt% (dry). Ion exchange with Ca acetate resulted in a loading of about 2.9 wt% Ca (dry).

Table 1 gives the elemental analyses of the starting raw and Dem + Ca-coal and selected Dem + Ca-chars prepared at 1275 K. Although the analysis of the ASTM ash and volatile matter content of the various chars[15] suggests that the devolatilization process at 1275 K is essentially complete after about 1 s, the results of *Table 1* indicate that H$_2$ evolution from the char is a very slow process. Consequently, there is a substantial increase in the C/H ratio of the chars with increasing pyrolysis time. The apparent substantial amount of oxygen in the short-residence-time chars (%S ≈ 1) is mostly an artifact since these chars readily chemisorb oxygen at room temperature.[10] Even though it is difficult to assess the effect (if any) of the differences in elemental analysis shown in *Table 1* on the activity of carbon active sites[10] and on the gasification behaviour of the chars, they should be kept in mind when interpreting the reactivity results.

Figure 1 shows the effect of demineralization and subsequent Ca^{++} addition on the reactivity of chars obtained by rapid pyrolysis at 1275 K for 0.3 s. The reactivity is expressed per unit initial weight of dry, ash-free (daf) char, i.e. as percentage conversion (burn-off) per unit time. The plots of char conversion *versus* time were in most cases essentially linear up to about 40% burn-off and
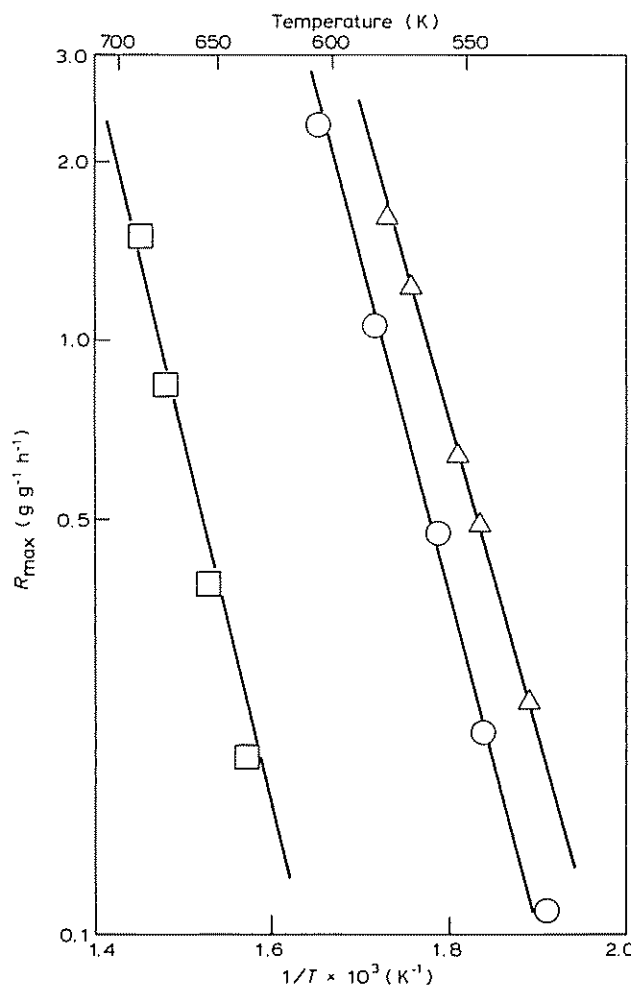

Figure 1 Effect of lignite demineralization and subsequent calcium addition on char reactivity. Pyrolysis temperature: 1275 K. Residence time: 0.3 s. ○, Raw char; □, Dem-char; △, Dem+Ca-char
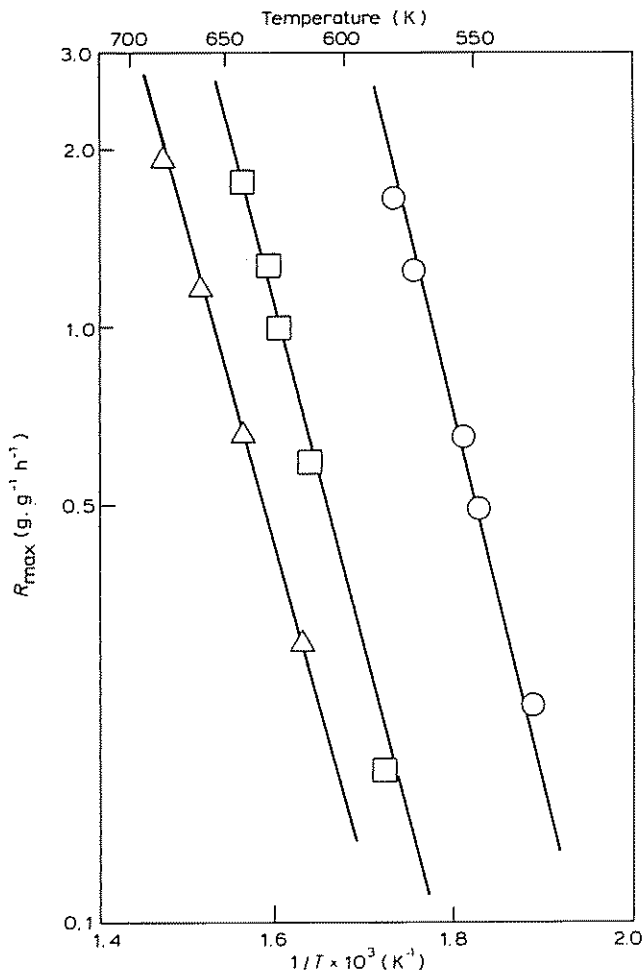
Figure 2 Effect of pyrolysis residence time on the reactivities of Dem+Ca-chars. Pyrolysis temperature: 1275 K. $\bigcirc$, R-0.3 s; $\square$, R-5 min; $\triangle$, S-1 h

subsequently exhibited a gradual decrease in slope. In all cases, the maximum slope was used in the calculation of reported reactivities. It is seen in *Figure 1* that the demineralized lignite was about 30 times less reactive than the raw lignite. When only Ca^{++} was added back to the demineralized lignite, the original reactivity was more than completely restored. The 50% reactivity difference between the raw and Dem+Ca-char is probably due to the greater amount of Ca^{++} present in the latter sample (1.5 *versus* 2.9 wt%). It is well known[12] that, in addition to exchangeable cations on the carboxyl groups, lignites contain discrete minerals such as clays, quartz and calcite. It has been shown by Tomita *et al.*[16] that these do not catalyse the gasification of carbon. Also, it has been shown in complementary reactivity experiments in 0.1 MPa air that they do not affect the dominant catalytic action of the Ca species.[17] Thus, the Dem+Ca-char behaves essentially in the same way as the raw lignite char and is a convenient system on which to investigate, from a fundamental standpoint, the effect of catalysis in lignite char gasification.

The Arrhenius plots in *Figure 2* show the effect of pyrolysis residence time at 1275 K from 0.3 s to 1 h on the reactivity of Dem+Ca-chars. A significant decrease in reactivity with increasing residence time is observed, by a factor of about 25 between 0.3 s and 1 h and by a factor of 10 between 0.3 s and 5 min. The reactivities of chars with

residence times between 0.3 and 1.5 s were essentially identical, i.e. within the reproducibility limits of ±15%. The activation energy in all cases was about 130 kJ mol^{-1}.

Figure 3 gives the XRD patterns obtained for the starting Dem+Ca-coal and chars as a function of pyrolysis residence time at 1275 K. The peak assignments for CaO (37.4°, 53.8°, 32.2°) are reasonably certain.[18] The assignment of the $CaCO_3$ (calcite) peak is based on the fact that the only reasonable (and expected) Ca compound with a peak maximum intensity at that particular angular position (29.4°) is, indeed, calcite. It is seen also that all the XRD patterns in *Figure 3* exhibit the very broad (002) and (10) carbon peaks which are characteristic of highly disordered carbonaceous materials. In *Figure 3* traces *d* and *e* clearly show that CaO is the predominant Ca species that is responsible for catalysis of lignite char gasification. On thermodynamic grounds this is, indeed, to be expected at 1275 K, since the standard free energy change for the reaction $CaCO_3 \rightarrow CaO+CO_2$ becomes negative between 1000 and 1200 K.

In the case of chars of residence times up to 1.5 s, in preliminary X-ray photoelectron spectroscopy (XPS) studies, CaO was also identified. *Table 2* gives the relevant electron binding energies obtained in this study, compared to published XPS data for CaO.[19] It is seen that
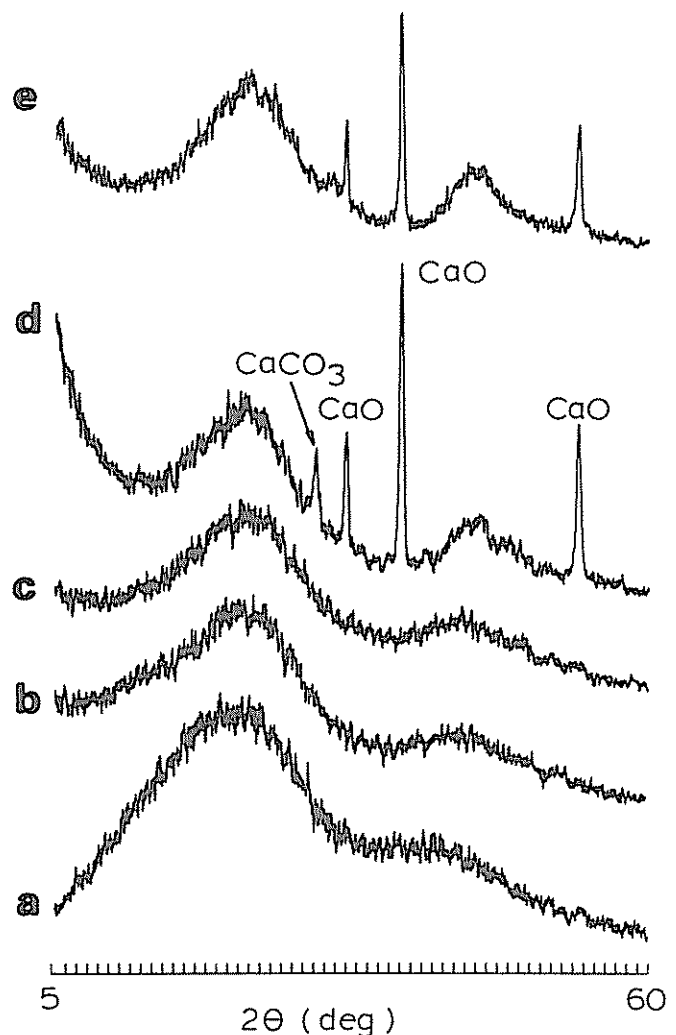

Figure 3 XRD patterns for Dem+Ca-coal and chars obtained at 1275 K. (a) Coal, (b) R-0.3 s; (c) R-1.5 s; (d) R-5 min; (e) S-1 h

Table 2 XPS data for CaO

Level	Peak position (eV)		
	R-0.3 s	R-1.5 s	CaO (Ref.19)
Ca 2p1/2	350.7	350.6	350.5[a]
Ca 2p3/2	347.0	347.1	347.1

[a] The measured values are uncertain to ±0.2 eV

Table 3 Average CaO crystallite size (*D*) and reactivities (R_{max}) at 600 K for various 1275 K Dem+Ca-chars

Sample	*D* (nm)	R_{max} at 600 K (g g^{-1} h^{-1})
R-0.3 s	—[a]	4.2
R-1.5 s	—[a]	4.0
R-5 min	24.5 ± 1.5	0.40
S-1 h	28.0	0.17

[a] Below the detection limit

the agreement is very good. In the light of these results, the absence of CaO peaks in the XRD patterns of these chars (*Figure 3*, traces *b* and *c*) strongly suggests that CaO is highly dispersed on the char surface and has an average crystallite size small enough to be below the detection limit of the instrument.

Table 3 gives the average crystallite size (*D*) for CaO particles on the various chars, determined from the (200) peaks using the Scherrer equation[20] in the form $D = K\lambda/(B^2 - b^2)^{\frac{1}{2}}\cos\theta$. The instrumental broadening (*b*) was determined to be 0.175° (*20*). The peak widths at half height (*B*) were determined from the scans made at 0.5° (*2θ*) min^{-1}. The commonly used value of the Scherrer constant (*K* =0.9) was adopted in all calculations. Also shown in *Table 3* are the reactivities (R_{max}) of the various chars at 600 K. It had been shown previously that normalization of reactivities with respect to the CO_2 surface area, as calculated using the Dubinin–Polanyi approach,[21] is meaningless, both in the case of demineralized[10] and raw[15] chars. It is seen that chars of residence time between 0.3 and 1.5 s have essentially the same, very high reactivity because in all of them CaO is highly dispersed, with crystallites of, say, <5 nm in size (usually cited lower XRD detection limit for supported metal catalysts). On the other hand, both the R-5 min and S-1 h char have a much lower R_{max} because in them CaO is not so highly dispersed. Furthermore, the latter is also less reactive than the former, as expected from their respective crystallite sizes: 28.0 vs. 24.5 nm.

Thus, as shown in *Table 3*, a correlation is established (for the first time, to the knowledge of the authors) between the observed lignite char reactivities and the dispersion (as measured by crystallite size) of the catalytically active CaO on the char surface. The gasification reactivity of lignite chars appears to be dominated by the concentration of the inherent catalyst sites. However, before this reactivity can be expressed as a turnover frequency (per unit catalyst site) it is necessary to determine the effect on reactivity of the concentration of carbon active sites.[10]

CONCLUSIONS

The relatively high gasification reactivity of lignites is due primarily to the catalytic effect of the highly dispersed CaO on the char surface that was identified by XPS and XRD. The decrease in char reactivity with increasing pyrolysis residence time is caused by CaO sintering and, therefore, a decrease in its dispersion. Thus, the char deactivation process is correlated with a measurable physical property of the char. It is felt that this approach gives an important contribution to the fundamental understanding of the gasification behaviour of lignite chars. However, before char reactivity can be expressed as a turnover frequency, it is necessary to determine how pyrolysis conditions affect the structure and activity of the carbonaceous solid itself.

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