

THE PREDICTION/CORRELATION OF CHAR REACTIVITY FROM DISTRIBUTIONS OF DESORPTION ACTIVATION ENERGIES

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INTRODUCTION

Recently, in our laboratory, we have been concerned with the determination of distributions of desorption activation energies of oxygen surface complexes on carbons and chars from temperature programmed desorption (TPD) spectra. In the current communication we report on the application of probability density functions of desorption activation energies to the prediction/correlation of CO₂ gasification reactivities for chars produced from Wyodak coal and phenol-formaldehyde resin, which are desorption rate-controlled under the experimental conditions examined here. The resultant technique represents what we believe to be the first truly *a priori* prediction of CO₂ gasification reactivity as a function of temperature.

EXPERIMENTAL

Chars were prepared from Wyodak coal obtained from the Argonne Premium Coal Sample Bank, and phenol formaldehyde resin *via* pyrolysis in ultrahigh purity helium at 1273K with a soak time of 1 hour. The resin was synthesized in our laboratory according to a previously described procedure [1]. Care was taken to insure that contamination by any potentially catalytic impurities was kept to a minimum. Subsequent analysis by atomic absorption spectrometry revealed only nominal levels of alkali metal impurities.

The TPD apparatus and methods have been described elsewhere [2]. The most salient experimental details are as follows. Char gasification was performed in a TGA apparatus in 0.1 MPa CO₂ at the temperatures noted. Following cooling to room temperature in the TGA apparatus, the samples were transferred to a TPD reactor. Tests involving comparisons of TPD spectra obtained using this procedure with those following *in situ* oxidation in the TPD reactor have shown that transfer of the sample in this manner does not affect the resultant spectra.

The TPD reactor was constructed from a high-purity silica tube, 1-cm inside diameter, within which a close-fitting, circular silica sinter is used to support the sample. Ultrahigh purity helium

carrier gas is passed over the sample in downflow. Heating is accomplished electrically via nichrome wire wrapped around the outside of the silica tube, powered by a high current variable transformer. The heating regimen is controlled by a microcomputer. The resultant TPD reactor has a low thermal capacitance which allows linear heating rates of up to 500K/min.

Detection of desorbed species is accomplished with a quadrupole mass spectrometer (MS) which samples a small portion of the carrier flow. The MS output is fed to a microcomputer which also provides for multiple species detection via mass programming.

Typical sample sizes for the TPD measurements were ~10 mg. This size resulted in less than a monolayer coverage on the silica frit that was used as the sample holder in the TPD reactor. This, when combined with high helium carrier gas sweep rates, insured the absence of secondary interactions between the bulk gas species and the char samples.

Repeated experiments with char samples obtained from the same batch indicate that the reproducibility of gas desorption rates is approximately $\pm 10\%$. This error is attributable to a combination of effects arising primarily from sample inhomogeneity, sample size and MS calibration. For this reason, the spectra reported are representative, rather than averages.

THE APPROACH

The specific gasification reactivity, W , is given by:

$$W = -(1/C) dC/dt = k_d C_t \theta, \quad [1]$$

where C is the amount of carbon, k_d is the desorption rate constant of oxygen surface complexes, C_t represents the total moles of active sites per mole of carbon, and θ is the fraction of the active carbon sites that are occupied by oxygen complex. For conditions where the surface is saturated with oxygen complex, $\theta = 1$ and Eq. [1] indicates that the specific gasification rate becomes desorption rate-controlled.

Eq. [1] applies explicitly to a homogeneous surface; i.e., one discrete surface complex with a single desorption activation energy. Actual char surfaces, however, are known to be distinctly heterogeneous, with a distribution of desorption energies. In a companion paper in this symposium [3], we present a method, based on the original work of Redhead [4], by which the the probability density function of desorption activation energies of oxygen surface complexes can be obtained by analysis of TPD spectra following gasification. The resultant transformation is given by:

$$d[CO]/dt = [C-O]_0 S(E^*) dE^*/dt, \quad [2]$$

where $d[\text{CO}]/dt$ is the desorption rate of oxygen surface complexes as CO, $[\text{C-O}]_0$ is the total amount of oxygen surface complex initially on the char surface, $S(E^*)$ is the probability density function of desorption activation energies, and dE^*/dt is the time derivative of the desorption activation energy during the TPD heating regimen. Since a TPD experiment yields the instantaneous $d[\text{CO}]/dt$ directly, then knowledge of E^* and dE^*/dt defines the initial energetic distribution of surface complex, $[\text{C-O}]_0 S(E^*)$. The expression for E^* and dE^*/dt are given by [3]:

$$E^*/RT = [\ln(v_0 T/\beta) - 3.64], \quad [3]$$

$$dE^*/dt = R\beta [E^*/RT] = R\beta [\ln(v_0 T/\beta) - 3.64], \quad [4]$$

where v_0 is the pre-exponential frequency factor for the desorption rate constant (assumed to be constant with energy and temperature), T is the temperature during desorption, and β is the local heating rate (constant for linear TPD).

The resultant energetic distribution can then be applied in a desorption rate-controlled reactivity expression similar to Eq. [1], with the exception that k_d must be energy-averaged over all surface complexes. In this case, the corresponding expression for W becomes:

$$W = \int_0^\infty v_0 \exp(-E^*/RT) [\text{C-O}]_0 S(E^*) dE^*. \quad [5]$$

RESULTS AND DISCUSSION

TPD spectra of oxygen complexes formed during burn-off of Wyodak and resin char samples at 850°C in 0.1 MPa CO_2 were compared after rapid quenching in helium, and after slow cooling in an atmosphere of CO_2 . These experiments were performed in order to ascertain whether or not the surface was saturated with oxygen surface complex (i.e., $\theta=1$) under these gasification conditions. It was reasoned that if θ is indeed a function of temperature, by cooling in CO_2 the resultant surface coverage would also change and differ from that obtained upon rapid quenching in helium. However, all the resultant spectra were virtually identical. This result implies that CO_2 gasification for these chars under these conditions is indeed desorption rate-controlled. This has also been concluded by other workers under similar conditions (e.g., see [5,6]).

Wyodak Coal Char. TPD spectra for a Wyodak subbituminous coal char sample are presented in Figure 1. In this figure, the rates of evolution of CO and CO_2 upon heating a Wyodak sample that has been gasified to 20% burn-off in CO_2 are presented as a function of temperature. As can be seen, the evolved gas is mostly CO, and its evolution is essentially continuous above a threshold temperature. The temperatures attained are quite high, indicating that the oxygen surface complexes from which the gases derive are quite thermally stable. The CO_2 evolved in

this case has been attributed to secondary reaction of desorbed CO with other surface complexes during TPD [2].

The energetic distribution, $[C-O]_O S(E^*)$, was obtained directly from these data using Eq. [2]. The result is presented in Figure 2. The prominent "bulge" on the leading edge of the distribution is also evident in the TPD spectra *ca.* 1000K. This feature has been attributed to catalytic mineral matter in the Wyodak char (most probably calcium oxide) in some of our work using demineralized samples. As is shown below, this feature accounts for practically all the reactivity of the char over the temperature range examined.

Since all the complex was not recovered in this experiment, due to the very high temperatures required, the entire distribution was also not determined. However, this could have been accomplished in principle by holding the sample at a final elevated temperature, T_f , until all the complex had desorbed. In any event, in order to predict the reactivity in the current temperature range of interest, knowledge of the entire distribution is not necessary, as explained below.

Predicted reactivities for the Wyodak coal char were determined from the preceding experimentally determined energetic distribution using Eq. [5]. The resultant parity plot of predicted versus measured reactivities (taken at 5% burn-off in other experiments in a TGA microbalance) is presented in Figure 3. As shown, the agreement between predicted and measured values is almost perfect for this char. It is noted that over the temperature range explored (*i.e.*, 650-800°C), the gasification reactivity increased by three orders of magnitude, and Eq. [5] predicts the exact same behavior.

The reason for the large change in reactivity is clearly evident in Figure 4 which presents the differential reactivity over the distribution (*i.e.*, the kernel of the integral in Eq. [5], along with the energetic distribution from Figure 2. As shown, as the temperature increases, an increasing number of surface complexes become involved in a highly nonlinear manner *via* the Arrhenius-dependent exponential term. It is also quite evident that gasification reactivity is controlled by only a very small fraction of the oxygen surface complexes located in the vicinity of the 1000K desorption feature; most of the complexes once formed are stable under these gasification conditions. Thus, this formulation shows in a very simple and graphic manner precisely why CO₂ gasification reactivity is so low at the lower temperatures and why it increases so precipitously with temperature.

Phenol-Formaldehyde Resin Char. In view of the suspected control of reactivity by mineral matter in the Wyodak coal char, we undertook some experiments with a "model compound" char produced from phenol-formaldehyde resin. A CO TPD from this char gasified to 11.7% in 0.1 MPa CO₂ at 1173K is presented in Figure 5. For this particular char, the amount of secondary CO₂ was negligible. As shown, the absolute amount of surface oxygen complex on this char is significantly less than for the Wyodak coal char gasified at even lower temperatures. In addition,

the CO spectrum is shifted significantly to higher temperatures than for the Wyodak char, and the low temperature "bulge," which controls the CO₂ reactivity for the Wyodak coal char, is noticeably absent.

The resultant energetic distribution of oxygen surface complexes, determined from Eq. [2], is shifted to higher energies than the Wyodak coal char. This fact should be directly reflected in significantly reduced predicted CO₂ gasification reactivity; and, indeed this is the case, as shown in the parity plot of predicted versus measured reactivities (taken at 5% burn-off in other experiments in a microbalance) presented in Figure 6. As shown, the agreement between predicted and measured values is quite good (to within a factor of two), although not as good as for the Wyodak reactivity predictions presented in Figure 3. It is noted that the CO₂ reactivity of the resin char is three orders of magnitude less than that of the Wyodak coal char at 1073K, and the current formulation predicts this considerable difference quite well.

It is also important to note that the oxygen reactivities measured for these same two chars at 623K in 0.1 MPa of oxygen are almost exactly the same on a total active surface area (ASA) basis, as measured by oxygen chemisorption. Therefore, it seems apparent that oxygen reactivity is not a good indicator of CO₂ reactivity, at least for these two chars. Therefore, it appears that correlations of char CO₂ reactivities according to ASA, as determined by low temperature oxygen chemisorption, can fail quite dramatically for certain chars.

CONCLUSIONS

We believe that this work represents the first truly *a priori* prediction of the CO₂ gasification reactivity of chars. With this method the reactivity of a char as a function of temperature can be predicted from a single TPD experiment following mild gasification at a single temperature. Currently, this prediction can be made for the case where gasification reactivity is controlled by the thermal desorption of oxygen surface complexes formed during gasification; however, the approach may be extended to arbitrary conditions as well. The implications of this work potentially affect all aspects of coal char behavior. It represents a foundation for the development of techniques for coal char characterization and reactivity prediction/correlation based upon knowledge of the energetic heterogeneity of the coal char surface as described by the appropriate probability density function.

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REFERENCES

1. Suuberg, E.M.; Wojtowicz, M.; Calo, J.M. *Carbon* 1989, 27, 431.
2. Hall, P.J.; J.M. Calo *Energy & Fuels* 1989, 3, 370.

3. Hall, P.J.; Calo, J.M. *ACS Div. Fuel Chem. Prepr.* **1990**, "Energetic distributions of oxygen surface complexes on porous carbons and chars," this symposium.
4. Redhead, P.A. *Vacuum* **1962**, *12*, 203.
5. Mentser, M., and S. Ergun, *A Study of the Carbon Dioxide-Carbon Reaction by Oxygen Exchange*, **1973**, U.S.Bur.Mines Bull. 664.
6. Yang, R.T., in *Chemistry and Physics of Carbon*, **1984**, Volume 19, P.A. Throver, ed., pp. 203-263, Marcel Dekker, NY.

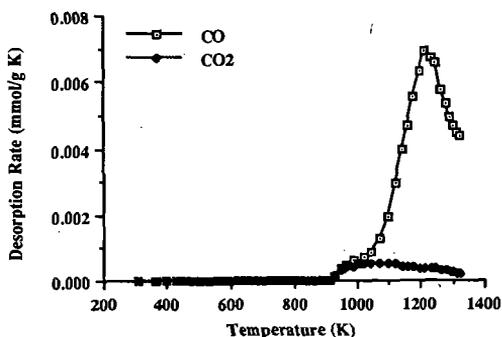


Figure 1. 100K/min CO and CO₂ TPD spectra from Wyodak coal char gasified to 20% burn-off in 0.1MPa CO₂ at 1173K, and cooled in ultrahigh purity helium.

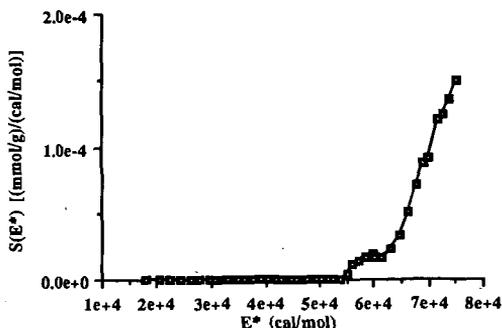


Figure 2. Probability density function of desorption activation energies, $S(E^*)$, for Wyodak coal char burned-off to 20% in 0.1MPa CO₂ at 1173K, and cooled in ultrahigh purity helium.

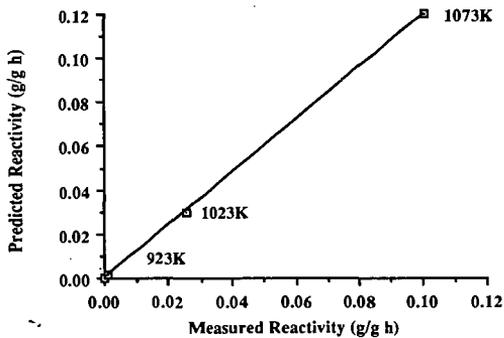


Figure 3. Parity plot of predicted vs. measured reactivities for Wyodak coal char in 0.1MPa CO₂ as a function of temperature.

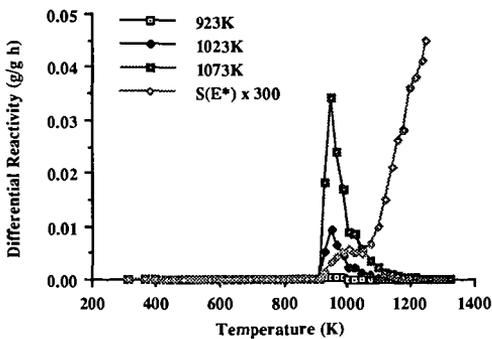


Figure 4. Differential reactivities as a function of temperature, and S(E*) for Wyodak coal char in 0.1MPa CO₂.

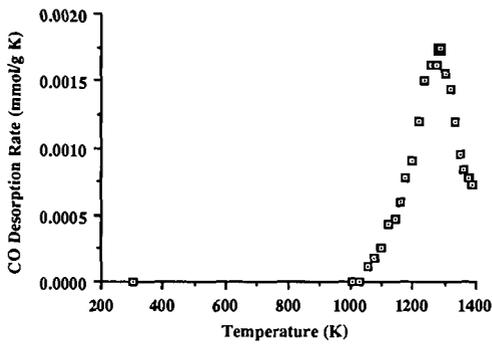


Figure 5. 100K/min CO TPD spectrum for resin char gasified to 11.7% burn-off in 0.1MPa CO₂ at 1173K, and cooled in ultrahigh purity helium.

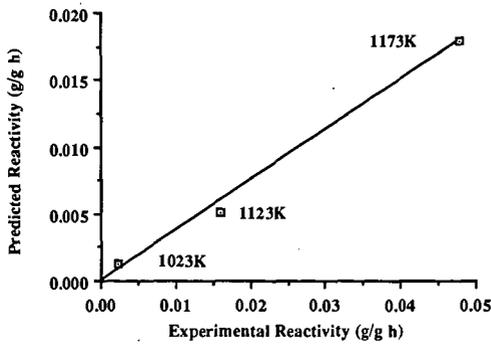


Figure 6. Parity plot of predicted vs. measured reactivities of resin char in 0.1MPa CO₂ as a function of temperature.