

## THE EFFECT OF CHAR "AGE" ON GASIFICATION REACTIVITY

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**Keywords:** Reactivity; char "age"; thermal desorption methods.

### INTRODUCTION

It is well known that, *ceteris paribus*, the overall gasification rate decreases with increasing pyrolysis severity [e.g., 1-7]. This effect can be attributed to various sources, including the loss of heteroatoms and annealing processes. All these types of processes affect the active site density of a char which is an important factor in determining its reactivity. In the current communication, we investigate the relationship between populations of oxygen surface complexes, which form on these sites, and char reactivity as a function of char "age."

### EXPERIMENTAL

The char samples used in the current experiments were produced from Wyodak subbituminous coal samples obtained from the Argonne Premium Coal Sample Bank [8], and a phenol-formaldehyde resin synthesized in our laboratory. The latter material was used as a prototype of a non-mineral matter containing char.

Char samples were produced in a tube furnace in flowing ultrahigh purity helium at various ultimate temperatures for two hours. Variation in char "age" was achieved by pyrolyzing samples at temperatures of 900, 950, 1000°C for resin char, and 1000, 1050, and 1100°C for Wyodak char, respectively, for two hours.

All the oxidation and thermal desorption experiments were carried out in the TPD-MS/TGA apparatus. For gasification, the samples were exposed to one atmosphere of carbon dioxide at a selected temperature to a desired burn-off. The thermal desorptions were all carried out at a heating rate of 50K/min to 1200°C in ultrahigh purity helium carrier gas [9].

### RESULTS AND DISCUSSION

*Reactivities.* As expected, the reactivities of the resin and Wyodak coal char samples all decrease monotonically with increasing pyrolysis temperature; i.e., the "younger" chars are more reactive than the "older" chars. Apparent activation energies, determined from Arrhenius plots, are presented in Table I. As shown, these values are well within the range reported by other workers (e.g., [6,7]) for different types of chars and carbons. These results suggest that the apparent activation energies of the "younger" chars are less than for the "older" chars, but only slightly so; certainly not enough to explain the significant differences in observed reactivities.

*TPD Spectra.* CO TPD spectra from CO<sub>2</sub>-gasified Wyodak coal char samples as a function of pyrolysis temperature are presented in Figure 1. As shown, the broad desorption peak is centered at about 950°C. The total amount of oxygen surface complexes decreases with char "age", but not homogeneously over the entire TPD spectrum. That is, the higher temperature surface complexes fall off more rapidly with "age" than the lower temperature complexes. In fact, the low temperature complex population in Figure 1 is practically invariant with char "age."

Figure 2 presents the corresponding data for resin the char samples. The same qualitative behavior is readily apparent, although the desorption is peaked at a higher temperature of about 1010°C. In addition, the total amount of oxygen surface complexes is about a factor of three or so less than for the Wyodak coal char samples. Just as for the Wyodak coal char, the "younger" char samples exhibit a greater amount of CO evolution than the "older" char samples, and the decrease in the population of oxygen surface complexes is not homogeneous over the entire TPD spectrum; the higher temperature population falls off more rapidly than that at lower temperatures. However, somewhat larger differences are apparent in the low temperature region than in the corresponding Wyodak coal char spectra.

*Distributions of Desorption Activation Energies.* The observation that the population of oxygen surface complexes does not decrease evenly over the entire TPD spectrum suggests that the char surface exhibits a distribution of desorption activation energies. Du *et al.* [10] and Calo and Hall [11] developed distributed activation energy models for the desorption of oxygen surface complexes from carbons following O<sub>2</sub> and CO<sub>2</sub> gasification. In the current work, the distribution of desorption activation energies was calculated using the method described by Calo and Hall [11]. The relationship between the instantaneous CO desorption rate and the distribution of desorption activation energies can be expressed as:

$$d[\text{CO}]/dt = [\text{C-O}]_0 S(E^*) dE^*/dt \quad [1]$$

where  $E^*$  is the local desorption activation energy, as approximated by an instantaneous step at energy  $E^*$ ,  $S(E^*)$  is the desorption activation energy probability density function,  $d[\text{CO}]/dt$  is the desorption rate of oxygen surface complexes as CO during TPD, and  $[\text{C-O}]_0$  is the total initial (i.e.

prior to the initiation of desorption) amount of CO-evolving oxygen surface complexes on the surface. Based on the classical work of Redhead [12], the parameters are related by:

$$E^*/RT = \ln [v_0 T/\beta] - 3.64 \quad [2]$$

which holds for for  $10^8 < v_0/\beta < 10^{13}$  ( $K^{-1}$ ), where  $v_0$  is the pre-exponential factor for the desorption rate constant,  $T$  is the temperature, and  $\beta$  is the heating rate. Since a TPD experiment gives the instantaneous desorption rate directly, and  $dE^*/dt$  can be obtained from Eq. [2], the distribution of desorption activation energies,  $[C-O]_0 S(E)^*$ , can be determined from Eq. [1].

The value of the pre-exponential factor,  $v_0$ , was assumed to be constant. A series of TPD runs was performed at various heating rates from 25K/min to 100K/min for the same oxidized char samples. It was determined that a value of  $v_0 = 10^{10} \text{ min}^{-1}$  yielded the best fit in that it produced essentially the same energetic distribution for all the heating rates. This proved to be the best value for both resin and Wyodak char. Consequently, this value was used for the determination of the distributions of desorption activation energies.

Figure 3 presents a comparison of desorption activation energy distributions determined for Wyodak coal char pyrolyzed at various temperatures. As shown, as the pyrolysis temperature decreases, the desorption activation energy distribution of the char also changes. A similar trend was also found for resin char, as shown in Figure 4. In comparison to the Wyodak coal char distributions, the energetic distributions for resin char samples are shifted to higher energies. It is noted that mineral matter (most probably calcium) in the Wyodak coal char plays a significant role in determining the population of the low temperature surface complexes which turn over most rapidly during gasification. The absolute amount of the low temperature oxygen surface complexes is considerably greater for Wyodak coal char than for resin char, which contains no mineral matter. Therefore the mineral matter in the Wyodak coal char preferentially catalyzes the formation of low desorption activation energy surface complexes. This represents the basis of the catalytic effect in this char. This is the principal reason that the reactivity of Wyodak coal char is significantly greater than that for resin char even at lower gasification temperatures.

*Mean Desorption Activation Energies and Active Site Concentrations.* Two important parameters that can be used to characterize reactivity are the apparent mean concentration of active sites and the average desorption activation energy. For conditions where the gasification rate is desorption rate-controlled, the reactivity can be correlated using the distribution of desorption activation energies. This is accomplished by integrating the desorption rate over the entire distribution:

$$r = \int_0^{\infty} v_0 \exp(-E^*/RT) [C-O]_0 S(E)^* dE^* \quad [3]$$

In order to address the issue of the rate-controlling step in the current work, the following types of experiments were performed. Following gasification, samples were rapidly quenched to room temperature in either pure helium or  $CO_2$ . This was done to assess whether or not the surface was saturated with oxygen surface complexes at gasification conditions. It was reasoned that if the gasification reaction was not controlled by the desorption step, unoccupied active sites would exist which by cooling in the reactant would form additional oxygen surface complexes as the temperature decreased. Consequently, the resultant TPD spectra would differ from those obtained following rapid quenching in helium. From such experiments it was found that gasification of both resin and Wyodak coal char in one atmosphere of  $CO_2$  is desorption rate-controlled under the current experimental conditions [13].

Equating the gasification rate expression for a single mean activation energy,  $E_d$ , with that described by a continuous distribution, as in Eq. [3], yields:

$$C_1 \exp(-E_d/RT) = \int_0^{\infty} \exp(-E^*/RT) [C-O]_0 S(E)^* dE^* \quad [4]$$

Figures 5 and 6 present the apparent mean active site concentration,  $C_1$ , calculated from Eq. [4], as a function of pyrolysis temperature for Wyodak coal char and resin char, respectively. These plots show that the mean active site concentration decreases as the pyrolysis temperature of the char samples increases. This result means that a "younger" char effectively has more active sites than an "older" char on a per unit mass basis. A similar conclusion has been reported by other workers (e.g., [3,6,7]). Since gasification occurs at active sites on which oxygen surface complexes are formed, a char with a higher active site concentration at low desorption activation energies will exhibit a greater reaction rate.

The mean desorption activation energies determined from Eq. [4] are presented in Table I. As shown, they are almost constant with "age" for both resin and Wyodak coal chars. These values of mean desorption activation energies are similar to the apparent values determined from the reactivity measurements. They are also quite close to that reported for  $CO_2$  gasification of a PVC char by Hüttinger and Nill [14]. It is clear that there is relatively little effect of char "age" on the mean desorption activation energy. Rather, the reactivity is controlled primarily by the active site

concentration, especially at the lower activation energies in the distribution. In a way, this is similar to the catalytic effect of metals and mineral matter on carbon gasification. That is, the catalytic effect in carbon gasification is predominantly an increase in the number of effective sites rather than the more typical catalytic effect of decreasing the effective activation energy.

#### SUMMARY AND CONCLUSIONS

The objective of this work was to explore the relationship among char "age", CO<sub>2</sub> reactivity, and thermal desorption techniques. The results indicate that the major influence of char "age" for the samples investigated is the concentration of active carbon sites, which is greater for the "younger" chars than for the "older" chars. There is little apparent effect of char "age" on the mean desorption activation energy. Comparisons of the apparent activation energies from reactivity measurements with those obtained from analysis of the desorption activation energy distributions show reasonably good agreement, which suggests that reactivities of both chars in one atmosphere of CO<sub>2</sub> at the temperatures investigated are desorption rate-controlled.

It was determined that both chars exhibit energetically heterogeneous surfaces for all the samples examined. For these chars, the distribution of desorption activation energies can be determined from TPD desorption spectra. Prediction/correlation of reactivities from the desorption activation energy distribution was shown to be feasible for the carbon-CO<sub>2</sub> reaction operating under desorption rate-controlled conditions for both resin and Wyodak coal char over the range of char "ages" investigated.

It is noted that we have found very similar behavior for steam-gasified chars as a function of char "age" [15].

#### ACKNOWLEDGEMENT

This work was supported by Grant Nos. DE-FG22-90PC90307 and DE-FG22-91PC91305 from the UCR Program of the U.S. Department of Energy.

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Table I. Mean activation energies as a function of char "age" for Wyodak coal and resin chars, as determined from reactivities and distributions of desorption activation energies.

Wyodak Coal Char			Resin Char		
Pyrolysis Temperature (°C)	Mean Activation Energy (kJ/mol) (Reactivity)	Mean Activation Energy (kJ/mol) (Desorption)	Pyrolysis Temperature (°C)	Mean Activation Energy (kJ/mol) (Reactivity)	Mean Activation Energy (kJ/mol) (Desorption)
1000	214	211	900	195	234
1050	233	212	950	207	237
1100	243	212	1000	230	238

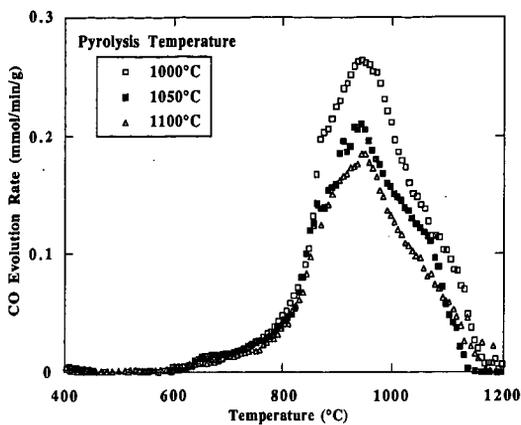


Figure 1. The effect of pyrolysis temperature on CO TPD spectra (50K/min) of Wyodak coal char gasified in 1 atm of  $\text{CO}_2$  at 825°C to 20% burn-off.

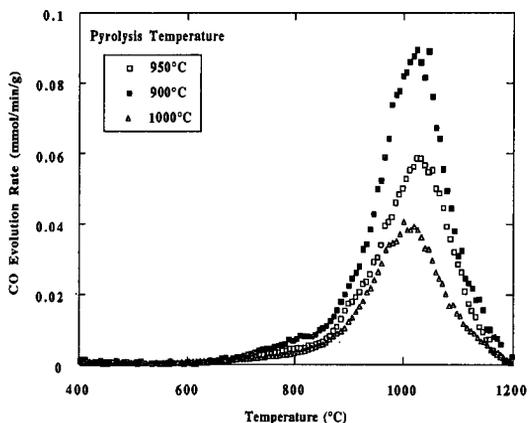


Figure 2. The effect of pyrolysis temperature on CO TPD spectra (50K/min) of resin char gasified in 1 atm of  $\text{CO}_2$  at 890°C to 5% burn-off.

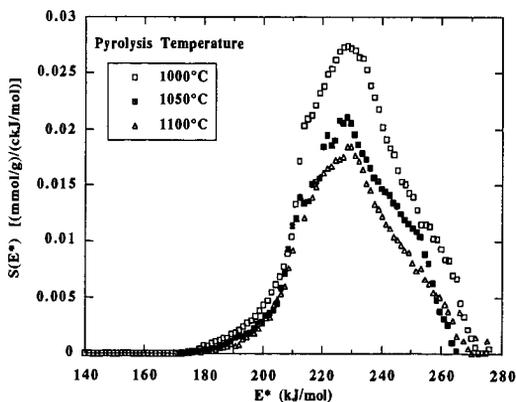


Figure 3. Comparison of desorption activation energy distributions for Wyodak char pyrolyzed at various temperatures and gasified in 1 atm of  $\text{CO}_2$  at 825°C to 20% burn-off.

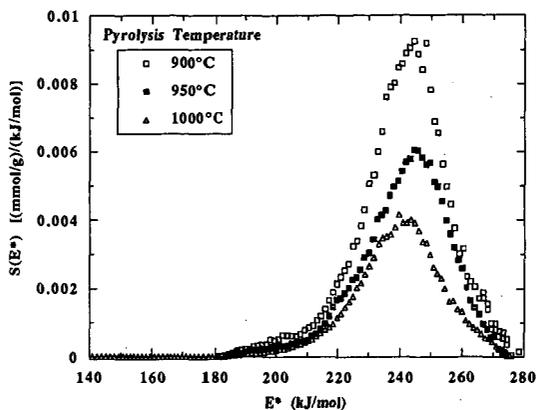


Figure 4. Comparison of desorption activation energy distributions for resin char pyrolyzed at various temperatures and gasified in 1 atm of  $\text{CO}_2$  at 890°C to 5% burn-off.

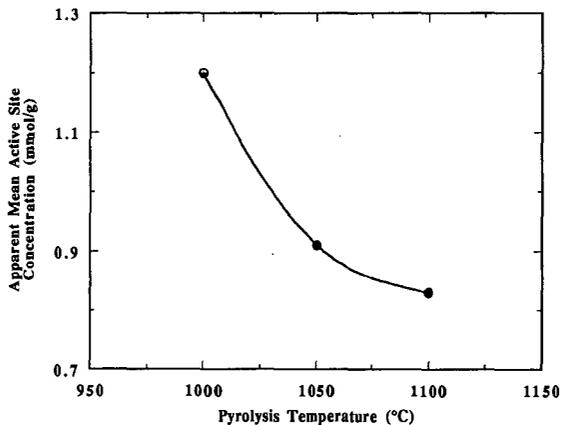


Figure 5. Apparent mean active site concentration as a function of pyrolysis temperature for Wyodak char gasified in 1 atm of  $\text{CO}_2$  at 825°C to 20% burn-off.

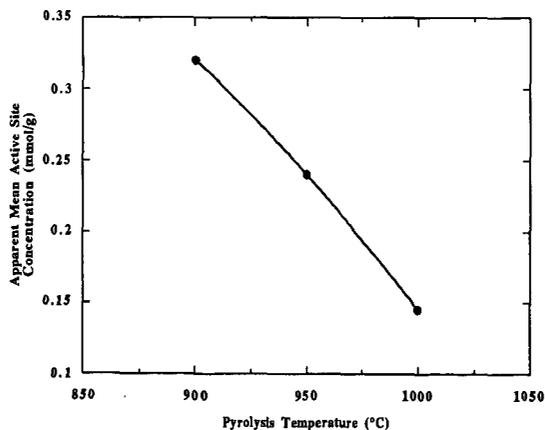


Figure 6. Apparent mean active site concentration as a function of pyrolysis temperature for resin char gasified in 1 atm of  $\text{CO}_2$  at 890°C to 5% burn-off.