CHARACTERIZATION OF POROSTY VIA SECONDARY REACTIONS

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SUMMARY

In this first quarterly technical progress report on this grant, we present the background of the project and the research program for the proposed investigations. Project activity during the reporting period included the following:

• A new digital recording microbalance (Cahn D-200) has been purchased. It is currently being incorporated into a TPD/TGA system from which transient desorption data will be obtained concurrently with transient mass variations. This system will become a principal apparatus for obtaining some of the data required for the development of porosity characterization techniques via thermal desorption methods.

• A new graduate student research assistant is being sought to become the focal point for the project.

Plans for the next reporting period include:

• Testing of the new TPD/TGA system and data acquisition.
1.0. PROJECT BACKGROUND

1.1. Overview.

Specific surface area, as well as its accessibility to gaseous reactants, are of paramount importance for all heterogeneous interactions occurring at coal char surfaces. Accessibility of this surface area is governed by the pore structure morphology of the char; i.e., pore size distribution, tortuosity, intersections, shape, etc. The morphology of porosity in coal chars varies over a considerable range and is determined by a large number of factors including the nature of the porosity of the precursor material prior to carbonization, the carbonization process, and extent and method of any subsequent activation or gasification. A persistent problem in this area has been the reliable, quantitative measurement and characterization of the resultant porosity, especially the micropores. For example, electron microscopy tends to be qualitative; small angle X-ray diffraction suffers from sensitivity to interpretive models, and the inability to distinguish porosity that communicates with the surface from that which does not; and gas adsorption techniques have several well known drawbacks. The latter, however, are perhaps the most reliable in general, but yield pore size distributions indirectly via surface area and pore volume measurements, and can also be laborious and time-consuming. Therefore, there is still a critical need for practical and facile techniques to characterize the porosity of coal chars.

The current project is directed at the development of a new approach to this old problem. During the course of recent work applying temperature programmed desorption (TPD) to the determination of energetic distributions of oxygen complexes on the surfaces of oxidized coal chars, we discovered that secondary interactions occurring within the char structure during TPD produce characteristic features in the resultant spectra that appear to be quite sensitive to char porosity. The relative and absolute extents of these secondary interactions form the basis of a potential characterization technique. The use of such a method to characterize coal char porosity is potentially attractive because the requisite spectra can be obtained in a single TPD experiment -- a very facile experimental procedure. However, the unambiguous and quantitative interpretation of such data in terms of parameters that can be used to characterize coal char porosity still requires
development and an improved understanding of the controlling phenomena. These issues define the primary focus of the current proposal.

1.2. **Secondary Interactions of the Oxides of Carbon Within Porous Coal Chars.**

When an oxidized char or carbon surface is subjected to a program of increasing temperature, the surface oxides desorb as the oxides of carbon, CO and CO$_2$. This process produces TPD spectra which can be interpreted in terms of the energetic state of chemisorbed surface complexes, and interaction phenomena occurring within the char structure during the TPD procedure. Typical TPD spectra from an oxidized Wyodak coal char are presented in Figure 1.

![Figure 1. 300K/min TPD spectra from Pittsburgh #8 coal char gasified to 11.5% burn-off in 0.1MPa of oxygen at 450°C.](image)

These results are noted to be fairly typical of oxygen-gasified chars, and are remarkably similar to those of Otake (1986) and Marchon et al. (1988a), among others, obtained with very different carbons. The CO features consist principally of a peak centered ca. 1000K, and a higher temperature shoulder (sometimes appearing as a separate peak) ca. 1200K. Tremblay et al. (1978) and other workers have explained this type of behavior by postulating two distinct kinds of CO-producing groups, although we have developed an alternate explanation (see below). The low temperature CO$_2$ evolution has been attributed to primary CO$_2$-producing oxygen complexes; e.g., lactones (Marchon et al., 1988a) and/or carboxylic acid anhydrides (Otake, 1986). The source of
the higher temperature CO₂ evolution under the CO peak is discussed below.

During the course of a recently completed study using TPD to probe the energetic distribution of oxygen surface complexes on oxidized coal chars (DE-AC21-MC23284), it was noted that the total integrated amount of CO₂ evolved is a function of the heating rate, and exhibits a broad maximum in the vicinity of about 100K/min (Hall et al., 1988; Hall and Calo, 1989). Oxygen balances for these chars demonstrated that this phenomenon amounts to a variation of the ratio of the evolved oxides of carbon, while the total amount of evolved oxygen remains constant. For example, for two TPD runs at 20K/min and 100K/min, conducted on samples of demineralized Wyodak coal char oxidized in a TGA (12h @ 300°C in 0.1MPa of O₂), the total evolved oxygen balance (i.e., CO + 2CO₂) closed to within 8% (i.e., essentially all the chemisorbed oxygen was recovered as oxides of carbon), whereas the ratio 2CO₂/(CO + 2CO₂) increased from 0.22 to 0.36, respectively. This behavior was attributed to secondary reaction via:

\[ \text{CO(g)} + \text{C(O)} \leftrightarrow \text{C}_f + \text{CO}_2(g) \]  

where: CO(g) represents "free," gaseous CO resulting from the desorption of a surface oxygen complex; C(O) is a surface oxygen complex; and C_f is an unoccupied surface active site (Hall and Calo, 1989). [It is noted that this reaction is the same as the reverse of the first step in the Ergun oxygen exchange mechanism for CO₂ gasification (Ergun, 1956, 1961).] In view of the high carrier gas flowrates that were used in this work, it is quite certain that these reactions do not involve the external bulk gas phase, but rather they must occur within the char pore structure between desorbed oxides of carbon and both occupied and unoccupied active surface sites during the process of out-transport to the bulk phase. The hypothesis that this phenomenon is associated with porosity is supported by other data on low porosity chars which exhibit virtually no variation in CO₂ production with heating rate; (Hall and Calo, 1989); e.g., as for 0% burn-off Pittsburgh #8 coal char with N₂ and CO₂ BETs of 2 m²/g.

Re-adsorption of "desorbed" species, diffusing within the char porosity, represents another type of secondary interaction with carbon surface sites. Recently, Marchon et al. (1988b) showed that CO can chemisorb on polycrystalline graphite surfaces to form complexes that are thermally stable to >1200K. These authors suggested that this high-temperature CO is "formed by
incorporation of the CO in the graphite lattice." The maximum rate of desorption of these species corresponds to the high temperature shoulder for CO in Figure 1. Therefore, this feature need not necessarily be due to stable, carbon-oxygen complexes produced by primary oxidation prior to TPD, but rather the result of re-adsorption of intrapore CO following thermal desorption.

These two secondary interactions were studied in our laboratory via gas "loading" experiments (Hall and Calo, 1989), wherein burned-off Pittsburgh #8 char samples were exposed to 0.1 MPa of either CO or CO$_2$ at 200°C for twelve hours, in order to saturate the char porosity with the respective gas. Comparison of the subsequent TPD spectra from the saturated chars with "normal" spectra from de-gassed, oxidized coal chars revealed that for the "CO-loaded," oxidized coal char the principal peak ca. 1000K (cf. Figure 1) is considerably broadened, and the high temperature shoulder becomes less distinct. This result was interpreted in terms of "additional" CO-producing surface complexes caused by direct CO chemisorption, which appear to desorb in the same temperature region as the shoulder observed in the "normal" CO TPD spectrum. The major difference in the evolution rate of CO$_2$ between the "normal" and "CO-loaded" oxidized chars was a considerable increase in the CO$_2$ peak at lower temperatures. Since the only difference between the treatment of the two samples was the low temperature CO exposure, the increase in CO$_2$ could only be due to secondary reactions between pore-trapped CO (from the loading) and oxygen surface complexes (from previous oxidation). The reaction of pore-trapped CO with itself (i.e., the reverse Boudouard reaction) to produce CO$_2$ was ruled out by performing a "blank" experiment with a "thermally-cleaned" (i.e., no oxygen surface complex) and "CO-loaded" Pittsburgh #8 coal char sample; no additional CO$_2$ was observed in this experiment.

1.3. Deconvolution of TPD Spectra.

Over the course of examining many TPD spectra from oxygen-oxidized chars, it was noted that the leading edge of the total oxygen (i.e., CO + 2CO$_2$) desorption feature ca. 1000K always seems to approximate a Gaussian distribution. For this reason, it was decided to deconvolute the total oxygen production rate into two contributions - one as a Gaussian centered at the maximum rate of production, with the variance determined from the leading edge of the 1000K peak, and the other as a higher temperature residual difference peak. The results of such a deconvolution for
spectra obtained from an oxidized Wyodak coal char are presented in Figure 2. As shown, the Gaussian approximation is quite reasonable for describing the leading edge of the total oxygen distribution, and the residual peak appears to be relatively smaller and non-Gaussian. However, as it stands, such a deconvolution is nonunique, and thus we are faced with the question of whether the high temperature end of the 1000K oxygen peak remains close to Gaussian in the region where it cannot be directly observed. There is some other experimental evidence in support of this hypothesis. Here we present one such example.

![Graph](image)

**Figure 2.** Deconvolution of 100K/min TPD spectra from Wyodak coal char gasified to 15.2% burn-off in 0.1MPa of O₂ at 623K into a Gaussian and a residual.

For the following experiments only the CO data were utilized, although similar results were obtained for the total oxygen spectra as well. A sample of the same gasified Wyodak char used in Figure 2 was partially cleaned by heating to 1100K at 100K/min, and was then quickly cooled (>200K/min) in ultra-high purity helium. This process not only removes complexes stable below 1000K but is also expected to effectively "titrate" the high temperature sites suspected to be involved in CO re-adsorption that give rise to the 1200K peak during TPD. A second sample of the same char was subjected to TPD to 1100K and quick cooling in He to room temperature. Then, a TPD was carried out to 1400K to measure the behavior of the residual complexes. This is the "HT"
CO spectrum presented in Figure 3. The "partially cleaned" sample, with high temperature CO remaining on the surface, was then re-oxidized in the TPD apparatus under non-gasifying conditions in 0.1MPa of oxygen at 473K for 12 hours. This treatment effectively reoxidizes almost all the surface sites created during the original gasification. TPD was then carried out on this char, and the result is designated as PC in Figure 3. The difference between the PC and HT spectra represents the oxygen added during reoxidation. This is designated as PC-HT in Figure 3.

![Graph](image)

Figure 3. 100K/min TPD spectra from partially cleaned Wyodak coal char originally gasified to 15.2% at 623K, and the re-oxidized for 12h at 473K; both in 0.1MPa O₂.

The difference spectrum in Figure 3 should be uncomplicated by CO re-chemisorption, and the resultant distribution should, therefore, be reflective of the original state of the oxygen chemisorbed during reoxidation. As shown, a Gaussian distribution does seem to fit the difference spectrum reasonably well. This agreement supports the hypothesis that the 1000K peak for oxygen production may indeed be Gaussian over its entire range.

### 1.4. Energetic Distribution of Desorption Activation Energies.

In view of such evidence in support of a Gaussian distribution for the 1000K peak, the question naturally arises as to what the physical basis may be for this type of distribution. In
considering this question, it is useful to transform the TPD spectra from temperature to desorption energy space. A procedure that we have developed for this purpose is outlined in Section 3.1-2 below. Eq. [9] indicates that this transformation is practically linear for constant heating rate, $\beta$; i.e., the logarithmic term does not vary appreciably over the TPD temperature range. Thus, for linear TPD, if the distribution of the surface complex desorption in temperature space is Gaussian, then the distribution of desorption activation energies will be close to Gaussian as well.

A Gaussian energetic distribution implies that the surface-bound oxygen exhibits a continuum, random distribution of binding energies. Oxygen functional groups that may be chemically distinct on an "open" surface, may ultimately "merge" into one another in a porous, multi-surface environment. For many typical coal chars, most of the surface area and, consequently, most of the oxygen complexes, are present in micropores. In these small pores of near-atomic dimensions, the effective binding energy of the complexes is strongly influenced by the local environment, the presence of neighboring complexes etc., and thus can be randomly distributed. For example, an oxygen atom could be bound to opposing walls of a micropore (e.g., an ether linkage). The binding energy of such a complex would vary according to the local width of the micropore, and, ultimately, in a very wide micropore, or a mesopore, the complex could be bound to only one wall, thereby becoming a semiquinone or carbonyl group.

This hypothesis suggests that the resultant energetic distribution should be a characteristic property of the char porosity. This latter hypothesis has now been examined in a preliminary fashion. A Gaussian was fit to a 100K/min total oxygen TPD spectrum, "corrected" for 1200K CO, from a sample of oxidized Pittsburgh #8 coal char (10% burn-off @ 723K in 0.1MPa O$_2$). This distribution was then transformed into an energetic distribution (cf. Section 3.1-2). Since the heating rate was linear, the resultant distribution is also quite close to Gaussian as well, as explained above. The value of the pre-exponential frequency factor of the desorption rate constant, $v_0$, was varied to obtain the best fit to spectra obtained at heating rates of 20 and 300K/min. These calculations were, therefore, iterative, and were performed using a spreadsheet program. A value of $v_0 = 10^{10}$ min$^{-1}$ yielded good predictions, although reasonable results were also obtained over a range of $v_0$, so this value may not be unique. The final distribution, obtained in this manner, appears in Figure 4.
1.5. The Relationship Between Secondary Interactions During TPD and Coal Char Porosity.

The conclusion that the resultant effects of secondary interactions are coupled to the char porosity, prompted us to consider the possibility of developing these phenomena into a char porosity characterization tool. To explore this possibility further, we performed a preliminary set of experiments with chars derived from Pittsburgh #8 and Wyodak coal as a function of burn-off, in
order to vary the porosity. These two coals were selected because it was expected that their chars would exhibit different porosity characteristics. Pittsburgh #8 passes through a fluid state during slow carbonization in which most of its original microporosity is lost (Mahajan, 1982). Thus, any subsequent porosity is solely due to the gasification process. Conversely, Wyodak is a subbituminous coal and, consequently, much of the original porosity is preserved or enhanced during carbonization. A number of studies indicate that the initial porosity of this coal char consists of a random network of pores with extensive "ink-bottle"-type restrictions and a significant amount of "closed" porosity (Mahajan, 1982; Larsen and Wernett, 1988). Gasification of the Wyodak coal char, therefore, not only develops new porosity but also tends to widen restrictions and render previously closed pores accessible.

![Figure 5](chart.png)

Figure 5. Standard deviations of Gaussian fits to total oxygen desorption rates for Pittsburgh #8 and Wyodak coal chars.

The leading edges of the total oxygen TPD spectra for these chars gasified to varying extents in 0.1MPa of O₂ were fit to Gaussian distributions, as described above. The standard deviations obtained from these Gaussian fits are plotted in Figure 5 as a function of burn-off. From this figure, it seems that the distribution of total surface oxygen is initially broadest for the Wyodak coal char.
char at low burn-off. The distribution then narrows with burn-off, and thereafter seems to be relatively constant over a broad range of burn-off. The distribution then apparently narrows sharply once again at higher burn-offs. From the limited data, the Pittsburgh #8 coal char seems to behave somewhat similarly, although the very high and low burn-off regions are not as well represented. This behavior is consistent with the char porosity initially "opening up" and then remaining fairly constant in "effective" (in terms of total surface oxygen energetics) mean pore size until the high burn-off regime is attained.

This picture is somewhat reminiscent of constant turn-over number (TON), or site-specific oxygen gasification reactivity, reported by Jenkins and Piotrowski (1987) over a broad range of intermediate burn-offs. This is consistent with the energetic distribution of surface complexes for oxygen gasification remaining constant (i.e., as in Figure 5) over this burn-off range. The absolute reactivity, however, is proportional to the active surface area, which, of course, does vary considerably over this range. Therefore, this picture is only part of the story; it does not indicate how the total amount of surface oxygen varies as a function of burn-off.

In order to explore this aspect, the Wyodak and Pittsburgh #8 data were analyzed in another manner. Gaussian distributions were fit to the leading edges of the CO TPD spectra alone. The total amount of CO represented by the integral under this curve was termed "1000K CO," and the residual (i.e., the difference between the total measured CO, and the amount accounted for by the distribution) as "1200K CO," as discussed above. The contributions to total oxygen desorption from these two sources plus secondary CO2 are summarized in Figures 6 and 7 for the Wyodak and Pittsburgh #8 coal chars, respectively. These figures reveal some interesting behavior. For both coal chars, the largest proportion of oxygen derives from the 1000K CO peak, except for the "0%" burn-off chars (i.e., O2 chemisorption at 250°C), where oxygen from CO2 predominates (57% and 51% for the Wyodak and Pittsburgh #8 coal chars, respectively). For the Wyodak coal char, the relative contributions of the three categories of oxygen seem to be fairly constant over a broad middle range of burn-off, and both the CO2 contribution and that from "1200K CO" increase precipitously at low burn-off. At high burn-off, another change occurs which favors "1200K CO."
Figure 6. Desorbed oxygen distribution for Wyodak coal char as a function of burn-off in O₂.

Figure 7. Desorbed oxygen distribution for Pittsburgh #8 coal char as a function of burn-off in O₂.

The Pittsburgh #8 coal char exhibits slightly different behavior. Although there is also a rapid increase in "1200K CO" and CO₂ at very low burn-off, both the relative and absolute contribution of CO₂ to total desorbed oxygen steadily increase with burn-off, while the 1000K and 1200K CO contributions follow each other quite closely over the burn-off range examined. It is also noted that
the Wyodak coal char accommodates roughly twice as much oxygen as the Pittsburgh #8 coal char for equivalent burn-offs, due to its lower total porosity.

As discussed previously, all the available data suggest that the 1200K oxygen complexes arise primarily from "free" CO re-chemisorbed during the TPD process, and not just from chemically different (i.e., from the 1000K complexes) oxygen complexes formed during steady-state gasification/oxidation. If these complexes did arise from the latter source, their population would tend to increase relative to the "low temperature" complexes with exposure under gasification conditions, rather than decrease, as generally observed, since they would be more stable. However, if CO can be re-chemisorbed during TPD, why should product CO, formed during isothermal, steady-state gasification, not also be re-chemisorbed, with the result that the "high temperature" CO sites would already be occupied prior to TPD, especially during long exposures? This can be explained in terms of CO chemisorption being a highly activated process with a low sticking probability, as concluded by Marchon et al. (1988b). As a consequence, at the relatively low temperatures of oxygen gasification, the rate of re-chemisorption of product CO may be too low to occupy the high energy sites available under gasification conditions. Moreover, any sites that may be accessible under these conditions would almost certainly react preferentially with oxygen, which is present in considerably larger amounts and exhibits much greater reactivity towards the formation of stable complexes. In addition, if CO chemisorption were appreciable under isothermal, steady-state gasification conditions, the amount of CO chemisorbed during gasification should increase steadily with increasing burn-off and/or exposure time. However, this has not been observed. In fact, as shown in Figure 6 for the Wyodak coal char, the 1200K CO shoulder is remarkably constant over a broad range of burn-off, and for both Wyodak and Pittsburgh #8, the 1200K CO shoulder actually decreases at high burn-off.

This latter behavior is believed to directly reflect the development of porosity. As noted above, it is known that much of the porosity of the Wyodak coal is preserved upon slow carbonization, and the resultant char is highly microporous. Such a pore network increases the probability of interaction of desorbed species with pore walls during their out-transport to the bulk gas phase and,
consequently, of secondary interactions. As gasification proceeds, "high residence time" restrictions, such as "ink-bottle"-type pores, tend to be preferentially gasified with a concomitant "opening up" of the porosity and an increase in the mean pore diameter. The development of porosity results in a decrease in the frequency of gas-pore wall collisions during TPD, and thus also a decrease in the probability of re-chemisorption. This behavior would result in a decreased 1200K CO peak, if, as hypothesized, it is predominantly due to CO re-chemisorption.

Available evidence suggests that secondary CO₂ production via reaction [R.1] is associated with the smaller pores (e.g., the micropores). For example, it has already been shown that the secondary CO₂-to-CO ratio is a maximum for zero burn-off Wyodak, which possesses a "Type I" N₂ adsorption isotherm, characteristic of microporous materials. Further evidence derives from other oxidation studies where, for example, it has been reported that, due to the large size of the nitrate ion, nitric acid oxidation does not oxidize the surface within the microporosity, but rather only that accessible in the meso- and macroporosity, as well as the external surface (Otake, 1986). TPD spectra of these nitric acid-oxidized chars exhibit virtually no secondary CO₂ in comparison to air oxidized chars; on the other hand, considerable 1200K CO was evident (Otake, 1986). This suggests that CO re-chemisorption can take place in the larger pores.

Secondary CO₂ production takes place primarily in micropores probably for the same reasons that a normal distribution of bond energies occurs, as discussed above. That is, the low temperature, less stable complexes present in the micropores would also tend to be more reactive towards attack by "free" CO. Consequently, although there is as yet no definitive explanation as to why CO re-chemisorption does not appear to be appreciable in the micropores during TPD, it may be overwhelmed by secondary CO₂ production. In any case, any "free" CO in micropores may preferentially be oxidized to CO₂, and thus may not survive to desorb in the higher temperature peak ca. 1200K. In summary then, these two secondary interactions appear to be complementary, in that they appear to be sensitive to different aspects of the char porosity.

The data presented here have shown that it is possible to have high secondary CO₂ production relative to CO re-chemisorption (significant gasification-developed microporosity, as in Pittsburgh # 8 char in the mid-burn-off range); low secondary CO₂ production with significant CO re-
chemisorption (low microporosity, as in low burn-off Pittsburgh #8 char); high secondary CO\textsubscript{2} formation and CO re-chemisorption (high micro- and mesoporosity, as in low to intermediate burn-off Wyodak char); and reduced secondary CO\textsubscript{2} production relative to CO re-chemisorption (reduced microporosity, as in high burn-off Wyodak coal char). This behavior forms a basis for the development of a quantitative technique to interpret the absolute and relative degrees of these secondary interactions in terms of coal char porosity morphology.

2.0. PROJECT APPROACH

2.1. Temperature Programmed Desorption.

2.1.1. Background. One of the principal experimental techniques to be used in the current work is continuous TPD. Basically the TPD procedure involves: preadsorption of a gas or gas mixture onto a solid surface; removal of any physically adsorbed gases; thermal desorption via a programmed temperature increase (usually a linear ramp); and detection of the rate of desorption by a suitable analytical technique. The result of this procedure is known as a desorption spectrum or chromatogram which usually consists of one or more peaks. The shapes of the peaks and their maximum temperatures are related in a fundamental manner to the desorption processes, and, therefore, provide basic information regarding the energetics of the adsorbed species.

The theory and application of TPD to energetically homogeneous surfaces is well understood. The corresponding situation for heterogeneous surfaces is more complex, and, therefore, has not been as well developed. However, recently we have devised a technique to transform TPD spectra into probability density functions of desorption activation energies. This approach has been successfully applied to carbon-oxygen surface complexes produced by CO\textsubscript{2} and O\textsubscript{2} to predict/correlate reactivity and to characterize coal char behavior (Calo and Hall, 1990). A summary of this technique follows.

2.1.2. Energetics of Surface Complexes on Heterogeneous Surfaces. For a heterogeneous surface consisting of a population of noninteracting surface species, each obeying a first order desorption rate law characterized by a single desorption activation energy, E\textsubscript{i}, the total desorption rate, d\Omega/dt, due to an increasing temperature heating regimen is:
The rate of thermal desorption as CO of complexes with desorption activation energies between E and E+dE is given by:

\[ \frac{\partial [C-O]_{E,t}}{dE} = -k_d(E) [C-O]_{E,t} \]

where the first order desorption rate constant, \( k_d(E) \), is given by:

\[ k_d(E) = v_o \exp(-E/RT) \]

Integrating and combining with the mass balance for surface complexes, yields:

\[ [CO] = [C-O]_o - \int_0^\infty [C-O]_o S(E) \exp\left\{-\int_0^E k_d(E) \, dE\right\} \, dE \]

in which the initial desorption activation energy probability density function, \( S(E) = [C-O]_0^O_{E,t} / [C-O]_o \), and \( [C-O]_o \) is the total initial (i.e., prior to the initiation of desorption) amount of oxygen surface complex on the surface. In this expression, the integral over the rate constant increases over a very narrow energy range from zero to unity. For this reason, it can be approximated (cf. Suuberg, 1986, and Du et al., 1990) as a step function occurring at a critical activation energy, \( E^* \).
In this manner, Eq. [5] becomes:

\[ [\text{CO}] = [\text{C-O}]_0 - \int_{E^*}^{\infty} [\text{C-O}]_0 S(E) \, dE = [\text{C-O}]_0 \left[ 1 - \int_{E^*}^{\infty} S(E) \, dE \right]. \]  

[6]

Taking the derivative of this latter expression with respect to time:

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

[7]

Since a TPD experiment yields the instantaneous \( \frac{d[\text{CO}]}{dt} \) directly, then knowledge of \( E^* \) and \( \frac{dE^*}{dt} \) defines the initial energetic distribution of surface complex, \([\text{C-O}]_0 S(E^*)\), experimentally.

For the reasons cited above, Eq. [3] can also be used to provide \( E^* \), which can be differentiated to yield:

\[ \frac{dE^*}{dt} = R \beta \left[ \ln \left( \frac{\nu_0 T}{\beta} \right) - 2 \right]. \]  

[8]

Combining Eqns. [7] and [8], then yields the energetic distribution of surface complexes as:

\[ [\text{C-O}]_0 S(E^*) = \frac{d[\text{CO}]/dt}{R \beta \left[ \ln \left( \frac{\nu_0 T}{\beta} \right) - 2 \right]}. \]  

[9]

From this expression, the energetic distribution of surface complexes can be determined experimentally from TPD spectra. We have shown that the resultant energetic distribution can be put to various uses (Calo and Hall, 1990). In the current proposed work it will be used to transform desorption features via the deconvolution process described above in Section 2.2.

3.1.3. The TPD Apparatus. As a result of work on a recently completed DOE-METC contract, we have developed an apparatus specifically for obtaining TPD spectra from coal chars. The reactor itself 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. The carrier gas for most of the work performed was ultra-high purity helium, passed over the sample in downflow. Heating is accomplished electrically via nichrome wirewrapped 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. In order to minimize the delay between species desorption and detection, and prevent potential re-interaction of external bulk gas phase species with the char sample, a high helium carrier gas flowrate was used, as well as a
minimal length of small bore sampling tubing. The resultant high velocity in the sampling tubing minimizes dispersion of the sampled gas. In addition, special attention was paid to the elimination of stagnant volume in the vicinity of the sampling point such that there was no noticeable integration of the desorption spectrum.

It is proposed to use the same TPD reactor system for the current work. The only anticipated change will involve the material of construction of the inner sample tube. As a result of our work, we have found that in some cases stable surface complexes can be retained on char surfaces to temperatures in excess of 1373K. Therefore, it is proposed to replace the inner quartz tube with a ceramic or metal (such as tungsten) tube that will extend the high temperature capability of the TPD reactor. Otherwise the experimental apparatus will remain the same.

The experimental procedure for a typical TPD run is generally as follows. Char samples are first "thermally cleaned" in a TGA at 1273K in ultra-high purity helium and the sample cooled in helium. Oxidation or gasification of the char sample can be carried out either in situ in the TPD reactor, or ex situ in a TGA apparatus. In the former case, no sample transfer is necessary. In the latter case, part of the oxidized sample (typically about 10 mg) is then transferred to the TPD apparatus [In our work we have observed that oxygen surface coverages and energetic distributions are not affected by transfer of oxidized samples after cooling in helium.], the reaction chamber flushed with ultra-high purity helium and the TPD performed. The resultant MS peak heights are normalized for sample size and species sensitivity, as determined by calibration with a known partial pressure of the appropriate gases. This allows determination of evolution rates in terms of absolute amounts of desorption products. Repeated experiments with char samples obtained from the same batch indicate that gas desorption rates are reproducible to within approximately ±10%. This error is attributable to a combination of effects arising primarily from sample inhomogeneity, sample size and mass spectrometer calibration. For this reason, the spectra reported are usually representative, rather than averages over multiple experiments.

2.2. Coal Char Preparation.

As a result of previous work, we now have considerable experience and data on chars produced from coals obtained from the Argonne Premium Coal Sample Bank; specifically, Wyodak,
Pittsburgh #8, and Stockton-Lewiston coals. Therefore, we will initially use these same coals to produce the char samples for the proposed work. The resultant coal chars will be used in their natural (dried) state and also in demineralized form for comparison, since certain spectral features have been attributed to mineral matter content (Kyotani, et al., 1988; Calo and Hall, 1990). It is noted that the demineralization process not only removes mineral matter but also significantly alters the macromolecular structure of the precursor coal such that the resultant char exhibits a larger surface area than the non-demineralized char. Thus, an increase in total oxygen surface complex coverage for demineralized chars may be accounted for by the increase in porosity due to demineralization. This effect has been noted previously in the literature (Tomita, 1977; Mahajan, 1978), and is also reflected in our TPD spectra (Calo and Hall, 1990). We will also continue to use our own synthesized phenol-formaldehyde resin char (Suuberg, Wojtowicz, and Calo, 1989) as a "benchmark" char, low in mineral matter impurities. We have also developed apparatus appropriate for pyrolyzing and reacting chars under a wide variety of conditions. These include: two tube furnaces for slower heating regimens; heated wire grid reactors; two TG systems; the TPD reactor discussed above; and a fluidized/entrained bed furnace. These systems cover a heating rate range of \( \sim 1-10^4 \) K/min, with maximum temperatures as high as 1100°C.

In addition to pyrolysis equipment, we have significant coal/char characterization capability as well (see Appendix C, Existing Facilities).

2.3. Coal Char Porosity Characterization.

2.3.1. Gas Adsorption Techniques. In order to interpret the degree of secondary interactions in terms of coal char pore structure, another independent technique is needed to characterize the porosity in some self-consistent manner. Of the available techniques listed in the Introduction, gas adsorption techniques are generally the most reliable.

Adsorption isotherms can be obtained in our laboratory using a commercial BET apparatus (Quantachrome Quantasorb) and/or a quartz spring McBain microbalance. Microporous materials (typically <20Å diameter pores) are usually characterized by Type I isotherms. Obtaining surface area and pore size distributions for such materials from gas adsorption data remains admittedly
controversial, but reasonable estimates can still be made. Chars and carbons with developed mesoporosity (20Å-500Å) usually exhibit a Type IV isotherm. Pore size distributions for the larger pores are routinely obtained from Type IV isotherms in terms of the Kelvin equation. Pore size distribution calculations invariably involve an assumption of pore geometry (usually cylindrical), and detailed procedures are reviewed in standard textbooks on surface area analysis (e.g., see Gregg and Sing, 1982; Lowell, 1979). Exclusion techniques, such as nonane pre-adsorption (Gregg and Sing, 1982, p. 239), can also be used to estimate micropore volume contributions.

N₂ and CO₂ are the two most common adsorbates used in char or coal surface area determination. N₂ is believed to adsorb non-specifically on most solid surfaces (Barrer, 1966), which makes it a particularly attractive adsorbate. CO₂, on the other hand, has a quadrupole moment, which makes strong interactions with oxygen-containing functional groups in chars much more likely (Deitz et al., 1964; Anderson et al., 1965). Thus, there is still some uncertainty concerning the role of these interactions in surface area measurements (Marsh, 1965; Ramsey, 1965; Walker and Kini, 1965), and thus CO₂ should be used with some caution.

Since the concept of mono- or multilayer surface coverage is of questionable validity in micropores, a mechanism of pore filling with liquid phase adsorbate appears to be a more adequate description of adsorption in micropores. Dubinin and Radushkevich (1947) developed an expression for the estimation of the micropore volume from the low and medium pressure regions of the adsorption isotherm. Although the validity of surface areas for microporous adsorbents remains an open issue (Gregg and Sing, 1982), these values are reported in the literature.

We have used these and related techniques in previous studies. In one study involving phenolic resin chars (Wojtowicz, 1988), adsorption isotherms, pore size distributions, and surface areas of these chars were obtained as a function of at burn-off, from both N₂ and CO₂ isotherms.

2.3.2. Morphology. Given that the preceding techniques can provide a measure of surface area and pore volume, then the one remaining part of the characterization process is a measure of the morphology of the pore system. Ideally, this should be reducible to a single parameter, or set of parameters. The most straightforward way to accomplish this is by interpretation of reactivity and/or transport data in terms of an appropriate model; e.g., random pore models (Bhatia and Perlmutter (1980); Gavalas, 1980; Ballal and Zygourakis, 1987), and pore tree models (Simons and Finson...
1979; Simons, 1979). For example, Bhatia and Perlmutter (1980) have shown that for coal chars with low mineral matter content and negligible closed pore volume, a characteristic structural parameter can be obtained for the char by analysis of surface area data as a function of gasification conversion. Ballal and Zygourakis (1987) have extended these types of models to accommodate additional complexities of the pore structure. This type of an approach will be tested for the coal chars to be used in the proposed work. The requisite gasification data can be easily obtained in our TGA apparatus, and the effective transport parameters can be measured using our gradientless reactor approach. (cf. Section 2.4).

Another potential means of characterizing the char porosity morphology is by direct correlation of an effective diffusion or residence time within the char porosity with the extent of secondary reaction. This requires the application of a numerical model of TPD that we have developed, and is explained further in Section 2.5.

![Figure 8. Effective diffusion time constants for CO₂ in Wyodak coal char burned-off to 15.2% in air at 350°C, measured using the gradientless reactor technique.](image)

**2.4. Measurement of Characteristic Diffusion Times.**

As a result of work on another project, we have developed an apparatus and techniques to measure characteristic transport times, $t_d$, of gaseous species in coal chars and other microporous materials (Calo, Perkins, and Lilly, 1989). This method is an outgrowth of and related to the
transient kinetics approach of measuring kinetic rate parameters for char-gas reactions that was developed in our laboratory (Sy and Calo, 1983). It can be shown that the initial transient behavior of a species introduced as a step-function into a "gradientless" reactor in which char is present, is controlled by the transport resistance offered by the char micropores. These data are analyzed for micropore diffusion time constants using a difference technique that we have developed (Calo, Perkins, and Lilly, 1989). A sample set of measurements of diffusion times of CO₂ in Wyodak coal char as a function of temperature obtained using this approach is presented in Figure 8.

2.5. A Numerical Model of TPD of Surface Complexes From CoalChars.

During the course of our previous work on the TPD of oxygen surface complexes, we developed a numerical model that was used to simulate the desorption behavior of oxygen groups from an energetically heterogeneous carbon surface (Calo and Hall, 1989). This model was based on the assumption of two distinct types of complexes: (1) intrinsic CO₂- liberated complexes (e.g., lactones, carboxylic acids, carboxylic anhydrides); and (2) intrinsic CO- liberating complexes (e.g., semi-quinones and carbonyls). It was further assumed that the population of active sites at which these complexes are formed can be distributed energetically. Although the model was run for the specific cases of uniform and Gaussian distributions of desorption energies, actually any arbitrary distribution of surface complexes can be used. Secondary reaction, according to [R.1], were also included. In addition, the model allows for transport resistance. We focused on a microporous char such that the primary resistance to transport was in microporous regions (i.e., the larger pores presented no transport resistance to the evolved gases), and that the transport was activated.

Mass balances, consistent with the preceding assumptions, were formulated for the species involved. For this case there were four of these -- two surface complexes and the two oxides of carbon, CO and CO₂. The resultant set of PDEs and boundary conditions comprising the model was solved using the code PDECOL (Madsen and Sincovec, 1979)

2.5-1. Sample Results. Some sample model results are presented in Figure 9. As can be seen, save for the high temperature shoulder on the CO peak (an effect which was not included in the model), these results are quite similar to the experimental spectra presented in Figures 1 and 2. The primary effect of surface heterogeneity is to broaden the desorption features over that for a single
desorption energy (i.e., a homogeneous surface), and to reduce the sensitivity to heating rate somewhat (not shown in Figure 9).

![Figure 9](image)

Figure 9. Model TPD spectra, including energetic heterogeneity and secondary reaction via [R.1], for a "base case" parameter set, as a function of diffusion times, \( t_d = 2, 20, \) and 200s.

One of the most interesting features of Figure 9, however, is the appearance of a second CO\(_2\) "reflection" peak under the major CO desorption peak, due to secondary reaction via the forward step of [R.1]. This "reflection" peak decays with significantly greater "tailing" than the CO peak. As can be seen, increasing the diffusion time over the range examined does not appreciably increase "tailing" of the "primary" CO\(_2\) and CO peaks. However, the degree of secondary reaction is quite sensitive to \( t_d \). The higher the diffusion time, the greater the conversion of CO to CO\(_2\) via [R.1], as manifested by a decreasing "primary" CO peak, and an increasing "secondary" CO\(_2\) peak. In fact, by \( t_d = 200s \), the "secondary" CO\(_2\) peak is greater than the "primary" CO peak in this calculation. In addition, it is interesting to note that the "secondary" CO\(_2\) peak progressively shifts to lower temperature, while the primary CO peak shifts to higher temperature with increasing degree of
secondary reaction. In fact, for $t_d = 200s$, the "secondary" CO$_2$ peak crosses the "primary" CO peak. This type of behavior has also been observed experimentally in our coal char TPDs. The enhancement of secondary reaction with increasing $t_d$ is due, of course, to the fact that increased intrapore residence time favors the conversion of free CO to CO$_2$ via [R.1].

2.5-2. Application of the Model to Data Interpretation. In its current form, the model can be used to obtain a quantitative measure of the degree of secondary CO$_2$ formation as a function of effective intrapore residence time, $t_d$. [CO re-chemisorption has not yet been included since the kinetic parameters are not known.] This latter parameter is related to the char porosity morphology. The absolute amounts of primary CO and secondary CO$_2$, can be obtained in TPD experiments. TPD and the absolute amount of secondary CO$_2$. [CO re-chemisorption has not yet been included since the kinetic parameters are not known.] In order to obtain a measure of secondary CO$_2$ formation, the following must be specified:

- The distribution of desorption activation energies (i.e., the desorption kinetics). This can be readily obtained by the deconvolution procedure described above in Section 2.1-2.

- Kinetics of reaction [R.1]. The equilibrium constant for [R.1] has been measured and is relatively well known (Mentser and Ergun, 1973; Strange and Walker, 1976). Kinetic parameters for this reaction [R.1] can also be estimated from these sources. This is in fact how the calculations presented in Figures 9 were done.

- The effective diffusion time constant, $t_d$. As shown above, the CO$_2$ production is sensitive to this parameter. The model can be used to obtain this parameter by matching the amount of secondary CO$_2$ to TPD data. Independent measurements of this parameter will be conducted as indicated in Section 3.4. The variation of diffusion times with temperature must be determined in order to be used in the model of the nonisothermal TPD regimen.
3.0. CONCISE STATEMENT OF THE PROPOSED WORK

The proposed work is organized according to the following tasks:

I. Char Preparation and Characterization.

I.1. Coal chars will be prepared via standard pyrolysis procedures.

I.2. The char samples will be characterized using the following techniques:

I.2-1. Surface areas and pore volume measurements using gas adsorption techniques.

I.2-2. Demineralized chars will be prepared using methods similar to those described by Morgan and Jenkins (1981). Atomic absorption will be used to monitor this process via alkali metal content.

I.2-3. Characteristic diffusion times, $t_d$, will be determined as a function of temperature using a gradientless reactor technique that has been developed in our laboratory.

I.2-4. Char porosity morphology will be characterized by analyzing TGA reaction rate data and/or diffusion time transport data in terms of pore models. A simple random pore model will be tested first for this application. Other models might be employed as needed.

II. TPD Experiments.

II.1. Oxygen Oxidation.

II.1-1. The chars, prepared and characterized as stated above, will be subjected to low temperature oxidation in oxygen to progressive burn-offs in a TGA apparatus.

II.1-2. The oxidized chars will then be subjected to linear TPD. The effect of heating rate on the extent secondary interactions will be explored. From previous work it appears that the maximum extent of secondary CO$_2$ formation occurs ca. 100K/min.

II.1-3. TPD spectra will be deconvoluted using procedures similar to those described in Section 2.2. Desorption rate data will be transformed to corresponding energetic distributions for analysis using procedures outlined in Section 3.1-2.

II.1-4. The various contributions to the total oxygen desorption will be correlated to surface area, pore volume, and morphology determinations (cf. Section 2.3) in order to
establish a quantitative relationship between these features and the nature of the porosity.

II.1-5. The extent of secondary interactions will be investigated from the viewpoint of the characteristic diffusion times determined above (Task 1.2-3; cf. Section 2.4), analyzed according to the TPD model (Section 2.5) in order to aid in the establishment of a quantitative relationship between these features and the nature of the porosity.

II.2. Other Oxidants.

II.2-1. NO has been observed to behave in a different fashion than O₂ in certain chars. Low temperature oxidation of Pittsburgh #8 coal char in NO indicated relatively little porosity development in comparison to comparable burn-offs in O₂ (Hall et al., 1989). Furthermore, high temperature (1200K) CO was much more prevalent than 1000K CO (Hall et al., 1989). If the NO gasification is restricted to "external" surface (i.e., the larger pores), as it appears to be for this char which exhibits little initial microporosity, then it should also be devoid of secondary CO₂, which also appears to be true. NO oxidation studies would then be ideal for studying the relationship between porosity and CO re-chemisorption in the larger pores. For this reason, oxidation studies in NO paralleling those in O₂ will be conducted.

II.2-2. Nitric acid oxidation has been observed to exhibit similar behavior; i.e., not forming complexes within the micropores (Otake, 1986). For this reason, this oxidant will be used as a probe to explore secondary interactions in the larger pores.
4.0. PROJECT ACTIVITY

Project activity during the reporting period included the following:

• A new digital recording microbalance (Cahn D-200) has been purchased. It is currently being incorporated into a TPD-MS/TGA system from which transient gas phase desorption data will be obtained concurrently with transient mass variations. The entire system will be computer-controlled using a Mac II microcomputer with a GW Instruments interface available in the laboratory. The TPD reactor will serve as the hangdown tube for the microbalance. A furnace is also being constructed to accommodate the new TPD reactor. This system will become a principal piece of apparatus for obtaining some of the data required for the development of porosity characterization techniques via thermal desorption methods.

• A graduate student research assistant is being sought to become the focal point for the project.

Plans for the next reporting period include:

• Testing of the new TPD/TGA system and data acquisition.

REFERENCES


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