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**REACTIVITY OF YOUNG CHARS VIA ENERGETIC
DISTRIBUTION MEASUREMENTS**

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SUMMARY

In this report, we present some preliminary work performed on the effect of "inert," diluent gases on the O₂ and CO₂ reactivities of chars, and the corresponding temperature programmed desorption spectra of the oxygen surface complexes. We also present some of the initial data obtained by operating the TPD reactor under vacuum.

The following was accomplished during the reporting period:

- TPD spectra were obtained resin for resin and Wyodak coal char samples gasified in mixtures of various "inert," diluent gases and either O₂ or CO₂ as the oxidants.
 - The effects of helium, argon, nitrogen, sulfur hexafluoride, and xenon diluent gases on reactivity were investigated. Although the diluent gas generally seemed to affect the reactivity, the expected trend in molecular weight was not clearly discernible. In view of these results, the reproducibility of the diluent/oxidant mixture compositions came under suspicion. As a result, we are now switching to pre-mixed gases for these types of studies.

Plans for the next reporting period include:

- The use of pre-mixed oxidant/diluent gas mixtures under batch reaction conditions in the TGA will be explored in order to improve the reliability and reproducibility of the reactivity data obtained for these types of runs.
- The steam addition system that has been developed for use with the TGA apparatus (*cf.* DE-FG22-90PC90307-2) will be tested.
- Work will also continue on adapting the TPD reactor system to operate under subatmospheric/vacuum conditions in order to enhance the sensitivity of the system and explore the nature of certain features in the TPD spectra which have been attributed to secondary interaction effects.

1.0. PROJECT BACKGROUND

The correlation and prediction of kinetic rates and mechanisms of the reactions of gas phase species with coal chars represent a difficulty undertaking under the best of circumstances. Solid phase heterogeneity and impurities, complex pore structure, transport limitation, and evolution of active surface represent just a few of the well known problems. Because of this complexity, this largely remains an unresolved but, nevertheless, important problem affecting many aspects of coal utilization. The only techniques available until now were empirical correlations which may be useful for a single coal, or, at best, a special subset of coals, but are by no means global because they are not *fundamental*. This severely constrains the predictive capability of such methods.

The temperature programmed desorption (TPD) has become a standard technique for investigating the physico-chemical state of adsorbed species on surfaces. The predecessor of TPD-type methods was the flash filament technique of Redhead(1962), whereby gases adsorbed on wire filaments are rapidly desorbed upon rapid heating in an ultrahigh vacuum. This technique was subsequently adapted to catalytic surfaces(e.g., see Cvetanovic and Amenomiya, 1967, 1971). Experimental method and interpretation of TPD spectra for well defined crystalline surfaces have been reviewed by King(1975).

TPD spectra usually consist of one or more peaks. The shapes of the peaks and the position of the peak maxima with respect to temperature are related in a fundamental manner to the desorption process, and, therefore, provide basic information regarding the energetics of the desorbed species.

As a result of previous work, we accomplished what amounts to a significant breakthrough in this long-standing, important problem. In short, we have developed what we believe to be the very first *a priori* prediction technique for the gasification reactivity of coal char. With this method the gasification reactivity of a coal char *as a function of temperature* can be predicted from a *single TPD experiment* following mild gasification at a *single temperature* (Calo *et al.*, 1989; Hall and Calo, 1990a). This approach has been demonstrated for CO₂ gasification of coal chars where the gasification reactivity is controlled by the thermal desorption of oxygen surface complexes formed during gasification. This approach may be extended to other oxidant species, such as steam, and

carbon-hydrogen complexes for hydrogen gasification as well.

In the current report, we present some data on the effect of oxidant partial pressure (i.e., CO₂) on TPD spectra of oxygen surface complexes.

2.0. EXPERIMENTAL

2.1. *The TPD Apparatus and Methods.*

The TPD apparatus consists of three principal parts:

- (1) The gas flow/metering system which provides an inert carrier gas to convect away desorbed species from the vicinity of the char samples;
- (2) The reactor where the sample is subjected to the controlled heating program for desorption of surface species; and
- (3) The detector (quadrupole mass spectrometer) for evolved species.

The experimental details are as follows. Char oxidation/gasification was performed in a TGA apparatus in 0.1 MPa total pressure of oxidant gas at specific temperatures. Following cooling to room temperature in the TGA apparatus, the samples were transferred to the TPD reactor.

The TPD reactor is 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 rate is controlled by a microcomputer.

Detection of desorbed species is accomplished with a quadrupole mass spectrometer (MS) which samples a small portion of the carrier flow. A simple programmer was developed which provides the DC levels required to automatically switch the mass spectrometer among four masses during the course of a TPD experiment. The MS output is fed to a microcomputer which also provides for multiple species detection via mass programming. For the current application, normally only masses $m/e=28$ and 44, corresponding to CO and CO₂, respectively, were monitored. The electron energy in the mass spectrometer ionizer was set to ~25V in order to eliminate cracking of CO₂ to CO upon electron impact. In this manner, the two measured peak

intensities reflect contributions from the parent species only.

The mass spectrometer was calibrated prior to each TPD run using 50/50 mol % CO/CO₂ mixture in order to determine relative species sensitivity. The MS signals were converted to an absolute basis *via* calibration with a series of pulse injections of calibration gas using a syringe, conducted in exactly the same fashion as the TPD experiments. The levels of the two peaks were recorded and the background at each peak was subtracted from these values. The background levels at M/e=28 and 44 were measured before and after each calibration, and were usually considerably less than the values measured with the calibration gas.

2.2. General Experimental Procedures.

The experiment procedure for a typical TPD experiment was as follows:

(1) The char sample was placed in a quartz sample bucket in the TGA apparatus. It was then thermally cleaned by heating in ultrahigh purity helium to a temperature of 1000°C, and holding at this temperature for approximately 20 min. The sample was then cooled to room temperature in ultrahigh purity helium.

(2) The sample was then heated to the desired chemisorption/gasification temperature and the oxidant gas (e.g., oxygen, CO₂ or other gas mixture) was introduced. The desired temperature was then maintained until a predetermined time or burn-off achieved.

(3) A small sample of the oxidized char was then transferred to the TPD apparatus, and the helium purge gas flow was initiated.

(4) The mass spectrometer was calibrated prior to each experiment, as indicated above.

(5) The sample was then heated in ultrahigh purity helium carrier gas at the desired heating rate to an ultimate temperature (usually 1100-1150°C), and the desorption rates CO and CO₂ were measured using the MS. The temperature and the analog output from the MS were digitized and recorded in a data file on a microcomputer.

3.0. EFFECT OF "INERT," DILUENT GASES ON REACTIVITY

One potentially important factor affecting the reactivity of chars from mild gasification processes, that has not yet received much attention, is the role of supposedly "inert," diluent gases on char reactivity. In a study involving both oxygen and CO₂ gasification of two carbons, Walker *et al.* (1977) noted that the presence of diluent increased the gasification rate in the order: N₂>Ar>He; and Xe was even more effective than N₂ for CO₂ gasification, effectively doubling the rate. This effect was probably first observed for the C-O₂ reaction (Prentz, 1959). The same effect has also been cited by Britten *et al.* (1987) as responsible for differences in CO peaks (both shape and total amounts) in TPD experiments conducted in different gases. In this latter work it was concluded that nonreactive gases influence the desorption step of the C-CO₂ reaction by affecting the transport rate of surface complexes to desorption sites. In Ar and Kr, the transport rates were higher than they were in He. Similar effects have also been observed in the catalytic oxidation of SO₂ over V₂O₅ (Hudgins and Silveston, 1975; Goodman, 1975; Rhodey *et al.*, 1976). Although some theories have been advanced to explain this effect (Walker *et al.*, 1977; Britten *et al.*, 1987), it is still far from understood.

In our study of the effects of "inert", diluent gases on gasification rate and corresponding TPD spectra, the rate of gasification of resin char and Wyodak was determined thermogravimetrically in various diluent gases and O₂ and CO₂ mixture. In this report, we mainly discuss the effects of diluent gases on TPD spectra.

3.1 *Experimental.*

The procedure for the reactivity experiments was as follows. Char samples were prepared by carbonization of phenol-formaldehyde resin and Wyodak coal at 1000°C for 2h in a tube furnace in a flow of ultrahigh purity helium.

The TGA was evacuated and refilled with ultrahigh purity helium three times to insure complete purging. A 90-100 mg sample of the char was then placed in a quartz sample bucket in the TGA, and a helium flow of 12 ml/min was established. The sample was heated at 950°C for 2h

in ultrahigh purity helium in order to clean the surface of oxides. The oxidant gas mixtures were made up dynamically by mixing calibrated flows of the two gases (i.e., oxidant and diluent). The Wyodak coal char samples were maintained at 475°C for the O₂ mixtures, and 800°C for the CO₂ mixtures to approximately 5% burn-off. The resin char samples were maintained at 500°C for the O₂ mixtures, and 850°C for the CO₂ mixtures to approximately 10% burn-off. The gas mixtures consisted of helium, argon, nitrogen, xenon, and sulfur hexafluoride, with either O₂ (20%) or CO₂ (50%) as the oxidants.

3.2. Reactivity Results.

The resultant reactivity measurements are presented in Table I. Figure 1 shows the reactivity of resin char in O₂ and CO₂ with the various "inert," diluent gases. In Figure 2, the corresponding reactivities for the Wyodak coal char in the various gases are presented.

3.2-1. Resin Char.

As shown in Figure 1, the reactivity results did not exhibit any monotonic trend with any of the properties of the diluent gases presented in Table II. The apparent reactivity is highest for argon for the O₂ reactivities, and xenon for the CO₂ reactivities.

3.2-2. Wyodak Coal Char.

As shown in Figure 2, the results for the Wyodak coal char were different than for the resin char, with the SF₆ and xenon reactivities being greatest for the O₂ reactivities, but argon apparently being the largest for the CO₂ results.

3.3. Discussion of Reactivity Results.

The enhancement of reactivity with the molecular weight of the "inert," diluent gas has been previously observed by Walker *et al.* (1977). In this latter work, various possible theories were put forth to account for this observation. However, the explanation that the diluent gas affected the surface transport of oxygen complexes to desorption sites is the one that was adopted without direct proof. As a result of TPD studies using helium and argon carrier gases, Britten *et al.* (1987)

concluded that the sweep gas can play a role in desorption by destabilizing a portion of the essentially destabilized a portion of the oxygen surface complex which would have been stable affected the oxygen surface complexes that were unstable with respect to desorption

The results obtained to date are ambiguous. There definitely seems to be an effect of the diluent gas in some cases, especially for the Wyodak coal char, but the results do not exhibit the expected trends with inert gas properties (i.e., molecular weight, polarizability, and size) as shown in Table II, for example. For these reasons, we have come to suspect the experimental procedure. As noted above, the reactivities were obtained under flow conditions, with the gas mixtures made up dynamically by mixing the flows of the two gases (i.e., oxidant and diluent) continuously in a mixing tee upstream of the TGA. If these gas flows drifted, and/or if the the flowrates affected the downstream pressures following calibration of the flowmeters, the mixtures may not have maintained a constant composition over the relatively longterm experimental runs. For these reason, we will attempt to conduct similar runs under static conditions using pre-mixed gas mixtures in order to compare with the dynamic results obtained to date. Thus, these investigations will be continued in this manner.

3.4. TPD Studies.

All the chars oxidized in the reactivity series discussed above will eventually be subjected to TPD. To date most of the O₂/diluent gas series have been run.

After a char sample was gasified in a particular gas mixture, part of the oxidized sample (about 20 mg) was transferred to the TPD apparatus; the reaction chamber was flushed with ultrahigh purity helium and a TPD performed. The heating rate used for every sample was 100K/min, and the maximum temperature attained was 1423K for resin char and 1373K for Wyodak.

3.4-1. Results and Discussion.

Figures 3 and 4 are the resultant TPD spectra from resin char gasified to 10% burn-off at 773K in various 20/80 oxygen/diluent gas mixtures. Comparison is made among helium, argon, and nitrogen diluents concerning their effects upon CO and CO₂ desorption processes. As can be seen, generally the TPD spectra obtained for these oxygen-gasified samples do not appear to reflect

much of an effect of the "inert," diluent gas. However, from Figure 3, it appears that the O₂/He sample exhibits the highest maximum desorption rate, while the O₂/N₂ sample the lowest; albeit the differences are quite small. Also the positions of peak desorption appear to shift slightly to higher temperature, the heavier the diluent gas.

The effects of "inert" diluent gases, helium, argon and nitrogen, on 100K/min TPD spectra for Wyodak gasified in 20/80 O₂/diluent gas mixtures at 748K are shown in Figures 5 and 6. As shown for this coal char, nitrogen diluent appears to give the highest desorption rate for both CO and CO₂; however, in this case the difference was more marked than for the resin char results, especially for CO desorption. Also, the maximum desorption rate appears to occur at the highest temperature for argon as the diluent.

3.5. Conclusions.

The desorption rates for CO and CO₂ do not appear to be sensitive to the diluent gas, except for the case of the nitrogen run for the Wyodak coal char (*cf.* Figure 5), which is not yet understood. However, if the primary effect of the diluent gas is to cause oxygen surface complexes to desorb which might otherwise be stable, non-desorbing complexes in the presence of another, less "intrusive" diluent gas (e.g., helium), we would not expect to see much difference in the TPD spectra following oxygen gasification in these mixtures. This is because the gasification rate is probably controlled by surface complex formation during oxygen gasification and thus, the oxygen complexes that are "turning over" during gasification would not survive on the surface to desorb during subsequent TPD; i.e., they would not be observed. However, it is known that gasification of some chars by CO₂ is oxygen surface complex desorption-controlled under certain conditions. In these cases then, desorption spectra from samples exposed to different CO₂/diluent gas mixtures should exhibit observable differences. Therefore, our experimental focus will shift to CO₂ gasification with respect to the "diluent" gas effect.

4.0. PLANS FOR NEXT REPORTING PERIOD

As noted in section 3.3 above, the reliability and reproducibility of the experimental procedure for the reactivity runs in the TGA using the dynamic flow method for producing oxidant./diluent gas mixtures is in question. Therefore, we will explore the use of pre-mixed gases under batch reaction conditions in order to improve the procedure.

The relatively low amounts of oxygen surface complexes and the small sample sizes used in the desorption experiments often produce "noisy" desorption spectra due to the low signal levels involved; e.g., in particular, see the CO₂ desorption spectra in Figures 4 and 6. These runs were all conducted at atmospheric pressure in the TPD reactor using a helium carrier gas flow. Due to this pressure level, the mass spectrometer actually samples only a very small portion of the total flow, and thus much of the desorbed species signal is not utilized. Therefore, one method which could be used to improve the sensitivity of the desorption spectra is to sample all the desorbed species directly into the mass spectrometer. This can be accomplished only if the total gas load to the mass spectrometer vacuum system is considerably reduced. This can be done by operating the TPD reactor under vacuum conditions, or using helium carrier gas under subatmospheric conditions. In an effort to attain this capability, the TPD reactor system has been made "vacuum-tight" and preliminary experiments have been performed. In Figures 7 and 8 are presented CO and CO₂ desorption spectra, respectively, obtained both under both atmospheric pressure using helium carrier gas and under vacuum. As shown, the sensitivity of the spectra is considerably enhanced under vacuum operation. For example, the low temperature CO₂ desorption features in Figure 8 are completely obscured under atmospheric pressure desorption conditions, whereas they are clearly resolved under vacuum conditions. However, even with this demonstrated enhancement in sensitivity employing vacuum desorption, the approach using helium carrier gas under subatmospheric pressures is more desirable because then the absolute pressure in the mass spectrometer vacuum chamber will not vary with desorption rate. In addition to improving sensitivity, subatmospheric pressure desorption capability will be useful for exploring the nature of certain features in the desorption spectra which have been attributed to secondary interaction effects during TPD (Calo and Hall, 1990).

Finally, as noted in previous reports, we have been developing a steam addition system for use with the TGA apparatus (*cf.* DE-FG22-90PC90307-2) in order to investigate the effects of steam gasification on the reactivity of young chars. This system is now essentially complete, but we have not yet had the opportunity to test it under steam gasification conditions. We will attempt to do so during the next reporting period.

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Table I. Reactivity results.

I. O₂ Reactivity Series: 80/20:Gas/O₂ @ T_{RC} = 500°C to 10% burn-off; T_{WD} = 475°C to 5% b-o; RC = resin char; WD = Wyodak.

<u>Run No.</u>	<u>Gas Mixture</u>	<u>Char</u>	<u>Reactivity (g/g/h)</u>
1	He/O ₂	Resin	0.242
2	He/O ₂	Wyodak	0.066
3	N ₂ /O ₂	Resin	0.256
4	N ₂ /O ₂	Wyodak	0.076
5	Ar/O ₂	Resin	0.275
6	Ar/O ₂	Wyodak	0.617
7	Xe/O ₂	Resin	0.205
8	Xe/O ₂	Wyodak	0.095
9	SF ₆ /O ₂	Resin	0.255
10	SF ₆ /O ₂	Wyodak	0.096

II. CO₂ Reactivity Series: 50/50:Gas/CO₂ @ T_{RC} = 850°C to 10% burn-off; and T_{WD} = 800°C; 5% b-o; RC = resin char; WD = Wyodak.

<u>Run No.</u>	<u>Gas Mixture</u>	<u>Char</u>	<u>Reactivity (g/g/h)</u>
11	He/CO ₂	Resin	0.032
12	He/CO ₂	Wyodak	0.023
13	N ₂ /CO ₂	Resin	0.027
14	N ₂ /CO ₂	Wyodak	0.034
15	Ar/CO ₂	Resin	0.021
16	Ar/CO ₂	Wyodak	0.033
17	Xe/CO ₂	Resin	0.040
18	Xe/CO ₂	Wyodak	0.026

Table II. Properties of "inert." diluent gases used in the current work.

Gas	Molecular Weight	Molecular Diameter⁽¹⁾ (Å)	Polarizability⁽²⁾ (10⁻²⁴ cm³)
He	4.0026	2.576	0.204956
N ₂	28.0134	3.681	1.7403
Ar	39.948	3.418	1.6411
Xe	131.3	4.055	4.044
SF ₆	146.0504	-	6.54

⁽¹⁾R.R. Bird, W.E. Stewart, and E.N. Lightfoot, *Transport Phenomena*, Wiley, NY, 1960.

⁽²⁾*Handbook of Chemistry and Physics, 66th Edition*, R.C. Weast, ed., CRC Press, Inc., Boca Raton, FL, 1985

Figure 1. Gasification reactivities of resin char in oxidant/diluent mixtures at 10% burn-off: (a) O₂/diluent - 20/80 at 773K; and (b) CO₂/diluent - 50/50 at 1123K.

Figure 2. Gasification reactivities of Wyodak coal char in oxidant/diluent mixtures at 5% burn-off: (a) O₂/diluent - 20/80 at 748K; and (b) CO₂/diluent - 50/50 at 1073K.

Figure 3. 100K/min CO TPD spectra from resin char gasified to 10% burn-off in 20/80 O₂/diluent gas mixtures at a total pressure of 0.1 MPa at 773K.

Figure 4. 100K/min CO₂ TPD spectra from resin char gasified to 10% burn-off in 20/80 O₂/diluent gas mixtures at a total pressure of 0.1 MPa at 773K.

Figure 5. 100K/min CO TPD spectra from Wyodak coal char gasified to 5% burn-off in 20/80 O₂/diluent gas mixtures at a total pressure of 0.1 MPa at 748K.

Figure 6. 100K/min CO₂ TPD spectra from Wyodak coal char gasified to 5% burn-off in 20/80 O₂/diluent gas mixtures at a total pressure of 0.1 MPa at 748K.

Figure 7. Comparison of normalized (at maximum desorption rate) 100K/min CO TPD spectra, obtained under helium carrier (0.1 MPa) and vacuum (<10 mtorr) desorption conditions, from resin char gasified to 10% burn-off in a 20/80 O₂/He mixture at 773K.

Figure 8. Comparison of normalized (at maximum desorption rate) 100K/min CO_2 TPD spectra, obtained under helium carrier (0.1 MPa) and vacuum (<10 mtorr) desorption conditions, from resin char gasified to 10% burn-off in a 20/80 O_2/He mixture at 773K.

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