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**PYROLYSIS AND GASIFICATION OF COAL
AT HIGH TEMPERATURES**

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SHORT DESCRIPTION OF TASKS

(A) Effects of Pyrolysis Conditions on Macropore Structure

Coals of different ranks will be pyrolyzed in a microscope hot-stage reactor using inert and reacting atmospheres. The macropore structure of the produced chars will be characterized using video microscopy and digital image processing techniques to obtain pore size distributions. Comparative studies will quantify the effect of pyrolysis conditions (heating rates, final heat treatment temperatures, particle size and inert or reacting atmosphere) on the pore structure of the devolatilized chars.

(B) Gasification Under Strong Intraparticle Diffusional Limitations

The devolatilized chars will be gasified in the regime of strong intraparticle diffusional limitations using O_2/N_2 and $O_2/H_2O/N_2$ mixtures. Constant temperature and programmed-temperature experiments in a TGA will be used for these studies. Additional gasification experiments performed in the hot-stage reactor will be videotaped and selected images will be analyzed to obtain quantitative data on particle shrinkage and fragmentation.

(C) Mathematical Modeling and Model Validation

Discrete mathematical models will be developed and validated using the experimental gasification data. Structural properties of the unreacted chars will be used to generate computational grids simulating the pore structure of the solid. Simulations will then provide the evolution of observed reaction rates with conversion. The size distribution of particle fragments obtained as the reaction front moves through the particle will also be obtained. Proper statistical averaging of the results from these simulations will yield the expected behavior for each char. Comparisons of experimental data and theoretical predictions will identify the fundamental phenomena that must be included in a mathematical description of the process, thus leading to the development of accurate models for the gasification of coal particles.

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1. SUMMARY

Images from five Illinois #6 chars were processed to quantify the effect of pyrolysis heating rates on particle swelling. Our preliminary results indicate that particle swelling does not appear to correlate well with the macropore surface area data. Changes in the internal macropore structure (like the appearance of small secondary vesicles in the walls separating larger cavities) are not reflected by differences in particle swelling. More data are currently being processed in order to further investigate this issue.

We have recalculated the porosity and macropore surface areas of five Illinois #6 chars after applying a novel image processing procedure to the binary images of char particle cross-sections. The new procedure smooths the binary images in order to minimize the errors introduced by noise in the video signal and pixelization effects. We believe that this procedure will significantly improve the accuracy of stereological measurements. The only disadvantage of this procedure is that the smoothed images are 16 times larger than the original ones and this results in significant increases of the computational time needed for these calculations.

The development of the thermogravimetric reactor system is virtually complete. We have debugged and tested the computer program that programs and controls the furnace temperature. Data are presented that show the accurate performance of the temperature controller during experiments with 10 °C/s and 20 °C/s heating rates. The furnace temperature shows no overshoot and the observed deviations from the setpoint during the ramps were very small. Long term operation of the controller is very stable. The observed temperature fluctuations were at the lowest possible noise level.

The same program also controls the operation of the mass flow controllers so that we can carry constant temperature experiments with accuracy and repeatability. During such experiments, the sample is heated to the reaction temperature in an inert atmosphere and gaseous reactants are introduced when the reactor temperature has stabilized. Data are presented to show that the current

setup minimizes the transients observed after the introduction of the reacting gases.

Some preliminary combustion runs with Illinois #6 chars were carried out and results are presented to show the rate vs. conversion patterns as we move from the regime of reaction control into the regime of significant diffusional limitations in the micropores. These patterns show a behavior predicted by our models.

2. TECHNICAL AND SCIENTIFIC RESULTS

(A) Effects of Pyrolysis Heating Rate on Macropore Structure of Chars

As mentioned in the previous quarterly report, a new procedure has been developed for smoothing the pore (and particle) boundaries in order to eliminate possible artifacts introduced by the pixelization errors. According to this procedure, each 640x480 image is converted to an artificial B&W image with only two grey levels (black and white). A filter with a 3x3 kernel is then applied to the BW image resulting in a "blurring" of the sharp boundaries. The filtered image is then segmented and magnified by a factor of 4 to obtain a binary image with smooth pore (and particle) boundaries. This procedure also filters out small pores consisting of one or two pixels. We believe that these small pores should not be considered for structural property calculations since they may be due to noise in the original video signal or in the digitizer.

This smoothing procedure was applied to all the binary images of cross-sections obtained for the five Illinois #6 chars produced at different pyrolysis heating rates (0.1 to 1000 °C/s). All the smoothed 2560x1920 pixel binary images were then analyzed to calculate the areas and perimeters of the macropore cross sections. *This was an extremely CPU-intensive operation since the smoothed images were 16 times larger than the original binary images.*

The macropore structural properties computed from the smoothed images are

shown in Figures 1 and 2. As expected, the smoothing procedure had a negligible effect on the porosity estimate ϵ that was again computed by

$$\epsilon = \frac{A_a}{A_c}$$

where A_a is the total area of the pore profiles and A_c is the total area of particle cross-sections. Figure 1 shows the increase of char sample porosity with the increasing pyrolysis heating rate. The average porosity (middle line in Fig. 1) was computed from 48 particle cross sections. Also, upper and lower bounds were computed from considering (for each char sample) 6 groups with 8 particle sections each.

Figure 1 also shows the average area-equivalent radius computed from 48 particle sections computed as

$$R_{avg} = \left[\frac{\sum_{i=1}^N A_i}{N \pi} \right]^{1/2}$$

where A_i is the area of the i -th particle cross-section and N is the total number of cross-sections. The maximum computed area-equivalent radius is also plotted on Figure 1. These data provide a good quantitative *measure of particle swelling* at the various pyrolysis rates.

The macropore surface area densities and specific macropore surface areas computed from the smoothed images are presented in Figure 2. As expected, the smoothed images yield surface area density values that are smaller (by an almost constant amount) than those computed from the raw (original) images. We believe, however, that the new values should be more representative of the true macropore surface areas since the smoothed images should be free from artifacts introduced by video noise and pixelization errors.

Another interesting observation from the data presented in Figures 1 and 2 is that the "swelling" (or area-equivalent radius) data presented in Figure 1 do not appear to correlate well with the macropore surface area data. This indicates that particle swelling may not be a good index of the internal macropore

structure. We are currently collecting additional data to further investigate this important issue.

(B) Gasification Under Strong Intraparticle Diffusional Limitations

The development work for the thermogravimetric reactor is virtually complete. Several gasification runs were carried to test the reactor and to verify its capabilities. We have rewound the furnace with wire made from a Kanthal A-1 alloy. This appeared to solve the problems we were experiencing with nichrome wires and the furnace has not failed again even though it was repeatedly heated to temperatures above 800 °C in oxygen atmospheres.

The computer algorithm that provides for temperature programming and control was fine tuned and extensively tested. We can now achieve linear heating rates between 600 and 1200 °C/min (10-20 °C/s) with excellent accuracy and repeatability. Figure 3 shows the temperature program (dotted line) and the actual temperature measured by the thermocouple (solid line) for a 10 °C/s ramp. The agreement is very good and the deviation of the measured pan temperature T_s from the setpoint T_r (defined as $\Delta T = T_r - T_s$) was in the ± 2 °C range. *The temperature shows no overshoot when the program shifts from the 10 °C/s ramp to constant temperature* (note that ΔT is positive at that corner). Equally impressive is the performance of the algorithm during the constant temperature periods. *During these periods the temperature deviation from the setpoint is in the ± 0.25 °C range.* This is equal to a ± 1 bit error in the temperature measurement performed with a 12-bit analog-to-digital converter. Note that is the *lowest noise level possible given our A/D interface.*

Figure 4 shows the performance of the control algorithm for a ramp equal to 20 °C/s spanning a range of 400 °C (200-600 °C). The maximum temperature deviation occurs at the beginning of the ramp, a temperature region of no importance for our experiments. Again, the temperature shows underdamped response at the end of the ramp and no overshoot (a highly desirable feature). We believe that the response can be improved and we are currently working on developing new sets

Figure 1: Effect of pyrolysis heating rate on the porosity of char samples (top), the average area-equivalent radius of particle sections (bottom, solid line) and the maximum observed area-equivalent radius (bottom, dashed line).

Figure 2: Effect of pyrolysis heating rate on the macropore surface area density (top) and specific macropore surface area (bottom) for five Illinois #6 char samples.

Figure 3: Measured temperature T_s and setpoint T_R for a temperature program with a 10 °C/s ramp. The bottom graph shows the temperature deviation from the setpoint $\Delta T = T_R - T_s$.

of controller settings that will decrease even further the observed temperature deviations from the setpoint. We are also working on identifying the possible ranges of achievable heating rates and final temperatures with the current setup.

We have also developed a protocol for carrying out constant temperature experiments. During such experiments, the coal sample will be heated to the final temperature in an inert atmosphere and the gaseous reactant will be introduced when the reactor temperature has stabilized. As previously mentioned, the operation of three mass flow controllers can be programmed, controlled and monitored by the computer (see quarterly report #5).

Figure 5 presents plots from a typical run to demonstrate the ease and accuracy with which constant temperature experiments can be carried out. For this run, a char sample was heated to the final reaction temperature in flowing N_2 gas (flowrate was 200 ccm). After reaching the final temperature, the computer switched a solenoid valve and a mixture of 10% O_2 and 90% N_2 started flowing through the reactor. The total flowrate was kept constant at 200 ccm. The unavoidable pressure change caused a small momentary decrease of the sample weight by 0.03 mg (from 3.265 to 3.235 mg), but within 2 s the sample weight jumped back up to a new steady-state value of 3.255 mg. For the next 40 s, the sample weight remained constant (see the shaded area in the top graph of Figure 5). Note the **lowest noise level possible with our weight measurement system is ± 0.0025 mg**. This corresponds to a ± 1 bit error in our 12-bit analog-to-digital converter.

We estimate that it takes about 45 s after switching for the O_2 to reach the char sample. Figure 5 shows that at that point the sample weight starts to decrease as the chemical reaction takes off. We are confident at this point that we will be able to get good estimates of initial reaction rates with this setup. Also, Figure 5 shows that the measured pan temperature is constant during this period (within the ± 1 bit error range). These results indicate that the current reactor/mass flow controller setup will allow us to quickly and reproducibly switch gases (e.g. from an inert to a reacting atmosphere) at any desired point

Figure 4: Measured temperature T_s and setpoint T_R for a temperature program with a 20 °C/s ramp. The bottom graph shows the temperature deviation from the setpoint $\Delta T = T_R - T_s$.

Figure 5: Char sample weight and deviation from temperature setpoint in the early stages of the reaction.

in the temperature program. Computer control will minimize transients during constant temperature gasification experiments.

Figure 6 presents the raw temperature data for 25 minutes after the switch to the O_2/N_2 mixture. The sample weight shows a very smooth decrease and the temperature remains in the ± 0.25 °C range, with only four very short excursions to $+0.50$ °C.

We have developed two programs that process the raw weight and temperature data obtained from the process control computer. Figure 7 shows the reaction rates computed from four runs at two different temperatures (500 and 550 °C) and two O_2 concentrations (10 and 20%). The important thing to notice in Figure is that an inflection point develops in the rate vs. conversion curves as the reaction temperature and the oxygen concentration increase. The appearance of this inflection point means that *significant diffusional limitations are present in the micropores*. This distinct feature of the rate vs. conversion curves is also predicted by our theoretical models for pore evolution in the regime of diffusional limitations in the micropores.

In the next quarter, we plan to investigate the combustion of some of our old chars under conditions leading to diffusional limitations in the large pores. We also plan to explore the new possibilities offered by our reactor setup for pyrolysis/gasification experiments. For example, pyrolysis experiments at fairly high heating rates can be performed in the thermogravimetric reactor. We should note here that our earlier pyrolysis experiments in the captive sample (heated grid) microreactor showed that the macropore structure of the produced chars exhibited the most drastic changes for heating rates between 0.1 and 10 °C/s. Chars produced at 10 °C/s already had the characteristic cellular internal structure with thin walled cavities and the specific macropore surface area appeared to reach a maximum at that heating rate. It thus seems possible now to carry out the bulk of pyrolysis and gasification experiments in one reactor system, thus simplifying the acquisition and interpretation of data.

Figure 6: Char sample weight and deviation from temperature setpoint for 25 minutes after switching to a reacting atmosphere.

Figure 7: Rate vs. conversion patterns for an Illinois #6 char reacted with oxygen at various temperatures and reactant concentrations.

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