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PYROLYSIS AND GASIFICATION OF COAL AT HIGH TEMPERATURES

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QUARTERLY PROGRESS REPORT
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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.

SUMMARY

The effects of particle size on the macropore structure of chars produced from an Illinois #6 coal were investigated. Three size fractions (100-120, 50-60 and 25-28 mesh) of coal particles were pyrolyzed in our captive-sample reactor at 10 °C/s. By analyzing digitized particle cross-sections, we obtained the macropore volume distributions and surface areas, and determined that all three char samples had almost equal macroporosities. We have also analyzed for the first time the shape or boundary tortuosity of the macropores. As the size of the pyrolyzed coal particles increased, the produced chars exhibited macropores with more tortuous boundaries. Tortuous pore boundaries result in higher values for the true macropore surface areas and should enhance the reactivity of the char samples. A systematic procedure was developed for analyzing and averaging the simulation results obtained with our erosion models. Such a procedure is necessary for comparing statistical model predictions to experimental data. Several simulations were carried out to investigate the gasification behavior of the three char samples mentioned above and the predicted reactivity patterns are presented. Finally, a thermogravimetric analyzer (TGS-2) was ordered and will soon be delivered to our laboratory.

TECHNICAL AND SCIENTIFIC RESULTS:

(A) Effects of Coal Particle Size on Macropore Structure of Chars

Heat transfer in pyrolyzing coal particles can be significantly affected by the particle size. If external heat transfer controls the pyrolysis process, particle temperature will remain constant during heatup and the heating rate will decrease with increasing particle size. On the other hand, if the rate of external heat transfer is high enough, high heating rates and large particle sizes can lead to significant temperature gradients within the particle. Under such conditions, the pyrolysis reaction rates will vary significantly inside the particles.

We have selected three size fractions from the plastic Illinois #6 coal for our studies: 25-28 mesh (589-710 μm particle diameter), 50-60 mesh (250-300 μm particle diameter) and 100-120 mesh (125-149 μm particle diameter). Thus, the mass of individual particles varied by about two orders of magnitude for these runs. A heating rate of 10°C/s was selected in order to facilitate the detection of differences in the pore structure possibly caused by changes in the internal heating rate of the particles.

Figures 1 to 3 present representative cross-sections of char particles produced from these runs. Note that these figures have different scales. The cross sections appear to show very different pore structures for the three chars. For the smallest size fraction (Figure 1), we observe fewer pores per particle and the pore shape is rather rounded. The largest size fraction, on the other hand, exhibits numerous pores per particle. The boundaries of the pore profiles are very tortuous and we see again the characteristic cellular pore structure (see Quarterly report #1) with numerous small pores embedded in the walls separating the larger cavities.

Figure 4 shows the normalized pore volume distributions for the three char samples. A large fraction of the pore volume for the smallest char particles (100-120 mesh) is associated with relatively large pores approximately 50 μm in radius. The pore volume distribution for the intermediate particles (50-60 mesh) is more uniform. The contribution of smaller pore sizes increases, however, in the case of the largest particles (25-28 mesh) due to the formation of small pores in the walls separating the larger cavities.

Table I summarizes the measurements for the macropore properties. The interesting result here is that the macroporosity of the particles was not affected by their size. This indicates that the internal heating rate of the particles was not affected by their size, pointing out that external heat transfer is not limiting for our pyrolysis reactor. It should be noted here that our earlier results (see Quarterly report #1) had shown that the macroporosity (and the degree of swelling) of the particles was strongly affected by the

heating rate. As expected, the equivalent pore radii observed in the three samples decreased substantially with decreasing particle size. The maximum pore radius observed fell from 284 μm for the 25-28 mesh sample to 51 μm for the 100-120 mesh sample. This decrease in macropore size was accompanied by an increase in the specific surface area of macropores per unit volume of char particle.

TABLE I
Effects of Particle Size on the Macropore
Structural Properties for Illinois #6 Chars

Coal Particle Size		Porosity	Surface Area (cm^2/cm^3)	Maximum Pore Radius (μm)
(mesh)	(μm)			
25-28	589-710	0.69	638	284
50-60	250-300	0.69	695	152
100-120	125-149	0.71	1440	51
Heating Rate: 10 $^{\circ}\text{C/s}$				

It must be noted here that maceral segregation may complicate the determination of particle size effects on the macropore structure of chars produced from plastic coals. Due to differences in the mechanical properties of the various coal macerals, grinding and sifting procedures may lead to enrichment of certain macerals in certain size fractions (i.e. small size fractions may contain more exinite). Thus, the well-known differences in the plastic behavior and volatile content of coal macerals can affect the macropore structure of different size fractions. Such effects will be investigated in the future stage of our studies.

Calculation of the True Surface Areas of Macropores

The macropore surface areas presented in Table I were calculated according to a stereological method that models the macropores by a population of non-overlapping spheres. By intersecting this ensemble of spheres with random planes, populations of circles are obtained on the sectioning planes. The population statistics obtained from the two-dimensional sections are distributionally related to the statistics of the three-dimensional objects. Thus, the structural parameters for the 3-D ensemble of spheres can be unfolded by analyzing the 2-D pore profile statistics via a stereological model.

Random sectioning of char particles is accomplished experimentally by preparing polished sections. A large number of particle cross-sections is then processed and analyzed to obtain accurate statistics for the macropore size distribution. The pore profiles for every section are identified and their areas are directly computed. The assumption of spherical pores necessitates the use of equivalent radii in the statistical calculations. Pore profiles are thus assumed to be circles and their equivalent radius r is computed by the formula

$$r = \sqrt{A/\pi} \quad (1)$$

As shown in Figures 1 to 3, however, the pore boundaries are very tortuous. By replacing the pore profiles with equivalent circles, we underestimate the true surface area of the macropores. These surface area estimates can be improved by employing a pore shape factor S defined as follows:

$$S = \frac{P^2}{4\pi A} \quad (2)$$

where P is the directly measured perimeter of each pore profile and A is its area. The value of this pore shape factor reflects the complexity of the pore boundary. A perfect circle yields the minimum value for the shape factor $S=1$, while complex cross-sectional shapes yield values for S substantially larger than unity.

Such measures of the tortuosity of pore boundaries are important for

reaction engineering calculations since they quantify more accurately the true surface area available for heterogeneous gas-solid reactions. In an effort to improve the accuracy of the macropore surface area estimates, our macropore size analysis software was enhanced to perform calculations of the true perimeter P and the shape factor S of each pore.

Shape factor analysis of the two-dimensional particle cross sections identified significant differences in the morphology of the macropores observed in the three char samples studied here. This analysis was based on the following probability density function:

$$f(S)dS = \text{fraction of total area attributed to pore profiles} \\ \text{with shape factors between } S \text{ and } S+dS$$

The computed probability density functions $f(S)$ for the three char samples are presented in Figure 5. Each histogram bar denotes the fraction of total area of pore profiles whose shape factor S (or boundary tortuosity) falls within a specified range.

Most of the macroporosity in 100-120 mesh sample is attributed to pores with shape factors between 1.0 and 3.0, with the maximum occurring at about 1.5. A distinct shift to larger values of shape factors is observed with increasing particle size. The corresponding distribution for the 25-28 mesh sample shows that a substantial fraction of the macroporosity is now attributed to pores with boundary tortuosity greater than 3. This increase in the shape factors is due to the large size of the pores observed in the 25-28 mesh sample.

The increasing tortuosity of pore boundaries observed in the larger char particles partially offsets the decrease in their specific area (see Table I) due to the increasing size of the pores. Thus, char samples with large particles are expected to exhibit higher reactivity than would be predicted on the basis of the specific surface areas reported in Table I.

(B) Gasification Under Strong Intraparticle Diffusional Limitations

A thermogravimetric analyzer has been ordered and will be soon delivered to our lab. We have decided to acquire an earlier version (TGS-2) of the PERKIN-ELMER analyzer since this earlier version is fully compatible with our data acquisition and control computer. Once the new unit is installed, the digital algorithms developed earlier to accurately program and control the reactor temperature will be tuned for the new instrument. The thermogravimetric reactor, its computer interface, the control programs and the gas-feed station are expected to be fully operational during the next quarter of this contract (3/15/1987 to 6/15/1987).

(C) Mathematical Modeling of Char Gasification

Reaction Rates Predicted by the Erosion Models

The previously described erosion models work on computational grids obtained from digitized images of char particle cross-sections. Several factors, however, complicate the statistical analysis and averaging of simulation results and a systematic procedure must be developed for comparing theoretical predictions to experimental data. Experimental reactivity data provide the specific gasification rates that are most often expressed in the form

$$R_o = \frac{1}{m_o} \frac{dm}{dt} \quad (3)$$

where m_o is the mass of unreacted char and (dm/dt) is the rate of change of the reacting char mass. Let $R_s(c, T)$ be the intrinsic reaction rate expressed in $(\text{kg of solid})/(\text{s})(\text{m}^2 \text{ of surface area})$. The solid volume dV consumed by the heterogeneous reaction over a time period dt is given by

$$\frac{dV}{dt} = \frac{S_g}{\rho_s} R_s(c, T) \quad (4)$$

where S_g is the total surface area available for reaction and ρ_s is the solid density. If the reaction rate is uniform over the entire surface area, a layer

of solid with uniform thickness dx will be consumed over the time period dt . Thus, $dV = S_g dx$ and Eq. (4) becomes

$$\frac{dx}{dt} = \frac{R_s(c, T)}{\rho_s} \quad (5)$$

This simple analysis can be used to normalize the reaction rates predicted by the discrete models. At every simulation step, we erode a single layer of pixels from the solid surface area available for reaction. Thus, every erosion step corresponds to a time interval $\Delta\tau$ that equals the time required to convert a solid layer of uniform thickness Δx , where Δx is the pixel size. From Eq. (5)

$$\frac{\Delta x}{\Delta\tau} = \frac{R_s(c, T)}{\rho_s} \quad (6)$$

If two simulations are carried out on images with different pixel sizes Δx and Δx^* , their time steps will be related according to the formula

$$\frac{\Delta x}{\Delta\tau} = \frac{\Delta x^*}{\Delta\tau^*} \quad (7)$$

Let now N_0 be the number of solid reactant pixels on the initial computational grid and let ΔN be the number of solid pixels converted during an erosion step. The specific rate R_0 for this step can be computed by the formula

$$R_0 \Delta\tau = \frac{\Delta N}{N_0} \quad (8)$$

Let Δx be the pixel size (in μm) for this image and let $\Delta\tau^*$ be the time required to react a layer of solid with uniform thickness equal to $\Delta x^* = 1 \mu m$. Eqs. (8) and (7) yield

$$R_0 \Delta\tau^* = \frac{\Delta N}{N_0} \frac{\Delta x^*}{\Delta x} \quad (9)$$

Eq. (9) provides specific reaction rates that are independent of the pixel size of the digitized images used in the simulations.

Using Eqs. (6) and (7), the value of $\Delta\tau^*$ can be computed from the value of the intrinsic rate $R_s(c, T)$ at the appropriate conditions. Most often, however, the reactivity data obtained at various temperatures and reactant concentrations

are normalized so as to obtain master curves that yield (within experimental error) the dependence of the active surface area on conversion. Such master curves can be obtained directly from the simulations by plotting the dimensionless rate $R_e \equiv R_o \Delta \tau^*$ vs. either the conversion or a dimensionless time θ where

$$\theta = \frac{t}{\Delta \tau^*} = \frac{t R_s(c, T)}{\Delta x^* \rho_s} \quad (10)$$

Since several simulations are performed for each char sample, the average rate R_e is computed by the formula

$$R_e = \frac{\sum (\Delta N)}{\sum N_o} \frac{\Delta x^*}{\Delta x} \quad (11)$$

where the summations are taken over all simulation runs performed for the same char sample. The reaction rates computed according to Eq. (11) can be directly compared regardless of the amount of solid in each sample or the magnification used when acquiring the digitized images.

Effect of Coal Particle Size on Char Gasification Rates

The surface erosion models were used to investigate the gasification behavior of the three char samples produced from pyrolyzing the three different size fractions of an Illinois #6 coal at 10 °C/s (see part A). For these runs, we assumed that the internal macropores were not initially accessible to the reactant. Once the reaction front reached an internal macropore, however, the entire surface area of the macropore would become available for reaction. Simulations were carried out on images containing 8 particle cross-sections each. The results from 6 such simulations (48 total particle cross-sections) were then averaged.

Figure 6 shows the variability in the predicted reaction rates R_e for the char sample produced from 50-60 mesh coal particles. All six runs exhibit a pronounced maximum since the internal cavities open up as the reaction proceeds. The rate vs. conversion curves plotted in Figure 7 show that this maximum occurs at about 35-40% conversion. Although significant rate variations exist among the

six runs, the sudden rate jumps observed in single-particle runs were smoothed out, since the simulations considered here eroded 8 particles simultaneously.

Average reaction rates for the three char samples are shown in Figures 8 and 9. Due to its small particle size and large external surface area, the 100-120 mesh sample exhibits a high initial rate, a sharp rate maximum and very short reaction times (Figure 8). As the particle size is increased, the reaction rates decrease and their burnout times increase significantly. However, the normalized reaction rate vs. conversion curves shown in Figure 9 show a slightly different picture. Now the 100-120 mesh sample exhibits the smallest relative increase in the reaction rate. This is clearly due to the increased tortuosity of the macropore surface observed with the large particle samples.

Diffusional Limitations in the Macropores

The surface erosion models have been extended to account for diffusional limitations in the macropores opening for reaction. When the reaction front reaches a previously inaccessible macropore, its surface area becomes progressively available for reaction according to an effectiveness factor. Some preliminary results demonstrating the effects of diffusional limitations are presented in Figures 10 and 11. A complete analysis of such phenomena is under way.

PLANS FOR NEXT QUARTER (3/15/88 - 6/15/88)

TASK (A): Analysis of macropore structure data for chars pyrolyzed at various heating rates in an inert (N_2) atmosphere will continue. Studies on three char samples produced from a lignite coal (Wilcox, Texas) at different pyrolysis heating rates are already under way. Particular emphasis will again be placed on obtaining estimates of pore roughness and tortuosity, since such structural features are essential for calculating the total pore surface area available for reaction.

TASK (B): The thermogravimetric analyzer will be installed and interfaced to our data acquisition and control computer. We expect to have the thermogravimetric reactor operational before the end of the 3rd Quarter of this contract.

TASK (C): The erosion model has already been extended to handle diffusional limitations in the pores opening for reaction. We plan to analyze and compare the gasification behavior of the seven Illinois #6 and the three lignite chars under various conditions leading to full or partial utilization of the macropores during gasification reactions.

Figure 4: Macropore volume distributions for three chars produced by pyrolyzing 100-120, 50-60 and 25-28 mesh particles of an Illinois #6 coal.

Figure 5: Histograms showing the fraction of the total area of pore profiles whose shape factor S falls within the specified range.

Figure 6: Temporal evolution of predicted reaction rates from six simulation runs with 50-60 mesh Illinois #6 char particles. Each run eroded 8 particle cross-sections simultaneously.

Figure 7: Reactivity vs. conversion patterns predicted from six simulation runs with 50-60 mesh Illinois #6 char particles. Each run eroded 8 particle cross-sections simultaneously.

Effect of Particle Size on Reaction Rates

Figure 8: Effect of coal particle size on the reaction rates predicted for the three Illinois #6 chars. Model predictions are averages for 48 particle cross-sections.

Effect of Particle Size on Reaction Rates

Figure 9: Comparison of predicted reactivity vs. conversion patterns for the three Illinois #6 chars. Model predictions are averages for 48 particle cross-sections.

Effect of Diffusional Limitations in Macropores

Figure 10: Preliminary results showing the effect of diffusional limitations in macropores on the reaction rates. The char sample was produced by pyrolyzing Illinois #6 50-60 mesh coal particles at 0.1 °C/s.

Effect of Diffusional Limitations in Macropores

Figure 11: Preliminary results showing the effect of diffusional limitations in macropores on the reactivity vs. conversion patterns. The char sample was produced by pyrolyzing Illinois #6 50-60 mesh coal particles at 0.1 °C/s.

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