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The Role of Pore Structure on Char Reactivity

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Quarterly Progress Report

P.I.: Adel F. Sarofim

Student: Angelo Kandas

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Massachusetts Institute of Technology

Department of Chemical Engineering

Cambridge, MA 02139-4307

Prepared for U.S. Department of Energy

Morgantown Energy Technology Center

P.O. Box 880

Morgantown, WV 26507-0880

Attention: Wu K. Lan

Date Submitted: January, 1996

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Introduction

In order to examine the role of pore structure, studies will be conducted on coal chars in the electrodynamic balance. Larger particles will also be examined using a fluidized bed to examine diffusion control reactions, and soots will also be investigated to examine the role of meso- and micro-pores without macro-pore interference. These studies will allow a full range of particles sizes and temperatures to be investigated and eventually modelled.

Progress Report

The project has examined the effect of the pore structure diffusivity changes on the generation of NO_x and N₂O from the Fluidized Bed Combustor. Furthermore, refinement of the techniques necessary to determine micropore characteristics from TEM imaging have been further refined.

The continuing focus of this research has been the examination of the evolution of model compounds such as spherocarbon during oxidation in order to simplify structural analysis. The structure of spherocarbon now has been fully analyzed at three conversions(0, 44, and 96% conversion).

Analysis of the spherocarbon structural rearrangement methodology, as explained in the October, 1995 progress report, involves digitizing electron microscope pictures taken at 590kX using a Akashi 002B. After Digitization, the program SEMPER 6P (Synoptics Ltd., Cambridge, UK) is used to manipulate the stored images. A fourier

transform of the TEM images is first obtained, and then successive masking/demasking operations, and extracted structure is established using an intensity threshold.

The two most important measurements are the lattice length and the d_{002} carbon

The lattice length, or lateral extent of fringes is defined as

$$La = A \cdot B \sqrt{m_{\max}}$$

where $m_{\max}$ is the maximum principal second moment, and A and B represent digitization constants specific to our system. The interlayer-planar spacing defined as the distance d_{002} between parallel fringes and is obtained by evaluating the center of area P_i and the long axis orientation α_i . The distance was then calculated using the following formula:

$$d_i = \frac{m_i(x_{i+1} - x_i) - (y_{i+1} - y_i)}{\sqrt{m_i^2 + 1}}$$

$$m_i = \tan\left(\frac{\alpha_i + \alpha_{i+1}}{2}\right)$$

where (x_i, y_i) represent the coordinates of P_i . Since the measurement must be repeated several times, the system is specified using means and standard deviations, although a graphical distribution is more meaningful.

The results of the Analysis are shown in Figures 1 and 2. As can be seen, there is little variation in the d_{002} spacing. However, due to the high variation in our measurements of the d_{002} spacing, changes less than 0.1 Angstrom would not be measurable. However, the fringe length does change significantly. This finding is

important in understanding char fragmentation. The micrographs, combined with EDB work performed in Israel, suggest that the fragmentation percolation threshold of 0.7 may be surpassed because of this type of structural rearrangement. The spherocarbon rearranges itself (densification) in such a way as to prevent final porosities of 0.7 to be reached in the micropores, maintaining the continuity of the spherocarbon particle during oxidation. A summary of this work has been submitted for publication by the Combustion Institute.

Future Work

Analysis of spherocarbon will continue to obtain the full spectrum of conversions. Furthermore, work on the further development of the combustion resistant grid used for single particle examination will be reported upon.

Figure 1. d002 Spacing of Sphercarbon, effect of oxidation

Figure 2. Comparison of lattice length for Sphercarbon, effect of oxidation

Structural Changes of Char Particles During Chemically Controlled Oxidation

X. Zhang¹, A. Dukhan¹, I.I. Kantorovich¹ and E. Bar-Ziv^{1,2}

¹Department of Mechanical Engineering
Ben-Gurion University of the Negev, P.O. Box 6531

²Nuclear Research Center-Negev, P.O. Box 90012
Beer-Sheva, Israel

A. Kandas and A. F. Sarofim
Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge, MA 02139

ABSTRACT

The structural changes -- particle diameter, shape, porosity, fine structure -- during the oxidation of highly porous synthetic char (Spherocarb) particles at kinetically controlled conditions were investigated in order to provide insight on the factors that govern fragmentation during combustion. More than a hundred experiments were conducted in an electrodynamic chamber in the temperature range of 700-1000 K, for particles of initial diameters of 150 to 250 μm and densities of 0.45-1.0 g/cm^3 for carbon conversions up to 99% conversion. Particle mass, density, size and shape were measured continuously. Similar experiments were conducted in a thermogravimetric analyzer in order provide samples for determination of the fine structure of the chars using high resolution transmission electron microscopy. For a subset of particles that were analyzed in detail, the total porosity increased from 0.60-0.76 to 0.83-0.88, when allowance is made for the observed particle shrinkage. Although the maximum porosity surpassed that the value of about 0.7 required for percolative fragmentation in a material of uniform porosity, little fragmentation was observed. The explanation for this is that the particles have a bimodal pore size distribution and the porosity of neither the macroporous nor the microporous regions exceeded the critical porosity. The maximum final macroporosity was calculated to be 0.55-0.60. The HRTEM images showed that there was an increased order in the microporous regions which accounts for the densification of the chars that is responsible for particle shrinkage and the maintenance of the particle integrity.

INTRODUCTION

The changes in particle structure during carbon oxidation are of importance because they can influence particle sizes and shapes, which in turn influence reaction times. Moreover, the changes in structure influence particle fragmentation, which affects combustion by changing the particle size and has a major impact on the number and size of fly ash particles produced per coal particle [1, 2]. There are several mechanisms of char fragmentation, including percolative fragmentation where the oxidation increases the porosity until the interconnectivity of the solid matrix is interrupted, fragmentation resulting from the enlargement of macropores until they interconnect and result in particle break up, and the fragmentation resulting from mechanical forces acting on weakened parts of a char particle. Reports of fragmentation in the combustion literature date back to the study of Davis and Hottel [3] on the oxidation of carbon spheres and include the studies of Walker et al. [4] and Dutta et al. [5].

The focus in this paper is on the changes in the particle structure during char oxidation in the chemically kinetically controlled regime (Regime I) and its impact on fragmentation. A useful reference point is percolation fragmentation, the theory of which has been developed for materials with a uniform pore size, for which various theories predict that the fragmentation occurs at porosities of around 0.7 (as summarized in [6]). Kerstein and Niksa [6] carried out experimental measurements on large carbon particles, 52 mm diameter and 1.5 mm thick disks, and observed that the samples disintegrated into very fine fragments at the predicted critical porosity. They

showed that this process is reproducible. However, coal chars tend to have a wide pore size distribution, ranging from the micropores, having dimension of 2 to 3 nanometers, which account for most of the internal surface area to the macropores, having dimensions in the tens of micrometers, which often account for the major fraction of the porosity. For macroporous solids, the enlargement of macropores can lead to fragmentation as the particle continuity is interrupted. This was shown early for diffusion controlled reactions and, more recently, by Weiss and Bar-Ziv [7] and Zhang et al. [8] in synthetic char particles (Spherocarb) of 200 micron reacting under chemically controlled conditions. Modeling of combustion of char that includes aspects of pore enlargement connected to fragmentation was carried out by Kang et al. [1], Salatino and coworkers [9-11], and by Kantorovich and Bar-Ziv [12, 14]. The problems in applying theory to chars are complicated by two factors. The first is the wide range of pore size distribution. The second is that the char particles shrink due to densification, a phenomenon which has a major impact on particle porosity.

The purpose of this study is to present the structural changes during oxidation to high porosity of a synthetic char -- Spherocarb. The Spherocarb particles have the advantage of being essentially ash free, being spherical, and yet having a high initial porosity in the range 60-80%, distributed approximately one-third/two-third between micro- and macro-porosity, respectively [13]. The work has been carried out in two laboratories: (i) at Ben-Gurion University, where single particle experiments were carried out in an electrodynamic chamber; and (ii) at MIT, where TGA experiments were performed and samples were characterized by high-resolution transmission

electron microscopy (HRTEM). The results of the study are to provide insights on how the macroporosity and microporosity evolve with increasing conversion under Regime I conditions and how this evolution impacts fragmentation.

Experimental

Electrodynamic Chamber (EDC) Experiments

Observation of the detailed process of fragmentation of single highly porous char particles in regime I were carried out in an improved EDC. The EDC and its diagnostic systems were described in detail in recent publications [7,15-17] and will not be discussed here. In these experiments a particle was heated vertically from below by a CO₂ laser beam. The DC voltage, responsible for the levitation of the particle, is proportional to the vector sum of the gravitational, photophoretic and free convection forces [7,15-17]. The three forces were uncoupled by periodical interruption of the laser [17]. The DC voltage was measured every second by a data acquisition system and a CCD camera recorded continuously the shadow of the particle for size and shape measurements. Freeze-frame capabilities and shutter control facilitated the digital analysis of individual images. A Mutech Corporation model IVP, frame-grabber board was used for image analysis. Size calibration was carried out by measurements of a 155 ± 1 micron diameter wire, which was placed across the center of the EDC.

Particle density was measured at zero conversion by the drag force on a particle due to imposed flow, also described in [7,15]. Figure 1 (top) presents the ratio of the drag force to weight (DV/V_0 , where DV is a voltage difference of flow and non-flow voltages, and V_0 is initial voltage without flow) of a polystyrene particle and a Sphero carb particle. The line shape depends on the flow field within the chamber (as has shown by D'Amore et al. [18]) and the magnitudes are inversely proportional to pd^2 [7]. Since the density of the polystyrene is known, the density of the Sphero carb can be obtained from the slope of a plot of $(\Delta EV/V_0)(pd^2)$ for polystyrene vs. $(\Delta EV/V_0)d^2$ for Sphero carb as shown in the lower half of Fig. 1, which yields a density for the Sphero carb particle of $579 \pm 2 \text{ kg/m}^3$. This method is valid for spherical particles. During char oxidation, as the particles become aspherical, the density of particles are obtained from ratio of mass (obtained from voltage) and volume (obtained from the images of a particle from two perpendicular angles).

TGA and HRTEM Measurements

Sphero carbon particles at various conversions were produced by reaction in a thermo-gravimetric analyzer in air at a temperature of 773 K. Carbon Conversions were determined by analyzing the weight versus time, starting from an initial weight of approximately 10 mg.

For HRTEM observation, the samples were ground for 5 minutes in a ball mill or a mortar and pestle for higher oxidation samples were sample size was limited. The

resulting powder was then ultrasonically suspended in ethanol and then dropwise deposited on lacey carbon TEM grids. An Akashi/TOPCON 002B transmission electron microscope with an LaB6 filament operating at 200keV was then used to record high resolution(590 kX) images of each sample. The images were then digitized, and an image analysis software (SEMPER6P, Synoptics Ltd., Cambridge, UK), developed specifically for application with high resolution electron microscopy was used to manipulate the stored images in order to extract data which could physically characterize the Sphero carb.

Characterization was accomplished using a Fourier Transform of the TEM images to establish periodicities. By then applying a mask to remove unwanted noise in the image, the annulus was reverse transformed to obtain a gray filtered image. This image was then converted to a two color 'extracted structure' by establishing an intensity threshold value for the pixel intensity. This extracted structure then became the basis for the statistical analysis of the lattice length (L_a) and d_{002} carbon spacing [19].

RESULTS

More than one hundred oxidation experiments were carried out in air and in pure oxygen, with moisture and without it, at temperatures varying from 700 K to 1000 K in the EDC for conversions up to 80%. Another twenty-two experiments were conducted up to near complete (up to 99%) conversion. The experiments in the TGA were carried

out in air at 773 K for conversions up to 96 percent. The structural transformations observed are summarized below.

Particle Size and Shape

In all experiments involving the EDC, the particle underwent non-uniform shrinkage, transforming an initially spherical particle into a disk at 50-60% conversion. It was observed that the particle rotated frequently up to about 40% conversion with a consequent uniform shrinkage. After that, the particle flipped occasionally and non-uniform shrinkage started, as observed previously [7,16,17]. The frequency of flips decreased noticeably when the particle evolved into a disk at about 60% conversion. At higher conversion (above 85%) the particle undertook one of the following three shape types: type I - a disk without a hole; type II - a disk with one or more holes; type III - an opened disk. Figure 2 shows the three types at high conversions (from two perpendicular sides) together with images of the initial particles.

In the experiments in the TGA, the particles maintained their spherical symmetry to high conversions (see Fig. 4). The differences between the shape particles assume during oxidation in the EDC and the TGA is due to the non-uniform heating of particles in the EDC [17]. This non-uniform heating, induced by the heating from below, results in a preferential reaction of the lower side of the particle, and explains the shape, the flipping of the particle as it becomes unbalanced, and the eventual formation of a hole in the center.

The results in the EDC and the TGA both show the dramatic shrinkage of the particles at high conversions. This is consistent with the previously reported densification of carbon during Regime I gasification or oxidation [20,21]. The rationalization for the densification was that the oxidation or gasification reactions induced reorganization of the fine structure leading to loss of pores and contraction of the microporous regions. This hypothesis was tested in this study by the use of HRTEM to study the changes in fine structure of the char with increasing carbon conversion.

Fine Structure

The results of the images abstracted from the HRTEM using image analysis are shown together with the parent samples in Fig. 3. The spacing between the fringes in the picture is around 3.4 Ångstroms, slightly larger than that expected for graphites. The images showed increased order with conversion. A quantitative measure of the increased order is provided by the lattice length L_a of the different 'graphitic planes'. These are shown in Fig. 4 for the original Spherocarb and the particles at high conversion (> 97%). At high conversions there is systematic increase in the longer lattice lengths (>15 Å). The interlattice spacing also decreased slightly. The peak in the distribution function for the original Spherocarb particles was at 3.41 Å, whereas at the high conversion (>97 %) the peak had shifted to about 3.3 Å (see Fig. 5). This

ordering of the microporous structure has important ramifications to the fragmentation of the particles.

Fragmentation

The particles chosen for this study had a high initial porosity (61 - 78%). From the percolation theory for particles with a uniform pore size, the particles started with porosities exceeding the critical value or should have fragmented after very little conversion. For more than 100 experiments carried out with conversions up to 80%, none showed fragmentation. For 22 experiments (listed in Table 1) in which the conversion approached completion (up to 99% conversion), five particles experienced minor fragmentation, and about half developed holes in the particle center. A particle break up is shown in Fig. 6, which presents a typical conversion vs. time curve with a sequence of shadowgraphs depicting the shape development of a Sphero carb particle of 204 micron diameter at various conversions, oxidized in air at $T=920$ K (experiment number e7-281, in Table 1). The particle conversion was obtained from the weight loss of the particle assuming that the charge remained constant, a good assumption at this temperature [15]. The initially spherical particle turned into a disk at about 60% conversion. Spatial dimensions of the particle are included in the figure. The projected images from two perpendicular directions at 88% conversion show that the disk diameter decreased to 0.75 of the initial particle diameter, while the thickness decreased to 0.62 of the initial diameter, and a hole appeared around the center of the disk. The hole grew with increasing conversion and, at about 98% conversion, evolved

into an opened ring. Further burning caused the particle to break into two fragments. The print at this conversion shows one half of the broken ring. In fact, both halves were suspended in the chamber after fragmentation. These two fragments were oscillating around the center at a large distance from each other. Since only one could be suspended in the center, the field parameters (AC and DC amplitudes and AC frequency) were adjusted such that one of the fragments drifted away and the other was kept. This fragment continued to oxidize and eventually broke into two other fragments at higher conversion.

Table 1 summarizes the results of only the experiments that were carried out to high conversions . From the 22 experiments only five particles fragmented. One can see that fragmentation occurred only for those particles that developed opened disks -- Type III particles. However, not all particles that developed holes fragmented, but only those in which the progress of the reaction produced shapes in which the particle continuity was broken.

DISCUSSION

In order to understand the lack of fragmentation at high conversions in these studies one needs to examine the separate behavior of the macro and micro porosities. The change in total porosity of the particles versus conversion were obtained for six experiments from the changes in particle mass and volume. The initial values and final values of the porosities were obtained by assuming the dense phase had the density of

graphite ($2,200 \text{ kg/m}^3$), a reasonable assumption given the proximity of the interlattice spacings of the micro-structure of the Spherocharb to that of graphite. The results in Fig. 7, demonstrate that although the porosity increase is less than would be expected in the absence of particle shrinkage, it is sufficient to provide final porosities in the range 0.83-0.87 in excess of the percolation threshold of about 0.7 for a homogeneous material.

If the material is considered as having a bimodal distribution, then one can assess the probability of exceeding the percolation threshold in either the macro-porous or micro-porous regions. With about one-third of the porosity of Spherocharb particles being in the micro-pores and two-third in the macro-pores [15], the initial macro-porosity is in the range 40-50%, well below the critical value, and the micro-porosity is half that value. The results of Hurt et al.[21] show that the macro-features, including macro-pores, in chars shrink in proportion to the shrinkage of the entire particle; therefore, the macro-porosity will stay constant during conversion. The micro-porosity will increase but the values, obtained as the difference between the total porosity and the macro-porosities, will always be well below the threshold value of 0.7. Therefore the lack of fragmentation of the Spherocharb particles even at high conversions can be explained by the bimodal pore distribution, where the micro-porous and macro-porous regions maintain their integrity since neither reaches a porosity equal to the percolation threshold.

The formation of holes around the center of the particle was a result of the uneven heating of the particle resulting in the local acceleration of the reaction rate. When the hole break through the walls of the particle a ring is obtained and the further selective reaction can result in the fragmentation for selected particles as was observed.

The results presented in this paper on the changes in the macro-structure and micro-structure of carbons can provide guidance to the development and refinement of models [e.g., 8, 12, 14] that can take into account the ordering that leads to shrinkage as well as the changes in the pore structure of chars with oxidation or gasification. The data that was obtained in the EDC showed that fragmentation is of less significance than might have been inferred from simple percolation theory. The information on the micro-structure of carbons provides insights on the reordering of the carbon structure which results in the densification of the chars and the preservation of the structural integrity of particles.

SUMMARY AND CONCLUSIONS

There was no observation of fragmentation of the entire particle structure in all numerous (well above hundred experiments) carried out (including the twenty-two conducted to high conversions). Experimental porosity data show that the total porosity increased from initial value of 0.6-0.76 to final value of 0.83-0.88. For the initial polymodal pore size distribution of Spherocarb, the macro-porosity is well below the

critical porosity of 0.7. Therefore, consumption of carbon inside the particle was compensated by reordering and shrinkage so that the percolation threshold is not attained for the entire particle. Evidence is provided from the examination of the micro-structure of particles at different conversion that the shrinkage is the result of the increased ordering of the graphite-like micro-structures in carbons with increased carbon conversion.

It was observed that holes were formed at 65% to 96% conversion in thirteen experiments. These holes are a consequence of non-uniform rate of reaction obtained under non-uniform laser heating. The expansion of such holes led to fragmentation in a few cases, but this mechanism of fragmentation is quite distinct from percolative fragmentation.

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Figure captions

Figure 1. Top - ratio of drag force to weight ($F_d/mg=DV/V_0$) vs. flow rate for polystyrene particle (x) and for Sphercarb (o) particles. Bottom - $(F_d/mg)rd^2$ of the polystyrene particle vs. $(F_d/mg)d^2$ of the char particle, and best fit (solid line).

Figure 2. Examples of three types of shapes of initially spherical particles at high conversion. Type I - a disk without a hole at 94% conversion. Type II - a disk with one hole at 98% conversion. Type III - an opened disk at 95% conversion. For comparison, next to each form, a print of the initial particle. The prints at high conversion are from two perpendicular sides.

Figure 3. Shadowgraphs of Sphercarb Particles (initial diameter 160 μm) reacted in air at 773 K and the HRTEM structures for each sample: top, 0% conversion; middle, 44% conversion; bottom, > 97% conversion.

Fig. 4. Distribution of lattice lengths L_a (in Ångstroms) for Sphercarb particles at zero and greater than 97 percent conversions.

Fig. 5. Distribution of interlattice spacings d_{002} (in Ångstroms) for Sphercarb particles at zero and greater than 97 percent conversions.

Figure 6. Conversion versus time and a sequence of shadowgraphs presenting the development of shape of a 204 microns Sphercarb particle oxidized in air at 920 K as a function of conversion; C is conversion, l is length, and w is width.

Figure 7. Ratio of porosity to initial porosity vs. conversion. Initial and final porosities are indicated in figure.

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