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The Role of Pore Structure on Char Reactivity

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Quarterly Progress Report

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Objective

The objective of this project is to experimentally determine the evolution of pore structure during char conversion and use this information to subsequently examine various pore models for char conversion.

Introduction

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

Progress Report

The study is proceeding in its focus on development of methodology. However, modeling work to explain the small perturbations encountered in the CO₂ profile of a single char particle burned in the fluidized bed. Significant progress has also been made in the production of the carbons to be used in the EDB to further examine the role between the relationship given between conduction and porosity. The tools to image and examine soots and other amorphous char has also been refined for use in studying the evolving microstructure of carbon during combustion.

The model discussed previously has been refined to point that it is being prepared for an article to help explain the combustion profiles of a single char particle. It was developed in order to explain the low frequency noise that generates variations of approximately $\pm 10\%$. This problem may be explained by considering the concept of inaccessible porosity, as given by Perlmutter and Zygourakis. Simplified, one can assume that not all of the porosity is accessible at a given time, due to blockage of pores in the solid that are reacted away. As the blockage is cleared, new regions are revealed that can significantly increase reactive area.

Our model follows this approach, although we have a great simplification available to us. From previous work, the Oxygen penetration depth is estimated to be $17\mu\text{m}$ (Sundback). Thus, our system can be largely based on the classic shrinking sphere model, with one important variation. Distributed throughout the sphere are a number of "pore" spheroids of uniform size that become accessible to the reactant gas only as the

reaction front reveals them. The spheroids are distributed randomly under the criteria that

$$\epsilon = \frac{R_{char}^3}{n R_{pore}^3},$$

where n is the number of pores needed to generate the appropriate porosity. To simplify the model, the following assumptions are also made about the pores: (1) The pores are independent of each other. (2) The pores do not grow during reaction. (3) The surface area will not be greatly disturbed, so areas based on that of a sphere can be made. A representation of the char under these assumptions is given in Figure 1.

Under the shrinking sphere assumption, one can assume for the basis of this analysis

$$rate = k A_{char}$$

that the reaction rate is proportional to the surface area exposed during reaction. Under the shrinking sphere assumption, there is no ϕ and θ dependence on the rate of combustion due to uniform combustion, so the evolution of surface area over time reduces to a one dimensional problem in R .

However, added to the area from the char is the area from the pores, giving a total surface area of

$$A = 4 \pi R_{char}^2 + \sum 4 \pi R_{pore}^2$$

where the summation is over the pores that are accessible to the reaction front.

Using the shrinking core model assumption of constant radial decrease, one can numerically generate curves for the evolution of the surface area as given By Figure 2. To allow for comparison of the effects of different areas, the initial concentration (with no exposed pores) was set to be 1000ppm CO_2 . With very small pores, a relatively constant area to radius ratio is developed, resulting in little perturbation. However, as the radius of pores increases, surface area peaks are generated due to the revelation of pores. These peaks become relevant at pore radiuses of approximately 0.5mm. While this may seem large, the char particles used were originally of the order 7 mm in diameter. It should also

Figure 1. Illustration of the pore model used. As the reaction proceeds, the previously unaccessible pores are revealed to participate in the reaction until the reaction front passes them.

Figure 3. Modeling results to explain the small (10%) variation seen in the combustion of single particles of char. Above a Pore radius of 0.5 mm, the required perturbation is seen, and these variations increase with increasing pore size.

be noted that our spherical pores can be inferred to model "pore" regions, not just pores. These pore regions would be clusters of smaller pores that are initially inaccessible but revealed during reaction.

To further refine the model, we will conduct tests on the fluidized bed, removing char particles and viewing them to see if the porosity is changing during reaction or it is constant(our model predicts that it will be relatively constant). Furthermore, a pore size distribution will be tied to the model to better represent the char.

For our work in helping to characterize the role of mesopores and micropores, and the change in porosity during combustion, we need various particles to work with in the EDB. These particles are being produced in conjunction with Professor Levendis of North Eastern University. The process to produce the particles has been discussed elsewhere, but it can be described as the pyrolysis of polymer carbons to produce highly uniform particles. The porosity can be varied by adjusting the production rate and/or by the addition of carbon black to the feed solution. The particles produced range in sizes of 100-200 microns, ideal for use in the EDB. However, particles in the range 150+ microns are quite difficult to produce due to the limitations and interrelationships between furnace temperature and viscosity of solution-which currently limits us to producing only cenospheres (hollow chars) in this range. In the next month, the particles will be characterized fully by BET and SAXS studies before work proceeds. Working with Barziv of Ben Gurion University, we will also test the combustion properties of these carbons as compared to other past carbons used in the EDB. The carbons will also be reacted in a TGA in order to compare the differences between the two instruments.

One of the main hindrances to working with soot and other disordered carbons(including high conversion char) in the past has been the difficulty in characterizing them without extremely time-consuming manual examination, which is prone to error. To that end, a computerized system of characterizing the soot has been developed at MIT. The system involves taking TEM photographs of the relevant carbon. The TEM photo is then scanned into an IBM PC equipped with SEMPER V©. A Fourier transform of the image is taken, and frequencies are selectively masked out and filtered. Then, transforming back to an image, one can obtain images as given in Figure 3. Using the software, characteristic line counts, spacing and the like may be determined. Although still in its formative stage, the system offers a great deal of promise in the simplification of this complex task.

Future Work

Original Image

Power Spectrum

Extracted Structure

Figure 3. Methodology used to characterize amorphous carbons. A power spectrum is taken of the original image to quantitatively measure lattice spacing and angular dependance. The extracted structure can then be used to measure the number of lattice fringes, their length, circularity and other properties.

There will be relatively little work performed in the next quarter due to the primary graduate student involved in the project due to his participation in a cultural science exchange program with Japan. However, the particles generated by the Levendis method will be characterized and subsequently, the method of image processing will be pursued on soots if time presents itself.

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