The Role of Pore Structure on Char Reactivity

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Quarterly Progress Report

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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 soot 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 modeled.

Progress Report

The project has stressed the examination of microstructure and micropores in the last few months. Exciting work has continued to be done on the development of methodologies to view small submicron particles with a combined TEM/image processing system. Furthermore, the alteration of microstructure is being explored by examination of the same particles under Small Angle X-Ray Scattering(SAXS). Examination of the use of N_2O for use as a tracer gas for following the evolution of pore structure is progressing as the FTIR is recalibrated for CO, CO_2 , N_2O and NO sampling.

The major work accomplished this quart has been done with the aid of a recent addition, Ghokan Senel, a NATO sponsored post doc that will be with our research group for approximately six months and an expert on surface area determination. With his help, a flowing CO_2 surface area measurement technique has been reexamined and implemented based on the thesis by Du and using the TGA. The basic premise is much like the classic BET systems, measuring CO_2 absorption from different partial pressures of CO_2 gas mixtures. However, the exciting feature of this system is that surface area's is measured directly after combustion in the same system. Therefore, losses due to transport are eliminated, although careful buoyancy correction factors must be made to correct for the effects of different gases on the measuring pan.

Using the TGA/ CO_2 area system, several experiments have been completed, reacting soot to various combustion levels and then measuring their CO_2 surface areas. This soot work will allow greater understanding of the role the nature of chemical structure

and porosity in the combustion of carbons plays. The resulting profiles of the reacted soot structures are plotted in Figure 1. Two soot profiles are plotted, the NIST soot, which is an environmental standard with high volatile content and low ash, and a soot provided by Professor Levendis of North Eastern University that has a much lower volatile content, but has extremely high ash content. As shown, there is a continuing increase in the surface area of the soot particles. The soot starts with an initial surface area of approximately 175 m²/g. Upon devolatilization to constant weight, the surface area increases by a factor of approximately two. A slow gradual increase is then seen up to a conversion of approximately 50%, when a much more dramatic increase begins to take place, up to the limit of our measuring technique, which becomes less accurate at higher conversions due to low sample weight. However, the data is of the same form as obtained by Du previously, but for an extended range of up to 90% conversion. Beyond the 60% conversion Du explored, the soot rapidly increases in surface area. This may be due to the low temperature graphitization of carbon due to reaction reported by Hurt.

This carbon densification is further being pursued by using Small Angle X-Ray Scattering(SAXS) and TEM on the samples generated with the TGA. As seen in Figures 2 and 3, the profiles generated by the graphs are of different magnitude and appear to follow a well-defined pattern. The profiles themselves are the intensity defined as counts/sec plotted versus q ,

$$q = \frac{4 \pi}{\lambda} \sin(2\theta),$$

which is an angle measure of the distance from the center of the X-ray beam. However, to arrive at quantitative results, the absolute magnitude of the intensity must be known. To accomplish this, a background subtraction must be made. Unfortunately, past a q value of approximately 0.8, the background unexpectedly becomes larger than the sample intensity. This is now realized to be due to increased absorption and scatter by the samples. Evidently, a great deal of difference in magnitude may be due to this absorption difference between sample and blanks. However, it is interesting that absorption seems to go down as conversion increases for the same thickness sample of soot particles. It is

quite possible that the packing characteristics of the particles may be causing the change in sample absorption, although this is only an assumption for now. These experiments will be repeated in February to remove the rise in background readings from a q value of 0.8 to 2.5. The system in place presently uses capton film to hold an inert atmosphere to limit scattering at long detector distances, but by moving the X-ray detector from a distance of 120 cm to approximately 35 cm, these items will be removed to improve performance.

Further work is continuing on the examination by the examination of the change in microstructure by using the TEM as explained in the previous progress report. Due to the slow nature of the TEM work, both the primary graduate student and the new post doc have been trained in the use of the TEM, which will allow access to the use of the TEM for microstructure characterization during off-peak hours.

Further work has also been done on developing the experimental apparatus necessary to confirm the use of the N_2O /char reaction as a tool for the monitoring of the evolution of not only pore evolution, but more important, the evolution of the accessibility of the pores. To accomplish this, detailed knowledge of the NO , N_2O , CH_4 , CO and CO_2 present in the off gases of combustion must be monitored. We have refurbished the FTIR cell's mirrors, and now can sample concentrations with less than 5% error quantities as low as 5 ppm for the NO , N_2O and CH_4 , and down to about 100 ppm for the fixed gases(CO and CO_2). The completed system is already being used to generate preliminary data using a sample of Illinois #6 coal.

Future Work

The soot structure during reaction will be characterized more fully by the use of the TGA, TEM, and SAXS apparatus. Furthermore, conclusive evidence as to the use of N_2O as a pore tracer will be generated using the Fluidized Bed. Due to movement of the laboratory area used to house the Electrodynamic Balance, no further work will be done on this tool at MIT for the immediate future due to the sensitive optics involved (approximately 3-4 months).

References:

Du, Z., Kinetic Modeling of Carbon Oxidation, MIT Mechanical Engineering PhD Thesis, 1990.

Hurt, R. H., Dudek, D.R., Longwell, J.P., Sarofim, A.F., "The Phenomenon of Gasification-induced Carbon Densification and its Influence on Pore Structure Evolution," *Carbon*, 26, pp 433-449, 1988.

Figure 1. Graph of Surface Area versus Conversion. The soot undergoes a relatively constant rise in surface area until about 60% conversion, when a rapid surface area growth to the limit of a graphite plane appears.

Figures 2 (Levendis Soot) and 3 (NIST Soot). The Levendis Soot would appear to keep approximately the same intensity profile, which can be related to pore density during conversion. The Nist Soot would seem have a greater portion of high q (small diameter) intensity, indicating that the density of smaller pores has increased. However, more runs with better data at higher q values need to be performed to validate this.