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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

Massachusetts Institute of Technology
Department of Chemical Engineering

Cambridge, MA 02139-4307

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Morgantown Energy Technology Center

P.O. Box 880

Morgantown, WV 26507-0880

Attention: Wu K. Lan

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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 stressed the examination of microstructure and micropores in the last few months. The most in depth work has involved the investigations of micropores using the Small Angle X-Ray Scattering to obtain measurements of the total surface area and comparing them to gas absorption surface areas.

As explained in the last quarterly report, investigation of soot structure has progressed by using the TGA to react soot particles at very low temperatures to obtain complete kinetic control. Various conversion levels have obtained for two types of soots, a high volatile, low ash diesel soot(NIST), and a low volatile, relatively high ash content soot(termed simply Diesel soot). Surface areas were examined by use of TGA flowing CO₂ isotherms at 25°C, as plotted in Figure 1.

As can be seen, the initial surface area of both soots is in the region of 50-100 m²/g for the soots as received. To obtain measurements of the levels of intrinsic rate without interference by the volatile material, the soots were devolatilized at 1150K for approximately 15 minutes until a constant weight was achieved. It is during this step that the greatest increase in surface area is seen, with increases of approximately 250 m²/g for both soots. This is the were much of the high surface area is generated in the system. The short exposure to high temperature cannot account for this variation, although this possibility will be checked by using TEM to examine the microstructure before and after devolatilization. However, the most plausible explanation is that this surface area is being generated-either through pore rearrangement or through

revelation of previously inaccessible pores. The soots do tend to show a similar trend once this initial surface area peak is generated until about 50% conversion, where the high ash Diesel loses much of its generated surface area. While the increasing mass fraction of the low surface area ash would account for some of this drop, it cannot account for all of the decrease. It is possible that the surface area is also decreasing due to simple reaction of material, or densification of the soot.

To further examine this evolution, Small Angle X-Ray scattering was used to examine the closed porosity of the individual soot particles. SAXS intensity profiles have been used in several studies to determine the shape and size of carbons. The basic principle involves scattering of X-Ray radiation by differences in electron densities. In most studies, two regions have been identified and used to characterize surface areas, the Guinier and Porod regions.

As the scattering angle becomes very small ($h \rightarrow 0$; $h = \frac{4\pi}{\lambda} \sin \theta$) the Guinier region is reached and the scattered intensity exponentially rises as

$$I(h) = V \rho_e^2 \exp\left(-\frac{h^2 R_g^2}{3}\right), \quad (1)$$

where R_g is the electron radius of gyration about the center of electronic charge, V is the irradiated volume and ρ_e is the electron density..

For larger angles of SAXS, the Porod approximation holds as $h \rightarrow \infty$ for collimated optics and a two phase system with distinct electron densities,,

$$I(h) = \frac{2 \pi \rho^2 S}{h^4} \quad (2)$$

where S is the total surface area of matter contained in volume V . To avoid the use of absolute intensity measurements, which are quite difficult to measure, it is common to

normalize the intensity by the invariant Q_0 , or the total integrated intensity given by

$$Q_0 = \int_0^\infty h^2 I(h) dh = 2 \pi^2 (\Delta\rho)^2 \frac{\Delta V}{V}, \quad (3)$$

where $\Delta\rho$ is the electron density of the difference between two phases.

Evaluation of Q_0 has proved difficult due to the limitations of the scanning equipment. The lower limit is not a significant problem, as $h^2 I(h)$ is small as h tends to zero, although it must be extrapolated due to the presence of the beam stop. However, at higher values of h , the small $I(h)$ can be influenced by extraneous sources, such as scattering by air molecules. Therefore, the numerical integration was divided into three parts,

$$Q_0 = Q_1 + Q_2 + Q_3 = \int_0^{h_{\min}} h^2 I(h) dh + \int_{h_{\min}}^{h_{\max}} h^2 I(h) dh + \int_{h_{\max}}^\infty h^2 I(h) dh. \quad (4)$$

where Q_2 is evaluated from the measured scattered intensity $I(h)$ between $h_{\min}$ and $h_{\max}$, corresponding to the minimum and maximum scattering vectors of the measured scattering curve. Q_1 was estimated using the Guinier approximation for $I(h)$, while the Porod approximation was used for integration to infinity. Figures 2 and 3 give examples of typical Guinier and Porod Plots for both diesel soots.

The total specific surface area may then be evaluated as

$$S_{sp} = \frac{\pi \epsilon (1 - \epsilon)}{\rho} \frac{\lim_{h \rightarrow \infty} h^4 I(h)}{Q_0} \quad (5)$$

where ϵ is the porosity and ρ is the apparent density of the sample respectively.

The most difficult issue when dealing with soots is the use of the apparent density/porosity. The small sample sizes (of the order of 10-50 mg) precludes the use of most analytical methods for determination of apparent density. Therefore, two limiting factors were considered, a constant density or a constant diameter during devolatilization, as the real density variation must fall between these extremes. To give

a more realistic approximation, alternative models were used for the evolution of porosity during oxidation. Hurt's densification method¹ was used, as the densification phenomenon has been found to hold over large ranges of particle sizes. Furthermore, his theory is supported by the work of Ishiguro² on soots, although he explained the results of the analysis are plotted in Figures 4 and 5.

As can be seen by the variation in the surface area, the most important variable in determining the surface area is the model used to account for devolatilization. However, discounting this factor, which will be solved by simply measuring the diameter during and after devolatilization and the density change, the trends are similar despite the increase differences in initial starting points. The NIST surface area is seen to be higher throughout the system by an appreciable degree, with a slightly increasing overall surface area during reaction. The most important factor is to look at the trend between 0 and 18% conversion. The surface area as measured by SAXS and by CO₂ are both similar in that there is a rise in area, although this is most striking for the Hurt approximation. This would indicate that the surface area of the soot is being generated by reaction, and not by opening up of inaccessible pores. The other Diesel soot also shows an increased surface area from the SAXS data. The most notable feature is that all measurements indicate a decrease in the surface area of the soot after 50% conversion. As expected for the low volatile soot, the increase in surface area is not dramatic in the CO₂ as in the NIST, although this may be due to the fact that the soot is exposed to elevated temperatures at 300°C for a considerable period of time during collection, so some rearrangement may have already occurred.

¹ 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.

² Ishiguro, T., Suzuki, N., Fujitani, Y. and Morimoto, H., "Microstructural Changes of Diesel Soot During Oxidation," *Combustion and Flame*, **85**, pp 1-6, 1991.

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 continuing 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). An article to be submitted to Carbon on the SAXS soot work is being prepared for publication.

References:

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.

Ishiguro, T., Suzuki, N., Fujitani, Y. and Morimoto, H., "Microstructural Changes of Diesel Soot During Oxidation," *Combustion and Flame*, **85**, pp 1-6, 1991.

CO₂ Surface Area Evolution

Figure 1. Evolution of the surface area of Soot during oxidation. The high initial surface is thought to be revaluation of previously inaccessible pores during combustion. The Diesel drop in surface area may be predominately due to the high ash content.

Figure 2. Example Guinier plot for the NIST samples. The Diesel exhibits similar trends.

Porod Invariant Plot for NIST Soot

Figure 3. Example of typical Porod invariant plots. Under the Porod theory, the lines should asymptote to a constant h^4I value. The data does not perfectly come to a straight line due to various other scatterings which interfere with the signal.

Figure 4. Evaluation of the SAXS data to obtain surface area. Two cases were examine in the Hurt model, a constant density and a constant diameter during devolatilization case. While the values for area are generally higher than the CO₂ surface area, an increasing and then decreasing trend is observed.

Figure 5. SAXS results for the NIST Diesel. All values tend to increase during conversion, although not to a large extent. The most interesting factor is the constant density plot, which agrees almost exactly with the CO_2 surface area. This would tend to support Ishiguro's work, as one can view his successive shell model as an indicator of constant density.