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Structural Evolution of Carbon

During Oxidation

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Abstract

The examination of the structural evolution of carbon during oxidation has proven to be of scientific interest. Early modeling work of fluidized bed combustion showed that most of the reactions of interest occurs in the micropores, and this work has concentrated on these pores. This work has concentrated on evolution of macroporosity and microporosity of carbons during kinetic controlled oxidation using SAXS, CO₂ and TEM analysis.

Simple studies of fluidized bed combustion of coal chars has shown that many of the events considered fragmentation events previously may in fact be "hidden" or nonaccessible porosity. This makes the study of the microporous combustion characteristics of carbon even more important.

The generation of a combustion resistant grid, coupled with measurements of the SAXS and CO₂ surface areas, fractal analysis and TEM studies has confirmed that soot particles shrink during their oxidation, as previously suspected. However, this shrinkage results in an overall change in structure. This structure becomes, on a radial basis, much more ordered near the edges, while the center itself becomes transparent to the TEM beam, implying a total lack of structure in this region. Although complex, this carbon structure is probably burning as to keep the density of the soot particles nearly the same.

The TEM techniques developed for examination of soots has also been applied to Spherocharb. The Spherocharb during oxidation also increases its ordering. This ordering, by present theories, would imply that the reactivity would go. However, the reactivity goes up, implying that structure of carbon is secondary in importance to catalytic effects.

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1. Introduction

Coal is an extremely heterogeneous material that is difficult to characterize. Coal is essentially fossilized organic matter formed by geological processes and is composed of a number of distinct organic entities called macerals and lesser amounts of inorganic substances (minerals). The macerals of coal consist of principally carbon with various amounts of hydrogen and oxygen, ranging from ~50 wt % to over 95 %. Char is the product of pyrolysis of coal, and is considered to be formed as an intermediate in combustion after the devolatilization stage.

The reaction of carbon (char) with oxidizing gases is controlled by the following steps:

- (1) Mass transfer (by diffusion) of gaseous reactants from the bulk gas to the carbon surface.
- (2) Adsorption of reactants on the surface.
- (3) Surface reactions and formation of adsorbed product.
- (4) Desorption of products.
- (5) Diffusion of products to the bulk gas.

The kinetics of carbon oxidation is determined by which governing step is slower. This determination is based on process parameters (temperature and pressure) and carbon properties (active site concentration and catalytic effects).

At higher temperatures, the reaction may be controlled by diffusion of reactants to the external surface of the particle (Regime III). At lower temperatures, the rate determining step is due to surface kinetics (Regime I). At intermediate temperatures, the reaction may be controlled by both

the chemical processes and diffusion through the pores and the external surface boundary layer (Regime II).

One measure of the overall chemical kinetics of the heterogeneous carbon reactions with oxidizing gasses is calculated by the following

$$R = -\frac{1}{W_0} \frac{dW}{dt} \quad (1)$$

where R is the overall reactivity at temperature T , W_0 is the initial mass and dW/dt is the rate of weight loss. A better measure of the kinetics is the rate of reaction normalized by the actual, rather than the initial mass of the carbon,

$$R = -\frac{1}{W_t} \frac{dW}{dt} \quad (2)$$

where W_t is the actual mass at time t . The intrinsic reactivity is expressed per unit surface area and is given by

$$R_i = -\frac{k_i P^m}{A} \quad (3)$$

where R_i is the intrinsic reactivity, k_i is the intrinsic reactivity (related to temperature by the Arrhenius expression $k = A e^{-E/RT}$), P is the partial pressure of reactant gas, m is the true reaction order, and A is the surface area. The overall reactivity R and the intrinsic reactivity R_i is related to the intrinsic reactivity by

$$R = \eta A_i R_i \quad (4)$$

where η is the degree of gaseous penetration and A_i is the total internal surface area.

The physical properties of carbon at various temperatures or mass can be experimentally evaluated accurately, but the "reactivity" of carbon is difficult to measure with precision. Smith¹

compiled intrinsic reactivities of large numbers of carbons and compared them, finding differences of up to four orders of magnitude (Figure 1).

The intrinsic reactivity of carbon is a function of the gas used, and a surface area evaluation method is necessary. The measurement of the surface area available to a reacting gas molecule is not a straightforward task. Methods of physical adsorption of gases to obtain isotherms and their interpretation often indicate pore volume rather than surface area.

The measurement of surface area is most usually determined by gas adsorption measurements using Brunauer-Emmett Teller theory. A clean surface is prepared by outgasing in vacuum, and then the gas (normally nitrogen or CO_2) admitted in precise amounts. The amount of gas adsorbed is calculated using pressure differentials. From the isotherm of the gas adsorption, a value of the surface area can be inferred. Another measure of surface area is active surface area (ASA), measured by chemisorption of oxygen on clean carbon surfaces,² which measures the active sites available to reaction.

The surface area can also be measured by the use of Small Angle X-ray Scattering (SAXS), of which a typical experimental setup is shown in Figure 2. SAXS is produced by the interactions of X-rays with variations in the electron density caused by variations in the scattering medium on a scale of 0.5 to 200 nm, and is able to measure micro- (width less than 2 nm), meso- (width between 2 and 50 nm) and macropores (width greater than 50 nm³). For porous solids, the greatest change in electron density is assumed to be at the solid void interface. Evaluation methods for obtaining the surface area include the Debye equation, Porod's Law and the Guinier equation. Although all three theories use different assumptions, the three theories use plots of the

intensity of scattering in one form or the other to obtain an estimation of the surface area (see Chapter 4).

The surface area measurements are actually a measure of the structure of the carbon. For most chars, the surface area is predominantly in the micropores, while the volume is predominantly in the macropores.⁴ Microporous carbons have a very disordered structure as revealed by high resolution transmission electron microscopy (HRTEM).⁵ The various models proposed to describe the microstructure differ in detail, but the essential feature of all of them is a twisted network of defective carbon layer planes cross linked by aliphatic bridging groups.

Transmission electron microscopy provides a means of obtaining high resolution images of carbon material. Figure 3 provides a rough schematic of a typical TEM microscope. The preparation techniques for TEM are quite difficult, as it is necessary to obtain very thin sections of carbon less than 100 nm of uniform thickness. Proper preparation can provide direct imaging of the layer planes in carbon materials, reveals the complexity of the most regular structures, and shows ordering down to the nanometer level,⁶ as shown in Figure 4 and Figure 5.

The principal parts of the more ordered structure are essentially graphitic. Small volumes have graphitic like structure, as exhibited in Figure 6. However, the presence of defects, distortions and hetero atoms destroys the regularity giving disordered media. Little energy is needed to slide the graphitic layers over one another due to the weak Van der Waals forces holding the layers together. Twisting them so that they are not aligned with one another is possible leading to structures which have roughly parallel and equidistant layers but with random orientation, so called "turbostratic" carbon. Heat treatment of some of these disordered carbons

can lead to decreases in these defects and subsequent increase in the graphitic nature of the carbon, as depicted in

Figure 7.⁷ The study of these defects is important to the understanding of mechanisms of gasification.⁸

The reason for the extensive study of graphitic ordering and its effects on oxidation is that the edge carbon atoms are more reactive than basal plane carbon atoms⁹ Geometrically, as the oxygen (or other gasifying agent) approaches the graphite lattice, it can undergo reaction either at the edge of the basal plane or on the basal plane itself. Rates at the edges are 10^2 to 10^3 times faster on the edges than on the basal plane.¹⁰ Even under high temperatures where diffusional control begins to effect reactivity ($T = 1100$ and $1500K$), the oxidation rates of edge carbons are still 10 to 29 times higher¹¹ than basal plane carbon

This study explores the effects of porosity upon the reactivity of model chars. The effect of large macropores on the combustion time of large particles in an FBC is explored in Chapter 2. The structural evolution of soots during oxidation, and a new technique for examining nanometer size objects is discussed in Chapters 3 and 4. The structural evolution of Spherocarb, a model compound frequently used as a char model is discussed in Chapters 5 and 6.

Figure 1. Data from Smith et al¹ showing intrinsic reactivities of carbons.

Figure 2. Schematic of the SAXS Apparatus.

Figure 3. Schematic of the TEM Microscope setup

Figure 4. An ordered graphitic tem structure produced commercially with anathraphene. The original TEM image was taken at 590kx, and is a prime example of the d_{002} structure of graphite. One cannot measure the lattice length (L_a) for this sample due to its extreme length.

Figure 5. A carbon with turbostratic structure. This TEM micrograph of Spherocharb was taken at 590 KX, and reveals some layering of the sample. However, unlike the graphite in Figure 4, there is not a definable area that is conducive to analysis.

Hexagonal Unit Cell

Rhombohedral stacking

Figure 6. Diagram of perfect structure of consisting of hexagonal or rhombohedral stacking of the perfect hexagonal planes of graphite(from Marsh, 1993⁶).

Figure 7. Generation of local graphitic level in carbons by heat treatment from Marsh et al⁷. As heat treatment temperature increases from 1000C to 2400C, ordering increases.

2. Evolution of CO₂ During Combustion in a Fluidized Bed: Random Pore Model

INTRODUCTION

Prediction of the carbon content in fluidized beds is important because carbon losses in the bed are proportional to the carbon loading, because of carbon's role in the reduction of nitrogen oxides formed in the bed and because of the importance of carbon content for final ash disposal. The carbon load is proportional to the carbon particle burnout time, which is in turn related to the particle diameter raised to a power between 1 and 2. Fragmentation and attrition producing smaller particle sizes will thus decrease the burning time and the carbon content.

Evidence for fragmentation is provided by the variation in products of combustion of single coal particles. Sundback et al.¹² explained this variation by postulating fragmentation of single char particle, using CO₂ profiles to obtain the size and number of coal fragments evolved during reaction. However, the Zygourakis and Sandmann¹³ explained the same behavior by the use of a discrete structural model, where reaction rate increased sharply when the reaction front reached large internal cavities that were previously unavailable for reaction. In this present study this approach is modified to simulate the variation in CO₂ emissions from single burning coal particles by using a simple system of randomly distributed pores throughout a spherical char particle. Only the penetration depth and initial pore sizes are used as structural model parameters.

EXPERIMENTAL

Batch combustion experiments were performed in a small-scale quartz glass bubbling fluidized-bed reactor with an inner diameter of 57 mm. A bed of silica sand (particle size 150-212 μm) with a bed height of approximate 50 mm was fluidized by oxygen in helium. The oxygen concentration in the inlet gas stream was varied from 1-15% by use of mass flow controllers. The flow rate was set to 2.5 L/min at STP conditions. Coal particles, of 5-10 mm in diameter were burned at temperatures between 700°C and 850°C. A nondispersive infrared (NDIR) detector was used to measure the overall conversion of carbon to CO_2 . An attached Fourier transform infrared (FTIR) spectrometer equipped with an MCT detector and a low-volume gas cell of 223 cm^3 was used to monitor CO_2 , CO , and CH_4 . All measurements of the off-gas indicated that except during the devolatilization step, the CO and CH_4 accounted for less than 1% of the total fixed carbon of the coals tested. A complete schematic of the system is given in Figure 8.

RESULTS AND DISCUSSION

The data shown in Figure 9 is representative of most CO_2 profiles of coal burned in a fluidized bed. The high initial peak is due to the devolatilization of the coal particle when it is initially introduced into the bed, while the smooth profile at high conversions is due to the multiple fragments which are generated toward the end of the run when attrition takes its toll. Very large values of variation for CO_2 profile may be explained as a large fragmentation event. However, throughout the burning of the particle, there is a random variation in the CO_2 profile of approximately 5-10% from the mean. According to the works of Zygourakis^{14,15} and Perlmutter^{16,17,18,19}, even in the kinetically controlled regime, not all the porosity is accessible at a

given time, due to pore blockage. As the blockage is cleared, new regions are revealed that can significantly increase reactive area.

Our model follows a similar approach as the Zygourakis model, but with assumptions that allow it to model Regime II combustion. The model relies on the fact that different pore sizes will have different depths of penetrations. One may numerically calculate the extent of this penetration by calculating the penetration depth of the oxygen for an assumed pore size. Smith²⁰ gave the penetration depth for a pore size of r_p as

$$L = \left(\frac{r_p D_{eff} C_{O_2}}{4 R_{chem}} \right)^{\frac{1}{2}}. \quad (5)$$

where r_p is the pore radius, D_{eff} is the effective diffusivity of the gas (O_2) of given concentration C , and R_{chem} is rate of reaction of the char.

The penetration depth as a function of pore radius and temperature are calculated and given in Figure 10 and Figure 11. For the FBC particles examined in our study, the temperature ranged from 950-1150K, while the particle size ranged from 5 mm to 10 mm in diameter. As seen in Figure 10 under these conditions, for virtually all pore sizes, the penetration depth is much greater than the average size of a pore. However, as seen in Figure 11, the penetration depth is smaller than the particle size for micropores, but for macropores, the penetration depth is of the same order of as the particle size. Therefore, one can make the assumption that micropores serve only as reaction sites for the gasification of the char. Furthermore, due to the low diffusion of gasses in these pores, only macropores which are directly accessible to the gas act as highways. Thus,

the variation in CO₂ generation may be a result of simply reacting away blocking shells of micropores and exposing macropores.

To test this hypothesis, a simple model was designed. Under the FBC conditions studied, we are typically in regime II for large particles, where only partial penetration of the char is achieved.

The base model we assume is the classic shrinking sphere model (regime III), with variations to account for the penetration of the particle by reaction gasses. Distributed throughout the sphere are a number of "pore" spheroids of uniform size that act as reaction pathway for penetration.

The spheroids are distributed randomly under the criteria that

$$\varepsilon = \frac{n R_{pore}^3}{R_{char}^3} \quad (6)$$

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 pore are independent of each other. (2) The pores do not grow during reaction. (3) The pores only participate in the reaction if the reaction front of the shrinking sphere passes through them. A representation of the char model under these assumptions is given in Figure 12.

Using our pseudo-shrinking core model, one can assume for the basis of this analysis that the reaction rate is proportional to the surface area exposed during reaction (Regime I),

$$rate = k A_{char} \quad (7)$$

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

$$A = 4 \pi R_{char}^2 + \sum \pi R_{pore}^2 \quad (8)$$

where the summation is over the pores that are involved in the reaction.

Using a constant radial decrease, one can numerically generate curves for the evolution of the surface area as given by Figure 13. With very small pores, a constant surface area is developed that decreases with R. However, as the radius of pores increases, surface area peaks are generated due to the revelation of pores. These peaks become relevant at pore radii of approximately 0.5 mm. While this may seem large, the char particles used were originally of the order 7 mm in diameter. It should also be noted that the 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.

CONCLUSIONS

A model of the combustion of char in Regime II has been developed to explain the variation in CO₂ generation during the combustion of char particles in a FBC. The model assumes that there is no penetration of the particle by reaction gases except for regions where porosity is evident. The model adequately explains the variations seen in the production of CO₂ for pore sizes greater than approximately 0.5 mm.

Figure 8. Schematic of Fluidized Bed Combustion Apparatus and attached data analysis mechanisms.

Figure 9. Typical Variation of CO₂ profiles during combustion of Illinois Coal #6, 750°C.

Figure 10. Penetration Depth.

Figure 11. Penetration depth as a function of pore diameter.

Figure 12. Schematic of Pore Model. As the reaction proceeds, pores that had been previously hidden are revealed and begin to participate in the reaction. Once the reaction front has passed, these pores are of course part of the ash layer.

Figure 13. Evolution of CO₂ profiles as a function of pore diameter.

3. Soot Surface Area Evolution During Air Oxidation As Evaluated By Small Angle X-Ray Scattering And CO₂ Adsorption

INTRODUCTION

Soot is produced by incomplete gas-phase combustion of fossil fuels and other organic matter. While soot is emitted from numerous sources, the desire to control soot emissions from diesel engines has resulted in research into the performance of filters designed for exhaust collection systems. The collected soot is then burned off, resulting in an interest in the oxidation reactivity of diesel soot. This oxidation process is also important particularly for carbon black, where high oxidation levels are used to generate high surface areas. Furthermore, due to its similarities to highly reacted carbons, soot is a good model of carbon reactivity. Therefore, a better understanding of the evolution of surface areas of soots during oxidation is desired.

Classically, in carbon combustion studies, pore structure descriptions have been used as a common parameter in reaction characterization. However, for soots, little is known about how the surface area and other physical properties vary during the reaction process. While soot is generally considered as non-porous material, the existence of porosity has been reported by some researchers. Neoh, et al.²¹ found evidence for increase in soot microporosity during oxidation as measured by N₂ adsorption BET, much larger than the hypothetical unconnected sphere average, suggesting this difference was due to micropore development. Wicke and Grady²² also reported that thermal desorption of the soot oxygen complex formed by pre-adsorption of oxygen atom at 298 K produced a significant increase in soot porosity. Du²³ found rapid increases of soot area

past 20% conversion in oxygen, concluding that this was due to the reacting away of a blocking "shell" layer. These internal micropores then become accessible, causing a rapid increase in surface area. Du also found that the rate of reaction was proportional to the surface area up to 70% conversion. Bonnefoy, et al.²⁴, also reported a linear conversion rate for various carbon blacks and soots doped with catalyst.

Another characterization method for soots and carbon blacks is offered by fractal geometry that characterizes structural heterogeneity by use of fractal dimensions.²⁵ As a general trend, high surface area soots (carbon blacks) will give high fractal numbers, while low surface area soots will give low fractal numbers. Xu et al.²⁶ found that the fractal dimension of graphitized carbon black was 2.0 ± 0.01 , corresponding to a smooth surface, regardless of carbon black grade. Ismail and Pfeifer²⁷ found similar results for carbon blacks and Aerosils that had not been subjected to graphitization, conforming to a fractal dimensions of 2.02 ± 0.04 . Darmstadt et al.²⁸ found that as pyrolysis pressure was increased, the fractal dimension of rubber grade carbon black decreased from a high of 2.6, indicating a smoothing out of the surface due to carbanaceous deposits.

The examination of the microstructure of soot is also important to further explain the morphological changes that soot undergoes during oxidation. Ishiguro²⁹ proposed that the rise in surface area, and the corresponding decrease in diameter, he reported was due to the growth of crystallites with a turbostratic structure and subsequent stripping of the outer layer. However, Hurt³⁰ has proposed that this process is due to the actual densification of the soot particles. Both processes will affect the surface area of the soot, and examination is warranted.

This chapter examines the surface area changes generated by oxidation of soot in air. In order to examine the surface area of the soot, Small Angle X-Ray Scattering (SAXS) and CO₂ gas adsorption methods were used. The SAXS measurements have the advantage of seeing total porosity, giving a surface profile for the entire sample, while the CO₂ measurement describe only the accessible regions of our sample. Furthermore, the fractal nature of the soots are also examined to aid in understanding the soots morphological evolution.

EXPERIMENTAL

Materials

Two distinct soots were used in this study. A commercially generated diesel soot from the National Institute of Standards (abbreviated as NIST soot, order number 1250) collected in a water cooled diffusion trap was used due to its low ash properties. Furthermore, the NIST soot is a standard material used. Thus, an analysis of its surface properties during combustion is desirable. The second soot (termed Diesel soot) was collected by Prof. Levendis of Northeastern University, Boston, as part of his diesel engine research program. The latter soot was collected in a hot trap, and subsequently blown off by a high pressure air stream. The ash content of Prof. Levendis' soot was high, due to fuel additives and possibly due to contamination by the ceramic filter. However, due to the hot collection temperature, the volatile matter was significantly lower than the NIST soot. A collection of pertinent information for both soots is given in Table 1.

Experiments were also performed on Spherocarb, a synthetic char furnished by Analabs that has been widely used in combustion studies. Spherocarb can be considered a relatively pure

carbon(97% C, 2% H, 1 % O), so contamination by metals and the like is not an issue.

Furthermore, the Sphero carb's high surface is ideal for testing methodologies as a standard.

Table 1. Pertinent Properties of Carbon Examined

Material	NIST DIESEL	LEVENDIS DIESEL	Sphero carb
% Moisture (at 110 °C)	5.6	.5	.7
% Total Volatile Matter (at 900° C)	31.5	14	-
% Ash Content	0.96	6	780 ppm
He Density (g/cm ³)	2.1	2.04	2.1
CO ₂ Surface Area, as received (m ² /g)	49	96	1000 ⁸⁰
CO ₂ Surface Area, after devolatilization (m ² /g)	273	367	
SAXS Surface Area, as received (m ² /g)	156	207	1240
SAXS Surface Area after devolatilization (m ² /g)	344	280	
External Diameter after devolatilization	36 nm	27 nm	150 μm
External Area (m ² /g) ^a	110	150	<1

Methodology

Reactivity and surface area determinations were carried out in a standard Cahn 113 TGA system with an attached electronic acquisition system described elsewhere²³. Approximately 50 mg of fresh soot was devolatilized in inert Helium atmosphere at 1173 K for 20 minutes after a heating

rate of 25 K/min. Subsequently, the constant mass soot, termed 0% conversion, was cooled to 773 K in approximately 20 minutes. The inert atmosphere was then switched to air, and oxidation proceeded isothermally. After oxidation to the desired conversion level, the sample was cooled to room temperature in inert helium atmosphere.

The average primary particle size was estimated by use of a transmission electron microscope (TEM). The soots were ultrasonically suspended in ethanol and deposited onto a carbon coated TEM grid. A Joel 200 CX operating at 200 keV was used to image the soots at typical magnifications of 100-150 kX. The resulting micrographs were digitized using a powerlook II scanner, and the diameter of the soots were measured and averaged using the computer program Semper 6P. The diameters for the devolatilized soots is given in Table 1, while the actual TEM micrographs are given in Figure 14.

The surface area of the oxidized sample was measured gravimetrically by using CO₂ adsorption. While the gravimetric method has fallen into disuse, it has advantages over the volumetric method used today. It can accurately measure smaller amounts of sample due to the sensitivity of the TGA, and both reaction rate and surface area can be measured by in the same TGA without transportation errors. The method consisted of introducing various concentrations of CO₂/He mixtures (0, 0.1, 0.2, 0.35, 0.5, and 1.0 mole fractions respectively) into the TGA, and recording the subsequent weight change. At least 45 minutes were allowed for equilibrium to be established for each point of the CO₂ isotherm. The weight change was then corrected for

^a Based on a Apparent density of 1.5 g/cc for the soots, 0.83 for Sphercarb.

buoyancy effects due to different gas densities, and the CO₂ surface area was then calculated. Full details may be found in Du³¹.

Small Angle X-Ray Scattering (SAXS) experiments were also done on each oxidized soot sample. The X-ray scattering experiments were carried out on a Nicolet two-dimensional position-sensitive detector with an associated Rigaku rotating-anode generator operating at 40kV and 20mA which provided Cu K α ($\lambda = 0.154$ nm) radiation. The primary beam was collimated by two Ni mirrors, which allowed for the X-ray beam to be focused onto a small beam stop. A sample to detector length of 28.5 cm was used for all samples. Full details may be found in Kofinas.³²

THEORY

CO₂ Surface Area Characterization

Characterization of the micropore capacity of the samples was estimated by application of the Dubinin- Polanyi (DP) equation

$$\log V = \log \frac{\Delta W}{W_0} = \log V_0 - k \left(\frac{RT}{\beta} \right)^2 \log^2 \frac{P_0}{P} \quad (9)$$

to CO₂ adsorption at 296K. V is volume absorbed at pressure P , ΔW is the change from starting weight W_0 , β is the affinity coefficient, k is a surface property constant, while the saturation pressure P_0 is evaluated by the correlation $P_0 = 10^{-874.34/T + 4.7386}$ atm. After using the DP equation to determine the intercept V_0 , the specific micropore surface area is calculated from

$$S_{sp} = \frac{V_0 N_0 \sigma_{CO_2}}{M_{CO_2}}, \quad (10)$$

where N_0 is Avogadro's number, M_{CO_2} is molecular weight of CO_2 , while σ_{CO_2} is the cross-sectional area of a CO_2 molecule (taken as 24.3 nm^2).

3.2 Small Angle X-Ray Scattering (SAXS) Characterization

SAXS intensity profiles have been used in several studies to determine the pore structure in carbons.³³⁻³⁷ Levendis and Flagan³³ used SAXS to characterize the micropores of carbon spheres of controlled porosity. Foster and Jensen³⁴⁻³⁵ used SAXS to investigate carbon pore structure evolution during CO_2 gasification. Guet et al³⁶ characterized the structure of different carbons activated by steam and CO_2 using SAXS. Hua et al³⁷ used SAXS along with contrast matching to compare the porous structure of various carbons and inorganic materials. The increasing use of SAXS is due to several reasons, such as the ability to measure open porosity and closed porosity, which is not measurable by gas adsorption techniques.

The basic property measured in all SAXS studies is the scattering intensity (I) of X-ray radiation caused by differences in electron densities of each phase. The surface area of a solid may be evaluated in the so called Porod region for larger angles of SAXS by assuming a randomly distributed porosity throughout a uniform solid. The Porod approximation holds as $h \rightarrow \infty$ ($h = 4\pi \sin \theta / \lambda$, where 2θ equals the angle of scattering of the x-ray beam) for collimated optics,

$$I(h) = \frac{2 \pi \Delta \rho_e^2 S}{h^4} \quad (11)$$

where S is the total surface area of matter contained in volume V , and $\Delta\rho_e$ is the difference in electron density. To avoid the use of absolute intensity measurements, which are difficult to obtain, the intensity may be normalized by the invariant Q_0 , or the total integrated intensity given by

$$Q_0 = \int_0^{\infty} h^2 I(h) dh = 2 \pi^2 (\Delta\rho_e)^2 \frac{\Delta V}{V}, \quad (12)$$

where $\Delta V/V$ is the volume fraction of scatterers.

Evaluation of Q_0 must proceed carefully. 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. At higher values of h , the small $I(h)$ can be influenced by extraneous sources. Therefore, the numerical integration was divided into three parts,

$$Q_0 = Q_1 + Q_2 + Q_3 = \int_0^{h_{\min}} h^2 I(h) dh + \int_{h_{\min}}^{h_{\max}} h^2 I(h) dh + \int_{h_{\max}}^{\infty} h^2 I(h) dh. \quad (13)$$

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. The integration from $h_{\max}$ to infinity was calculated using Porod's approximation for intensity.

Extrapolation for small angles was accomplished by using the Guinier approximation. As $h \rightarrow 0$, the Guinier region is reached and the scattered intensity exponentially rises as

$$I(h) = V \Delta\rho_e^2 \exp\left(-\frac{h^2 R_g^2}{3}\right), \quad (14)$$

where R_g is the electron radius of gyration about the center of electronic charge.

The total specific surface area (S_{sp}) may then be evaluated as

$$S_{sp} = \frac{\pi \varepsilon (1 - \varepsilon)}{\rho} \frac{\lim_{h \rightarrow \infty} h^4 I(h)}{Q_0} \quad (15)$$

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

Another measure of the surface irregularity is the fractal dimensions of an object. True fractal objects are scale-invariant or self-similar, in that they look similar at all levels of magnification.

The earliest work in fractal analysis has shown that the degree of surface roughness, or

irregularities can be expressed by the parameter D_s ,^{38,39} where $2 \leq D_s \leq 3$. D_s may be taken as a measure of the space filling ability of the surface.²⁵ For a Euclidean, perfectly smooth surface, $D_s = 2$, and the value of D_s increases with the degree of surface irregularity, and for a very rough, disordered surface, the value of D_s approaches 3.

A surface fractal object is rough on a length scale small compared to its radius, e.g., rough pore boundaries in a porous solid.⁴⁰ The intensity scattered on fractal surfaces is proportional to a negative power of the wave vector h for $h\xi_s > 1$,

$$I \propto h^{-\alpha} \quad (16)$$

where ξ_s is the correlation length for surface fractal behavior, or in other words, ξ_s is the upper limit of the length range in which the surface is fractal. For surface fractals,

$$\alpha = 6 - D_s \quad (17)$$

When $D_s = 2$, the intensity is proportional to h^{-4} which is Porod's Law.

RESULTS AND DISCUSSION

REACTIVITY MEASUREMENTS OF SOOT

During reaction in the TGA, volatile matter would be driven off until a constant weight was reached. This freshly devolatilized material was termed 0% conversion, and oxidation proceeded at 773 K in air. The reaction rate was calculated by normalizing the rate of change in mass by initial sample mass (mg/mg-min) on a dry ash free basis. The variation of the intrinsic reactivity with conversion is plotted in Figure 14. For the NIST soot, a relatively linear rate of mass loss was observed, followed by a leveling off of reaction at very high conversions. The Diesel soot passed through a maximum rate at approximately 30% conversion. Both the Diesel and NIST soots had, assuming first order kinetics, rate constants of 0.15 s^{-1} at 30% conversion, in good agreement with Bonnefoy et. al.²⁴, who reported rate constants of 0.06 to 0.2 s^{-1} for diesel soots. The high initial rate for the NIST soot may be a function of loosely bound organic matter that is not devolatilizable in an inert atmosphere, or as Ishiguro described, the soluble organic fraction²⁹.

SURFACE AREA

The original and oxidized products were characterized with CO_2 to determine the specific surface area. The Dubinin-Polanyi plots were all fitted to straight lines with minimum correlation coefficients well above 0.997 for all tests. The resulting CO_2 surface areas calculated using Equation 10 are plotted in Figure 16. As shown in Figure 16, there is approximately a two fold or greater increase in surface area during reaction. The greatest increase in surface area occurs during the initial devolatilization step. Surface areas then rose to a maximum surface area at

around 50% conversion for both soots. However, while both soots' surface areas decreased at higher conversion levels, the Diesel soot exhibited a much more rapid loss of surface area. The most plausible explanation for this is that the ash content plays a significantly greater roll in the surface area calculations as reactions proceeds (78% weight conversion is equivalent to nearly 83% conversion on an ash free basis for the Diesel). Furthermore, the accompanying small, but measurable decrease in surface areas at higher conversions for the NIST soot may be evidence of Hurts' densification phenomenon at higher conversions.

The significant overall increase in surface area during devolatilization and oxidation can be explained in two ways:

1. Micropores are created in soot particles during oxidation, or
2. The micropores are inherently contained in the soot particle, but are inaccessible.

Devolatilization and oxidation reacts away the shell that initially blocks these pores, increasing porosity.

To check these hypothesis, SAXS measurements, which have the inherent ability to measure total porosity, were performed.

SAXS MEASUREMENTS

SAXS profiles of the converted soots were measured at each conversion level. The resulting two dimensional profiles did not exhibit any isotropic effects, so the average intensity at each value of h was found by radially integrating the circular profiles measured by the 2-D detector to eliminate noise. Typical profiles are shown in Figure 15 for the NIST and Diesel data. Intensity data were

corrected for background noise for by using the high h range to obtain the correct background subtraction factors and treated with the aid of a set of programs furnished by Glatter^{41,42}.

The Guinier plots for typical runs are shown in Figure 17. The linear range is quite broad for most samples, suggesting that there is a narrow pore size distribution. Typical $h_{\min}$ values were approximately 0.25 nm^{-1} , and the intensity for values of h less than $h_{\min}$ were obtained by extrapolating the data with Equation 14. The applicability of Porod's Law was checked by plotting $h^4 I$ versus h^4 , as shown in Figure 18. The invariant plot does not show significant variation from Porod's law at high h , exhibiting more or less a flat $h^4 I$ value. At very high values of h , the plots exhibited a higher variation in $h^4 I$, due probably to the small intensity values as compared to other sources of radiation in this range.

The invariant was calculated using the Guinier and Porod's approximations to extend the integration region from zero to infinity. The surface areas of the soots were then calculated using the Porod's law approximation given in Equation 11. However, the porosity and density of the soot particles are essential components in this analysis to obtain specific surface areas.

Unfortunately, the small sample sizes precluded measurement of these factors to any degree of accuracy. Therefore, three alternate density/porosity variations are assumed to give the limits of the variability in porosity for the purposes of calculating surface area. For all approaches, measured true densities 2.1 g/cc and 2.04 g/cc for the NIST and DIESEL soots were used respectively. An initial starting apparent density of 1.5 g/cc after devolatilization was assumed for

both soots, based on values reported in the literature ranging from 1.3 to 1.8⁴³. The three models were:

- 1) Constant density oxidation. The soot is assumed to burn at with no variation in densities. As density does not vary, the porosity given by

$$\epsilon = 1 - \frac{\rho_{app}}{\rho_{true}}, \quad (18)$$

remains the same. This corresponds to reaction in Regime III, or pure external diffusion control of reaction.

- 2). Constant diameter oxidation. The soot is assumed not to change size as oxidation proceeds. Therefore, density will decrease and porosity increase with increasing conversion. This assumption will break down at higher conversion levels due to collapse of the soot structure. This assumption corresponds to reaction in regime I, or pure kinetic control.

- 3). Ishiguro's²⁹/Hurt's³⁰ diameter variation is assumed. As Ishiguro investigated diesel soot oxidation under similar conditions as this study, the diameter variation can be assumed to be the same. Furthermore, measurements with a TEM of the NIST soot diameter during oxidation agree well with Ishiguro's results (see Chapter 5.)

The results obtained using these three assumptions are plotted in Figure 19 for each soot, along with the CO₂ areas for comparison. As can be seen in the figures, there is a striking variation between the results obtained for the three different cases. The constant density assumption gives relatively low values of surface areas that do not vary dramatically with conversion. The constant diameter assumption gives rapidly increasing surface area values, rising to over 800 m²/g for both

soots. The Hurt/ Ishiguro curve falls between the constant density and constant diameter approaches. One should also note that the relative values assumed for density can cause a great deal of variation in the actual values reported, although the trends remain the same.

Examining the NIST CO₂ and SAXS area curves (Figure 19), one quickly notes that there are evidently two regions where the agreement in trends is evident, below 40% conversion and above it. Below 40% conversion, all assumptions other than the constant density approach gives the same upward increasing trend. However, past 40% conversion, only the constant density approach gives trends that are reasonably the same between the two area evaluation methods. The diesel soot also follows a similar trend. The constant density approach again yields a relatively flat surface area profile. However, the surface area profiles for all three methodologies provide trends that agree somewhat with the CO₂ surface area, including the decrease in surface area past 50% conversion.

The fractal nature of the soot surfaces was calculated on a length scale ($= 2 \pi/h$) of 2 to 40 nm, ranging from the mesopore diameter of the soots, and is given in Figure 19. Both soots have low fractal dimensions initially, with dimensions slightly less than 2, in reasonable agreement with Xu et al.²⁶ This is probably indicative of the mass fractal nature of the agglomerates of the soot. Devolatilization of the soots increases the surface roughness of the system, but the surfaces are still relatively smooth. The smoothness of the soots is probably due aromatic layers that are deposited and loosely held on the surface of the soot during soot generation, of which devolatilization causes their pyrolysis.

The introduction of oxidant to the system radically alters the surface roughness of the soot, as indicated in Figure 21. The fractal dimension increases from about 2.2 for the devolatilized soot to about 2.7, even at very low levels of oxidation. The fractal dimension then increases with oxidation, up to a maximum of 2.9, very near the theoretical limits for a solid. Both soots follow the same trends, although the Levendis and NIST soots differ somewhat at high conversions, probably due to the impurities in the Levendis soot. The high values of surface roughness are comparable to the range of surface roughness obtained by Sahouli et al⁴⁴ for vacuum pyrolysis generated carbon blacks (range 2.69-2.91). The high degree of surface roughness also agrees well with Ehrburger-Dolle et. al.,⁴⁵ who found that high surface area furnace carbon blacks exhibited surface fractal while low surface areas did not exhibit fractal character.

That the constant density assumption gives the trend that agrees best with the CO₂ data is troublesome, as penetration depth analysis would indicate complete penetration of all pores at 773K. This analysis would also indicate that the diameter remains constant during reaction. However, the diameter does change significantly, as evident in direct measurements of the soot diameter.^{29,30} However, in light of the increasing fractal nature of the soot during oxidation, A closer examination of the physical changes during oxidation is called for.

CONCLUSION

Reaction of soots at 773 K was performed in air to various conversion levels, and SAXS and CO₂ surface areas measured. The surface area as shown by CO₂ absorption increased by a factor of two as soot oxidized. SAXS areas could also vary dramatically for our soots, depending on the model assumed for the density variation with conversion. The combined effect would indicate

that the rapid increase in CO₂ surface is due to the initial opening of previously blocked pores, followed by a constant density gasification.

Figure 14. Variation in Reactivity as a function of conversion.

(a)

(b)

Figure 15. Typical SAXS profiles for (a) Diesel Soot and (b) NIST soot.

Figure 16. Evolution of CO₂ Surface area with conversion. The points before zero represent the soots as received(no treatment).0

(a)

(b)

Figure 17. Guinier plots for (a) Diesel Soot and (b) NIST soot as a function of conversion

(A)

(B)

Figure 18. Porod invariant plots for (a) Diesel soot and (b) NIST soot as a function of conversion

(A)

(B)

Figure 19. Variation in SAXS calculated surface areas for (a) diesel and (b) NIST soots assuming constant diameter, constant density, and the ishiguro/Hurt variation in structure.

Figure 20 Fractal evolution of Soot. Devolatilization increases the fractal character of the soot, while oxidation increases its character even more.

4. Generation Of A Combustion Resistant Grid: Application To Single Particle Studies

INTRODUCTION

A large variety of carbonaceous solids are of interest in combustion, including soots, cokes from liquid-fuel combustion and chars from high temperature decomposition of organic solid precursors. The oxidation of these solids can occur uniformly throughout the solid under certain conditions, notably low rates of reaction, small particle size, and high porosity. For small particles in the nanometer size range, it is difficult to distinguish experimentally measurements that occur at a single particle level from bulk phenomena. A phenomenon of interest is gasification induced densification, in which structural rearrangements result in particle contraction during oxidation. This densification phenomenon was inferred from the studies of particles in the 20 nm to 13 mm range, including Spherocarb,^{46,47} Pittsburgh #8 Coal,⁴⁸ and form coke.⁴⁹ Hurt et al.⁵⁰ attributed the densification to the microstructural rearrangement of the carbons on oxidation, but had no direct corroboration of these changes.

Ishigiro et al.⁵¹ also observed the reduction of primary particle diameter during the oxidation of diesel soot at 500°C. The authors attributed this particle size reduction to surface ablation of the particles. Hurt et al.⁵⁰ suggested that a more likely explanation for the size reduction was oxidation induced densification. Interestingly, Ishiguro et al. provided high resolution electron micrographs and EELS data on the soot at different extents of oxidation that supported the

increase in ordering (graphitization) of the soot with increased extent of oxidation. Data on the evolution of the size and microscopic structure of the same soot particle would be useful in resolving this issue.

Heckman and Harling⁵² have reported a method for obtaining transmission electron microscope (TEM) micrographs of the same carbon black particles before and after oxidation, but did not report the details of their experimental procedure. The key to the methodology is the development of a sample holder that will withstand oxidation and allow imaging of soot particles at the same location on the grid after the soot particles on the grid have been subjected to different amounts of oxidation external to the microscope.⁵³ Controlled atmosphere electron microscopy (CAEM) for examining the soot particles during oxidation have been developed but so far only with lower resolution microscopes.⁵⁴ Higher resolution microscopes use electron energies which would cause structural rearrangements for the long reaction times involved for chemically controlled soot oxidation⁵⁵ so that CAEM cannot be used to pursue structural changes at high resolution without due precautions.

A modification of the Heckman procedures for obtaining and processing a labeled TEM grid that survives oxidation has been developed. The generation of this grid and its application to the study of soot shrinkage during oxidation are the subject of this chapter.

SAMPLE PREPERATION

Standard TEM grids are available in a variety of materials, typically a thin metal mesh with an overlaying amorphous carbon layer that provides sample support. For examination of carbon

structure, in which the amorphous carbon layer would interfere with sample characterization, a lacy carbon layer grid is preferred. The material to be imaged is examined by only looking at material that falls over these holes. Unfortunately, unlike highly unreactive graphitic carbon, the very thin carbon layer is quite fragile, and reacts under slightly oxidizing conditions, destroying the structure of the grid and its usefulness as a sample holder. The problem of fragility is solved by coating the grid with a non-reactive coating producing by depositing aluminum onto the grid. The grids used were obtained from Ted-Pella, consisting of a labeled nickel grid for grid location assistance, coated with lacy carbon, of typical hole diameters of 300 nm. The grids were coated front and back with approximately 7.5 nm to 10 nm of aluminum on each side with a thermal evaporator, and thickness was confirmed with a profiler. While it is preferable to have as thin a coating as possible, this was the minimum thickness that was found to provide a robust "sandwich" to protect the grid structure. After coating, the grids were subjected to a temperature stabilization period, typically 1 hour at 900K in air after a mild (10K/min) heat ramp. The mild heat ramp allows for stabilization of the metal and an evening out of the aluminum coating, which may deposit at uneven intervals or in large crystal domains before the aluminum is oxidized to aluminum oxide at the elevated temperatures. The stabilization step also acts as a first-pass removal method for grids that are not capable of withstanding elevated temperatures, due probably to lack of metal deposition the side of the grid, which may leave carbon exposed to the oxidizing environment. The sample to be examined, in our case, NIST diesel particulate matter (NIST item 1050), a standard diesel soot used in environmental studies, was ultrasonically suspended in ethanol and deposited dropwise onto the grid. The grid and deposited soot were

then subjected to a "heat shock" step consisting of a rapid heating to above the reaction temperature to allow for thermal stability to be achieved (550°C in our case) and to minimize changes in structures of the agglomerates due to heating after imaging.

After preparation, the sample was imaged using a Joel 200CX TEM with LaB₆ filaments operating at 200 keV. For a typical sample, 4-5 regions were identified and photographed at magnifications of 100-150 kX, along with lower magnification micrographs used to identify of the grid location in later microscopy work. The grid with deposited sample was then oxidized at 500°C in air using a Cahn TGA. The conversion level was calculated using a control sample of the same material to measure the change in oxidation level versus time, as the level of sample was too small to measure weight loss. After oxidation, the grid was again imaged using the electron microscope. The regions photographed before oxidation were located, and the sample again examined. Typically, only one or two of the regions were locatable with the same soot agglomerate. The micrographs were then digitized using Adobe Photoshop® with attached scanner (UMAX model II) and analyzed with Semper 6P®.

RESULTS

TEM micrographs of the same region taken before oxidation and after oxidation to 40% weight conversion are shown in Figure 21 and Figure 22. From Figure 21 and Figure 22, it can be seen that individual soot particles, such as those at point A and B, can be selected for the purpose of examining structural changes during oxidation. Comparison of the two figures also shows that the agglomerate itself has retained its overall shape. The upper portion has moved from its

attachment point C in the pre-oxidation micrograph to point D in the post oxidation micrographs, resulting in a shrinkage of the agglomerates overall area without loss of overall structure.

In Figure 23, the soot primary particle at Point A has been isolated. The pear shaped region is the result of the overlapping and fusion of two primary particles. The particle diameter is measured using software tools, and the differences in diameters are obtained. The plot of the overall trends in particle volume (assuming a spherical volume) is given in Figure 24, along with comparisons of the data from Ishigiro⁵¹.

While only the pear-shape particle was measured in the subregion depicted in Figure 23, there are important trends to note from the isolated region. The first is that the overall structure is maintained. A large fraction of sample has been oxidized, yet there is little change in the structure that is not due to rotation or shrinkage. This indicates that the particle is burning without removal of outer layers, since the agglomerate does not lose its shape. One would expect that primary soot particles would not be retained to a large extent after any oxidation if surface layer recession were occurring. That shrinkage occurs throughout the agglomerate is evidenced by the increase in the number of soot primary particles in the subregion region of Figure 23, indicating that shrinkage has occurred not only for the measured particle, but for the entire soot agglomerate.

The usefulness of the technique is exhibited in Figure 25, showing a very high oxidation sample. The same soot agglomerate is imaged before and after oxidation to 90% by weight. Due to the high degree of oxidation, and loss of the particles due to structural breakdown, the same individual particle may not be measured with a reasonable degree of accuracy. However, the

particles are in the same agglomerate, removing possible differences between possible sources of primary particles.

CONCLUSIONS

A combustion resistant grid has been used to examine the shrinkage of single soot particles during kinetically controlled oxidation. The retention of soot agglomerate shape and structure agrees well with the hypothesis that soots undergo homogeneous shrinkage during oxidation.

The examination of soot is only one potential application of this grid, and studies with different materials may be of interest. While only low oxidation temperature experiments were performed with this grid, the alumina structure can withstand a higher temperatures, and would be of use as a collection grid during in-situ combustion studies.

Figure 21. TEM micrograph of NIST soot before oxidation (original image: 200keV, 120kX magnification).

Figure 22. TEM micrograph of NIST soot after oxidation to 40% conversion (original image: 200keV, 120kX magnification).

Figure 23. Magnification of Region A of Figures 1a and 1b. The primary particle size is seen to visibly shrink

Figure 24. Comparison of sample data using Ishiguro's data and the data generated using the grid.

The error bars represent the maximum variation in diameter observed

Base diesel soot on carbon grid
 $D_s = 23.7 \pm 4.1$ nm

90% weight conversion at 550°C
 $D_s = 12.8 \pm 4.2$ nm

Figure 25. Very high conversion of soot on the TEM grid. The high oxidation level makes comparison difficult, but some regions are isolatable. The "bumps" seen on the grid are due to aluminum migration during extended periods of oxidation

5. Radial Distribution Of Soot Structure Obtained With High Resolution Transmission Electron Microscopy

INTRODUCTION

Widely used techniques used to measure porosity and surface area, such as gas absorption (BET) and Small Angle X-Ray Scattering (SAXS), when performed on particulates such as soot, yield average sample characteristics, and do not provide details on the variation of the physical structure within a particle. The morphology of carbonaceous materials is the direct result of their oxidation history. One result of oxidation is that certain carbon blacks yield cenospheric particles, suggesting that the outer layers are less reactive than the core. Another result is the observation of large increases in the surface area of soot after only a small fractional oxidation. This can be attributed to "blockage" of the internal area of individual particles by a relatively impervious shell of carbonaceous material^{56,57}.

Diesel soot consists of spherical primary particles, approximately 20-30 nm in diameter, that are aggregated in grapelike clusters of 1 to 2 μm .⁵⁸ In diesel engines, soot usually forms in the fuel-rich pockets and may undergo oxidation before being released to the atmosphere. Using high resolution transmission electron microscopy (HRTEM), it has been found that bearing different loads on diesel engines will result in different structural elements in the soot.⁵⁹ It has been found that an increase of lattice ordering and a decrease in primary particle size is the result of oxidation of soot.⁶⁰ Similar results have been observed for carbon black.⁶¹

The purpose of this study is to examine the effect of oxidation on the microstructure of soot. The consequences of radial variation in the porosity and reactivity of soots and carbon blacks as function of oxidation will be shown by analyzing the soot structure using a recently developed methodology based on image analysis of high resolution transmission electron micrographs.

EXPERIMENTAL AND ANALYTICAL METHODS

Diesel emissions are complex in structure and composition. High resolution electron microscopy (HRTEM) coupled with image-analysis techniques that apply high level computer software has been used to analyze the structure of a diesel soot that has been exposed to oxidizing conditions (air, 773K). A standard soot used in poly aromatic compound research generated by NIST was used for this study. The sample, NIST 1050, corresponds to a medium load diesel engine with a diffusion trap capture mechanism to minimize contamination.

In order to minimize interference from the polycyclic aromatic hydrocarbons (PAHs) absorbed on the soot surface, the soot was devolatilized in inert (He) atmosphere at 1173K for 15 minutes, until a constant sample weight, measured by a standard Cahn 2000 thermogravimetric analyzer (TGA) was obtained. The samples were then oxidized in air at 773K using the TGA.

A small portion of each sample was ultrasonically suspended in ethanol and deposited dropwise on a lacy carbon TEM grid. An oriented gold crystal was used as a calibration standard and subjected to the same techniques as the diesel soot samples. The use of a specifically oriented

gold crystal allows only the lattice locations in one plane to be diffracted. Then, precise measurements of the lattice distances may be made and compared to the experimental samples.

An Akashi/TOPCON 002B transmission electron microscope with an LaB₆ filament operating at 200 KeV was used to record high resolution images of each sample. The micrographs were digitized with a UMAX PowerLook II model scanner operating at a scanning resolution of 993 dpi. The high level language computer software, SEMPER 6P™ (Synoptics, LTD., Cambridge, UK), developed especially for high resolution electron microscopy, was then used to manipulate the digitized images in order to extract data that could be used to characterize each soot sample. Optical diffraction patterns showing the periodicities present were generated from these images. The optical diffractogram is a power spectrum calculated by squaring the modulus of the Fourier transform. Intensity profiles characteristic of the range of contrast in the diffractograms were then produced. A series of "filters" were also applied to the digitized soot images to eliminate noise and isolate the significant structural data from the image. The extracted structure then becomes the basis for statistical analysis.

The parameters that can now be quantified are the lateral extent of fringes and interlayer spacing. The angular dependence of the structures may also be measured, and was used to obtain the reference axis of the primary soot particle so that the mean of the orientation of all structural elements was as close to zero as possible.

The lateral extent of fringes is defined as:

$$La = AB\sqrt{m_{\max}} \quad (19)$$

where m is the principal second moment of area. A second moment is a mean square of all pixels about a line through the center of area of a structural element (fringe). The principal second moments are the second moments with respect to a pair of mutually perpendicular axes in directions that achieve minimum and maximum moments. The constant B is a physical conversion factor from pixels to Angstroms. The factor A , usually between 3 and 4 depending on the shape of the object in question, was determined experimentally to be 3.56 pixel^{-1} .

To get the characteristic interlayer spacings for the sample, the total area of the fringes was determined with minimal filtering, which corresponds to eliminating repeated frequencies below 0.3 nm and above 0.5 nm. Then, in order to eliminate differences in illumination between each sample, the intensity range was narrowed and shifted to a position in which the number of fringes showed a maximum.^{62,63}

RESULTS

The electron micrographs in Figure 26 show the turbostratic lattice structures of the untreated and oxidized diesel soots, respectively. The turbostratic structure is the random orientation of the carbon atoms layers in the soot lattice, in contrast to the highly oriented lattices of graphitic structures. These micrographs were digitized and stored as 1024 x 1024 pixel images. In Figure 27, a circular portion of the base soot has been masked off using the image analysis software in order to isolate the soot particle for comparison purposes. An example of the structural data extracted from the soot images after a series of filters is shown in Figure 28.

Care was taken to eliminate any regions in which overlap of primary particles occurs. The overall distribution of lattice lengths for each particle, along with a comparison of lattice length as a function of radius is shown in Figure 29.

DISCUSSION

The results of the three oxidation conditions that we have examined show some similarities and some differences for the overall soot imaging. The average lattice length for all samples is approximately 15 Å, although there is a difference in the distribution of lattice lengths of each sample. As oxidation conditions increase, lattice length tends to shift more to the smaller average values. This may be an indicator that the longer lattice lengths are being oxidized preferentially. It is important to note that the untreated soot has more individual lattice fringes due to its much larger area than the oxidized samples (approximately 2x), making comparisons difficult.

A better method of comparing the samples is to examine the radially sectioned averages. Each of the soot samples starts with a small lattice average in the center and increases to a maximum value near the edge of the soot before again beginning to decrease. The untreated soot starts with an average lattice length of approximately 12 Å, and slowly increases to a maximum of about 16 Å near the edge of the soot particle. In contrast, both of the oxidized soot samples have higher maximum values for the radial section, but start with lower center values for the average lattice length. The relative error is large for these samples due to the low number of fringes in the center. The actual average for all samples is about the same due to the high total number of small

fringes for all particles. As conditions become harsher, the radially sectioned maximum average (occurring near the edge of the sample) becomes greater. At a radius of 10 nm, the radial average for the base soot is 14.4 Å, while the oxidized soots have an average of approximately 16 Å. This indicates that the soot is chemically transforming during oxidation because these maximum averages occur at different locations due to shrinkage of the particle.³⁰ Ishigiro et al. observed similar crystallite growth which they said resulted in the stripping of smaller crystallites from the outer surface⁶⁰.

For all of the soot samples, the lattice fringe length decreases near the edge. While this may be due to interference from other particles that influence the average, careful examination of Figure 28 reveals otherwise. As the edge of the particle is neared, the extracted structure reveals fewer long lattice lengths, and more indentations where no ordered structure can be seen. This may be due to the carbon not being oriented in the direction of the beam, so that the Bragg angle condition necessary for diffraction and viewing of the structure is not satisfied. These most probably are the less reactive layers observed in surface area studies of soot(56, 57). The blocking layer appears to be younger structures that have not coalesced into an extended structure, although they are stable to high thermal conditions(1173K devolatilization). Another possible explanation is that during formation of the soot, high temperature oxidation only effects the outer layers of the soot particle, leaving an imperfect structure at the surface of the soot particle.

While the soots are different in absolute scale, it is interesting to compare the running lattice averages as a function of non-dimensional radius, where the radius of the soot is defined as the

radius where the running average begins to decline. The change in the lattice average follow the same general trends, for the base and mild conditions. While the heavily oxidized soot also reaches the same average, and follows the same slope, the average is approximately 2 Å greater until the ends converge. This again indicates that there is a fundamental difference between the heavily oxidized samples, due to the as high temperature conditions that facilitate thermal graphitization.

We were unable to compare the interlayer spacing differences between the center and edge layers. Except for the untreated case, we were unable to measure any lattices in the center of the particle. This is either indicative that the oxidation has preferentially oxidized the interior of the particle, as indicated by Heckman and Harling,⁵² who observed a hollowing out of particle cores during oxidation, or the inability to image the center of the particle due to the absence of Bragg conditions. The untreated soot case had the same interlayer spacing of 3.44 Å between the center and edge of the soots, in good agreement with Marsh et al.⁶ who found that the interlayer distances were the same in the core and the periphery of the primary particle. It is interesting to note that there is a considerable difference in the standard deviation of the spacing. We measured roughly twice as many fringes on the edge of the soot, yet the standard deviation went from 0.14 Angstroms to 0.18 Angstroms. This may indicate that the chemical species involved in formation of the soot differ between nucleation and outer edges, either in absolute size of the species or in its orientation. The difference may also be due to exposure time differences during formation, since center of the soot particle will have a longer residence time during formation than the outer

edges, allowing for more thermal annealing. Lahaye and Prado⁵⁸ observed that the layer planes of soot are oriented around some randomly distributed centers in the particle, much like an onion⁵⁸.

The differences between the untreated and oxidized soots show a difference between nucleation and growth species which supports some formation theories. From the higher degree of reactivity in the center (shown by preferential oxidation), one can conclude that the carbon species involved are fundamentally different in either their structural or chemical properties. The concept that at inception the particles should be considered liquid droplets⁶⁴ would seemingly only apply to the initial 1-2 nm particle due to the disordered, small lattice structure found in the center of the particle.

CONCLUSIONS

Differences in the carbon structure of soot has been shown to be a function of radius for untreated soot. Oxidation of the soot increases the radial differences in lattice structure for soot increasing order was found for carbon blacks with increasing oxidation, while Buseck et al. showed an ordering of the structure of amorphous coke, where increasing annealing temperatures and increasing linearity of the coke precursors resulted in more orderly structures when imaged by TEM.⁶⁵

Figure 26. Digitized TEM images of soot. (a) Initial soot (b) Soot Oxidized at 500°C for 1 hour (Weight conversion = 70%); (c) Soot oxidized at 1500°C

Figure 27. Isolated Soot particle of Figure 1a used for analysis.

Figure 28 Extracted Structure of Figure 27 showing lattice fringes. The outer edge shows more variation than the middle shells. The right of the figure is excluded in the analysis due to overlap of the connecting regions of the agglomerate.

(b)

(c)

Figure 29 Overall distribution of lattice lengths for (a) base soot; (b) mildly oxidized; and (c) harshly oxidized. The average lattice length for these samples are 15.3 ± 10.4 , 15.5 ± 11.8 , and 15.8 ± 10.9 respectively.

Figure 30. Overall comparison of soot lattice fringe length based on non-dimensional R.

At a radius of 0.8 R_0 , interference with other soot primary particles begin to decrease overall lengths.

6. Structural Changes of Char Particles During Chemically Controlled

Oxidation

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^{66,67}. 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 Hottel⁶⁸ on the oxidation of carbon spheres and include the studies of Walker et al.⁶⁹ and Dutta et al.⁷⁰.

The focus in this chapter 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 [71]). Kerstein and Niksa⁷¹ 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-Ziv⁷² and Zhang et al.⁷³ 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. [66], Salatino and coworkers^{74,75,76}, and by Kantorovich and Bar-Ziv^{77,78}. 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 phenomena 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, respectively⁷⁹. 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 [^{72,80,81,82}] 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^{72,80-82}. The three forces were uncoupled by periodical interruption of the laser⁸². 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^{72,80}. Figure 31 (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 Spherocharb particle. The line shape depends on the flow field within the chamber (as has shown by D'Amore et al.⁸³) and the magnitudes are inversely proportional to pd^2 ⁷². Since the density of the polystyrene is known, the density of the Spherocharb can be obtained from the slope of a plot of $(\Delta V/V_0)(pd^2)$ for polystyrene vs.

$(\Delta V/V_0)d^2$ for Spherocharb as shown in the lower half of Figure 31, which yields a density for the Spherocharb 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

Spherocharbon particles at various conversions were produced by reaction in a thermogravimetric 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 Spherocarb.

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 spacing⁸⁴.

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^{72,81,82}. 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 32 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 Figure 33). 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 EDC⁸². 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^{30,85}. 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 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.. The spacing between the fringes in the picture is around 3.4 Å, 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 Figure 34 for the original Sphercarb 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 Sphercarb particles was at 3.41 Å, whereas at the high conversion (>97 %) the peak had shifted to about 3.3 Å (see Figure 35). This ordering of the micoporous 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 Ratio of porosity to initial porosity vs. conversion. Initial and final porosities are indicated in figure. which presents a typical conversion vs. time curve with a sequence of shadowgraphs depicting the shape development of a Spherocarb 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 temperature⁸⁰. 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-pores⁸⁰, 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.⁷⁹ 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., 73,77,79) 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.

Table 2. Summary of results of Sphercarb particles oxidized in EDC, in air at various temperatures (values in parenthesis in density column is porosity in %), where T is temperature, d_0 is initial diameter, ρ_0 is initial density, ϵ_0 is initial porosity.

Exp. no.	T (K)	d_0 (micron)	ρ_0 (g/cm ³)	ϵ_0	Hole formed @ conversion	Fragmented @ conversion	Shape type @ final burnout
e7-271	930	247	0.76	0.65	83.8	89.8	3
e7-273	880	172	0.58	0.74	86.1	none	3
e7-281	920	204	0.59	0.73	87.7	97.5	3
e7-312	900	176	0.59	0.73	none	none	1
e7-314	900	177	0.71	0.68	none	none	1
e7-315	940	200	0.78	0.64	95.9	none	2
e8-11	910	198	0.61	0.72	none	none	1
e8-12	940	189	0.45	0.80	70.9	95.1	3
e8-14	860	206	0.50	0.77	90.8	none	2
e8-21	850	212	0.58	0.74	91.0	none	2
e8-22	880	215	0.85	0.61	none	none	1
e8-23	870	187	0.78	0.65	none	none	1
e8-24	910	205	0.48	0.78	66.3	none	2
e8-31	870	219	0.68	0.69	none	none	1
e8-32	850	176	0.71	0.68	66.0	none	2

e8-33	970	187	0.63	0.71	82.8	none	2
e8-34	940	186	0.69	0.69	none	none	1
e8-41	920	185	0.51	0.77	none	none	1
e8-51	930	185	0.56	0.75	91.1	92.6	3
e8-52	900	177	0.53	0.76	none	none	1
e9	780	205			86.0	97.0	3
e10	830	205	.579	.74	64.7	none	3

Type 1 is a disk without a hole.

Type 2 is a disk with one hole or more.

Type 3 is a disk that opens.

Figure 31. Top - ratio of drag force to weight ($F_d/mg = DV/V_0$) vs. flow rate for polystyrene particle (x) and for Spherocharb (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 32. 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 33. 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.

Figure 34. Distribution of lattice lengths L_a (in Ångstroms) for Sphero carb particles at zero and greater than 97 percent conversions.

Figure 35. Distribution of interlattice spacings d_{002} (in Ångstroms) for Sphero carb particles at zero and greater than 97 percent conversions.

Figure 36. Conversion versus time and a sequence of shadowgraphs presenting the development of shape of a 204 microns Spherocarb particle oxidized in air at 920 K as a function of conversion; C is conversion, l is length, and w is width.

Figure 37. Ratio of porosity to initial porosity vs. conversion. Initial and final porosities are indicated in figure.

7. Reactivity of Spherochar: Predictions by TEM

INTRODUCTION

The combustion of coal char can, depending on char temperature, occur in three regimes. At higher temperatures, the reaction rate is controlled by boundary layer diffusion to the particle surface (Regime III). At low temperatures, the reaction rate is controlled by the kinetics of the surface reaction of carbon with oxygen. The oxygen can diffuse throughout the pores of the particle faster than the particle can react, so the oxygen concentration is uniform throughout the porous particle (Regime II). At higher temperatures, the reaction rate increases to the point that diffusion of oxygen through the pores as well as surface reaction determines oxidation rate (Regime II). In Regime III, only a thin layer of char will oxidize, leading to the classic shrinking sphere model. In Regime I, the carbon loss will occur uniformly so that diameter stays essentially constant while the density decreases linearly until conversion is nearly complete.

In char oxidation studies at temperatures low enough ($T < 900\text{K}$) to be in Regime I, Hurt et al⁸⁵ observed that some chars, notably Spherocharb and sucrose char, did not gasify at a constant diameter as expected, but instead "shrank." Shrinkage has been observed in various other studies^{86,87,88} for highly porous synthetic chars oxidized in regime I. It has been shown⁸⁹ that shrinkage is a general phenomenon occurring for a variety of carbonaceous materials at ranges varying from tens of nanometers⁹⁰ to 70 mm.⁹¹ The observed shrinkage either means that the coal structure has changed, as postulated by Hurt and others, or that the particles did not burn in the kinetically limited regime. Hurt et al.

also observed that external features, such as pore diameters, decreased in size at the same rate as the particle diameter. If the reaction was occurring without shrinking, the pore diameters would be expected to enlarge as the particle reacted.

Hurt et al.⁸⁹ speculated that as the char loses carbon, atomic rearrangements causes the loss of pore volume in the fine pores. These atomic rearrangements lead to the graphitization accompanied by an increase in the density. This is consistent with the observation of Levendis et al.⁹² that as the oxidation temperature increased, there was increased graphitization of synthetic chars, but that little graphitization occurred when the char was heated in nitrogen. Oxygen accelerated the graphitization process. Thus, there is evidence that as chars react in oxygen, the carbonaceous material undergoes graphitization.

The extent of graphitization is of importance to the model of char oxidation. It has been found that the reactivity of graphite prism planes is an order of magnitude higher than for that of the basal plane.⁹³ Graphitic oxidation occurs mainly at the prism faces in uncatalyzed reactions, although basal plane defects cause pitting corrosion, creating additional prismatic faces during gasification.⁹⁴ Davis et al.⁹⁵ found that for pulverized coal ($T > 1800\text{K}$) oxidation, three dimensional graphitization did not occur due to insufficient reaction time, but rather lead to the growth of regions of turbostratic order. This growth in turbostratic order was accompanied by decrease in char reactivity. Following the assumption that the structure of the Spherocarb is changing, one can apply high resolution transmission electron microscopy techniques to examine the

microstructure of Sphero carb. This paper examines the microstructural evolution of Sphero carb for oxidation in Region I using high resolution electron microscopy.

EXPERIMENTAL METHOD

Sphero carb particles were oxidized to different extents of conversion at 773 K in air using a Cahn 2000 TGA with attached data collection equipment. Carbon conversions were determined by analyzing the weight versus time, starting from an initial weight of approximately 10 mg. The structure of the particles was then determined by the combined use of high resolution transmission electron microscopy (HRTEM) and quantitative measuring techniques using software (SEMPER 6P).

After combustion, the samples were imaged using an optical microscope with an attached 35 mm camera in order to get overall dimensions of the final product. For HRTEM observation, the samples were ground for 5 minutes in a ball mill. A mortar and pestle was employed when the sample size was limited, such as at high carbon conversion. Analysis of unoxidized Sphero carbon prepared by the two methods showed no differences between mechanical grinding and hand crushing. After grinding, a small portion of each sample was ultrasonically suspended in ethanol and deposited dropwise on a lacy carbon TEM grid. An oriented gold crystal was used as a calibration standard and subjected to the same image analysis techniques as the Sphero carbon samples. The use of a specifically "oriented" gold crystal allows only the lattice locations in one plane to be

diffracted. Then, precise measurements of the lattice distances may be made and compared to the experimental samples.

An Akashi/TOPCON 002B transmission electron microscope with an LaB₆ filament operating at 200 KeV was used to record high resolution images of each sample. These samples were then digitized with a UMAX powerlook II model scanner. The high level language computer software, SEMPER 6P™(Synoptics, LTD., Cambridge, UK), developed especially for use with high resolution electron microscopy, was then used to manipulate the stored images in order to extract data for each Spherocarb sample. From these digitized images, optical diffraction patterns were generated. The optical diffractogram is a power spectrum calculated from the modulus of the Fourier transform. Intensity profiles characteristic of the range of contrast of the diffractograms were then produced. A series of "filters" was also applied to the digitized images to extract only the significant structural data from the image while eliminating unwanted characteristics. This then becomes the basis for statistical analysis of the structures.

The parameters that can now be quantified are the lateral extent of fringes, fractional coverage and interlayer spacing. The lateral extent of fringes is defined as:

$$L_a = \sqrt{\frac{m_{\max}}{m_{\min}}} \quad (20)$$

where m is the principal second moment of area. A second moment is a mean square of all pixels about a line through the center of area of a structural element (fringe). The

principal second moments are the second moments with respect to a pair of mutually perpendicular axes in directions that achieve maximum and minimum moments.

To get the characteristic interlayer spacing value for the sample, first the total area (Original Area) of fringes was determined with minimal filtering, which corresponds to eliminating repeated frequencies only below 0.3 nm and above 0.5 nm. Then, in order to eliminate possible differences in sample image illumination, the intensity range was narrowed and shifted to a position in which the area of fringes showed a maximum. The fractional coverage is then simply the ratio of total area of fringes in this two-color image at the maximum to total area of image.

RESULTS

A typical weight loss curve is shown in Figure 38 for complete oxidation of spherocarbon, while the reactivity of spherocarbon may be found in Figure 46. The oxidation rate of 2g/g₀-s agrees well with the data reported by Hurt⁴⁶ and Gavalas⁴⁸ for Spherocarb, with a high degree of repeatability. Figure 46 shows the reactivity of Spherocarb plotted on a normalized weight basis (initial and instantaneous). The reacted Spherocarb particles were imaged to confirm the shrinkage observed in previous studies^{30,86,89}, and are shown in Figure 33.

A typical TEM micrograph for Spherocarb taken with the HRTEM is given in Figure 39 showing the turbostratic structure. The turbostratic structure is the random orientation of the carbon atoms layers in the Spherocarb lattice, in contrast to the highly oriented lattices

of graphitic structures. This micrograph was digitized and stored as a 1024 x 1024 pixel image. A circular portion of Figure 39 is masked off using the image analysis software in order to isolate a section for analysis. A power spectrum is then generated from the image to show the periodicities present in the soot sample, and is shown in Figure 40. This also provides a check of microscope technique, since for the randomly oriented spherocarb, the power spectrum should not show any orientation preferences

The image in Figure 41 was further manipulated by applying a series of "filters" using a series of software commands to extract only the significant structural data from the image while eliminating any unwanted characteristics. Figure 41 shows sample extracted structures of Spherocarb at various levels of conversions.

The lattice fringe length and d_{002} distributions derived with the Spherocarb extracted structures are given in Figure 42 and Figure 43 respectively. It is important to note that in order to minimize variations that could arise locally in the Spherocarb, these distributions are based on a minimum of 3 observed regions, typically 2 from the same negative and an additional area as a check.

DISCUSSION

Modelling Of Reactivity Using Fringe Length Change

The lattice imaging shown in Figure 42 reveals that there is an observable change in lattice length with oxidation. While Marsh et al⁹⁶ observed an increase in lattice structure with La going from approximately 1 nm to 2.5 nm at heat treatment temperatures of 750 and

1148 K respectively, we observe a change of 1 nm to 1.5 nm. As the Spherocarb is essentially a pure carbon, it is ideal to test whether the lattice length is a factor in the reaction rate of the carbon particles. In this analysis, we assume that the lattice length measured is measure of the aromatic, graphitic like structures. Marsh et al⁹⁶ suggested that these carbon structures may line up to yield apparent length comparable to those of longer molecules. However, we assume that for the thin edge samples examined that this is not a factor.

In order to derive a model for the oxidation of Spherocarbon, the following assumptions are made:

- 1) No generation of lattice fringes occur during oxidation.
- 2) The porous region where reaction takes place does not change significantly during oxidation.
- 3) The rate of reaction for a given fringe length is constant. Changes in reactivity for a fringe of a given length due to changes in interlattice spacing or changes in any catalytic activity are neglected.

Letting NdL represent the number of fringes in length $L + \Delta L$ as

$$NdL = \text{Number of Fringes in Length } L + \Delta L \quad (21)$$

A population balance on the number of fringes of length L to $L + dL$ yields

$$\Delta L \frac{d}{dt}(N) = N\left(\frac{dL}{dt}\right)_L - N\left(\frac{dL}{dt}\right)_{L+\Delta L} \quad (22)$$

where the term on the left gives the time rate of change of the number of fringes. The first term on the right gives the growth into (out of) the size range of the fringe of smaller size when dL/dt is positive(negative), and the second term gives the growth out of(into) the size range to (from) large sizes when dL/dt is positive (negative).

Making use of the definition of the derivative with respect to L , one can then find that

$$\frac{dN}{dt} = -\frac{d}{dL}\left[N\frac{dL}{dt}\right] \quad (23)$$

$$= \frac{dN}{dL}\left(-\frac{dL}{dt}\right) + N\frac{d}{dL}\left(-\frac{dL}{dt}\right) \quad (24)$$

The change in lattice length with respect to time is essentially the reaction rate of the lattice, so

$$r = -\frac{dL}{dt} \quad (25)$$

substituting r for the expression, one can then find that

$$\frac{dN}{dt} = \frac{dN}{dL}r + N\left(\frac{dr}{dL}\right) \quad (26)$$

It is important to note that all of the terms in equation 6 except for r are known quantities, as

$$\frac{dN}{dt} = \text{Change in number of fringes} \quad (27)$$

$$\frac{dN}{dL} = \text{Derivative with respect to } L \text{ of the distribution function} \quad (28)$$

$$\frac{dr}{dL} = \text{Change in reaction rate of fringes with changes in } L \quad (29)$$

One must now relate the TEM measurements of the fringes to the model, as the TEM only gives a representative sample, not a full measurement of all the fringes (N). An estimate of the number of fringes must now be made using a mass or atomic balance. The absolute number of carbon atom, N_T , may be derived by the weight of the sample if Spherocarb is assumed to be 100% carbon. We assume that there are essentially two types of carbon in our system, an ordered carbon giving rise to TEM diffraction patterns (N_O), and a disordered, randomly oriented sample that gives rise to no lattice fringes (N_R).

$$N_T = \text{Total Amount of atomic Carbon} = N_R + N_O \quad (30)$$

We can make use of the coverage, C , the fractional coverage of an area by the lattice fringe, which only applies to ordered carbon. Assuming that this area variation extends to three dimensions, the fraction of random of random carbon is given as

$$f_R = 1 - \Theta - F \quad (31)$$

Where Θ is the microporosity measured experimentally and F is the fractional coverage of ordered carbon in the TEM image, assumed equal to 2 times the coverage C .^b The total amount of ordered fringes may then be assumed to be

^b $F = 2C$ as the coverage counts only the fringe area, and not the area between fringes, which in the calculation of the coverage is counted as a void.

$$N_o = \frac{F}{f_r + F} N_i \quad (32)$$

Therefore, the total number of carbon atoms in an ordered matrix is can be determined.

However, this still does not give the number of fringes. Two methods are available to

estimate the total number of fringes, which assumes that the carbon length in the

horizontal is the same in the depth field. Once can assume that the fringes occupy a disk

volume $\pi \bar{L}^2 d_{002} / 4$, where $\bar{L}^2$ is the average fringe length. This then gives a final number of fringes of

$$N_f = \frac{4N_o}{\pi \bar{L}_{avg}^2 d_{002}} \quad (33)$$

However, one can note that the number of carbon atoms per atomic distance is not a linear

profile, as given in Figure 44. Once can use the relationship of Figure 44 for the number

of carbon atoms at a given fringe length, n_L , and the actual distribution of length L to find

the number of fringes:

$$N_f = N_o \cdot \sum_0^{\infty} f_L \cdot n_L \quad (34)$$

Modeling Results

A plot of lattice reaction rate r as a function of lattice length is given in Figure 45. The

reactivity at short range order is approximately 75 times the reactivity of the long range

order fringes. This reactivity corresponds well to the 100 to 1000 magnitude difference in

reactivity reported by researchers¹⁰.

Using the reactivities of the fringes, one can use the fringe distribution to derive the total reactivity of the Sphero carb using the following relationship

$$R = \sum_{l=0}^{\infty} r_l \cdot f_l \cdot L_w \quad (35)$$

where L_w is the length per unit weight for a given lattice length, as derived from Figure 44. The results of the calculation and a comparison with the reactivity obtained with the TGA is given in Figure 46. The reactivity at low conversion agrees well with the reactivity as measured with the TGA. However, since the initial reactivity is included in the calculation as a base case, this is not surprising. What is more important is the trend involved. As conversion level increases, the reactivity of the Sphero carb, when normalized with the remaining carbon, actually increases, whereas the reactivity predicted by the model decreases.

If one examines the model from a qualitative approach, the results agree well with the supposition that ordered carbon has a lower reactivity. The extracted structures shown in Figure 33 clearly show ordering to be occurring in the samples, yet reactivity increases.

Possible explanations for this lack of correlation between data and model

1. The contribution to the reaction of nonimagable carbon distorts the changes in reaction rate.
2. Changes in catalytic effects with time influence the reaction rate
3. The ordering we see is different than other orderings previously observed.

The contribution of nonimagable carbon to controlling the reaction could well be a factor. However, the reactivity of this disordered carbon should be quite high (essentially,

all carbon atoms can be considered edge carbons). For Regime I oxidation, this reactive carbon would be consumed at the beginning of oxidation, resulting in lower reactivity with conversion as the less reactive species begin to predominate.

Catalytic effects could well be a factor. At high carbon conversions, the ratio of catalyst to carbon increases with a consequent possibility of increasing reaction with conversion. Such effects have been observed with mobile catalysts such as potassium, but it is uncertain what role the trace elements play in Sphero carb.

We are now left with the supposition that the ordering we are seeing is somewhat different from orderings observed in the past. Studies of the effect of ordering of carbon on reactivity have mostly focused on thermal annealing, with very high activation energies (400-800 kJ⁹⁷) requiring extended treatment. It is possible that the "oxidative annealing" shown in these experiments proceeds in a manner so as to preserve many of the active sites where gasification occurs.

CONCLUSIONS

The use of HRTEM and image analysis provides a possible means of obtaining the reactivity of carbon of different lattice length. The results of the exploratory study here shows the potential of the method even though results leave some unanswered questions.

Figure 38. Weight loss of Sphercarb as a function of time at 773 K.

Figure 39. Typical micrograph of Spherocarb.

Figure 40. Powers spectrum of Spherocarb.

Figure 41 Typical extracted structure of Spherocarb.

Figure 42. Lattice length variation as a function of oxidation. The duplicates represent different TEM images from the same sample.

Figure 43. D002 Spacing variation as a function of oxidation

Figure 44. Variation in lattice length as a function of carbon atoms. The aromatic molecules depicted are the symmetric molecules that are assumed to represent the lengths images.

Figure 45 Reactivity of Fringe Lengths as a function of Lattice fringe length. The reactivity reaches an asymptotic value at about 15 A.

Figure 46 Reactivity of Sphercarbon as a function of conversion. The theory does not predict the right trend from the TEM.

8. Summary of Work done for this Project

The examination of the structural evolution of carbon during oxidation has proven to be of scientific interest. Early modeling work of fluidized bed combustion showed that most of the reactions of interest occurs in the micropores, and this work has concentrated on these pores. This work has

- 1) Shown that the oscillations of CO_2 profiles during oxidation in a fluidized bed can be attributed to changes in the number of accessible pores.
- 2) Shown that the soot densifies during combustion by generating a novel TEM grid that can withstand extended periods in an oxidizing environment and still allow for imaging of the same nanometer size particle
- 3) Shown as soot oxidizes, the SAXS and CO_2 surface areas change. This change can be attributed somewhat to a phenomenon known as densification, although the true extent of this change depends on the modeling parameters chosen. However, the SAXS and CO_2 models do agree on overall trends in surface area during oxidation.
- 4) As soot densification proceeds, the particle shrinks. This shrinkage is concurrent with a growth in the number of long lattice lengths.

The growth in lattice length also occurs during oxidation of Sphero carb. This densification explains why high conversions of carbon may be obtained without fragmentation. However, as oxidation proceeds, the lattice length changes, becoming longer in length. According to current oxidation theories, the more order that is evident, the lower the reactivity should be. However, as ordering increases in Sphero carb, the

reactivity actually goes up. This may be due to catalytic inclusions, but should be examined more fully in the future.

Appendix A: TEM Analysis Technique

Much of this work relies on image analysis of TEM micrographs. The analysis of TEM micrographs quantitatively for structural order and other characteristics has traditionally been quite difficult. Methods such as defocusing, axial illumination, tilted illumination and the like often have been used to characterize the complex, randomly oriented crystals in carbons. Issues such as sample thickness can also cause difficulties due to diffraction from different layers. Taylor and Lipson⁹⁸ and Ban⁹⁹ used laser sources to obtain optical diffraction patterns when the laser light passed through a TEM negative. The resulting diffractogram were then analyzed. Building on the fact that these diffractograms were essentially Fourier Transforms of the images, Palotás¹⁰⁰ used computerized image analysis to characterize the same information. The technique presented in this appendix is based on the work of Palotás⁶³ on soot, extended to Spherocarb and other thicker samples of carbons which can be sectioned thin enough for TEM examinations.¹⁰¹

SAMPLE PREPARATION AND HARDWARE HANDLING

For the HRTEM observation a small portion of each sample of carbon was ultrasonically dispersed in ethanol. Generation of the samples thin enough for measurement in the TEM was accomplished by use of a ball mill and/or a mortar and pestle. Figure A-1 shows digitized Spherocarb images and the resulting extracted structure and analysis for each of the two methods. No significant differences were found between the sample methods. Once a fine powder was generated, the dispersed suspension was deposited dropwise on a

copper TEM grid coated with a lacy carbon film. The examination of the samples was carried out on areas that extended over the holes in the supporting film in order to avoid interference from the amorphous carbon background film.

An Akashi/TOPCON 002B transmission electron microscope, operated at 200 keV, with a LaB₆ filament was used to record high-resolution images of each sample. These images were then digitized with a VIDEK™ image acquisition system equipped with a Kodak MEGAPLUS™ Model 1400 camera and stored as 1024×1024 pixel computer images for the first part of this project. The digitization process was replaced by directing scanning using a UMAX POWERLOOK II digital scanner to confirm that the two different systems gave the same results, the same negative area was digitized with the two different methods. An analysis of the structure of the resulting images showed no significant difference in the resulting data(Figure A-2).. Analysis of the images was accomplished using the high-level language computer software, SEMPER6P® (Synoptics Ltd., Cambridge, UK), developed specifically for use with high-resolution electron microscopy, was then used to manipulate the stored images.

Using SEMPER6), optical diffraction patterns were generated. The optical diffractogram is a power spectrum calculated from the modulus of the Fourier Transform. Intensity profiles characteristic of the range of contrast of the diffractograms were then produced. A sample power spectrum of Sphero carb is given in Figure A-3. The diffraction pattern is a circular cloud as the fringes are approximately evenly distributed over all possible directions with a wide range of interlattice spacings.

Filter Pass

The Fourier transform is filtered (masked out) in the high and low bands by specifying the minimum and maximum layer spacing(d_{002}). The range chosen was between 3.0 and 4.5 Angstrom in order to capture only fringes of reasonable interlattice spacing. This corresponds to the AA and BB parameters in Appendix B. The value of 235.62 was obtained by measuring the pixel distances between lattice points for the gold standard in Fourier space.

Threshold Intensity

This is the minimum in intensity of a pixel considered as part of a fringe in the processed image. Figure A-4 shows the results of varying the intensity threshold and filtering parameters. The lower the intensity, the fewer number of fringes are seen as fewer pixels satisfy the intensity parameter. As can be seen in Figure A-4, there is a great deal of variation in image with intensity, which poses a problem due to varying thickness and microscope parameters, which will change the intensity of the fringes. To solve this problem, a plot of the fraction coverage versus intensity threshold is created for each image, as shown in Figure A-5. The intensity used analysis corresponds to the intensity where the maximum number of lattice fringes can be found, and was well explored by Palotás.⁶³

Using a correlated gold standard, the number of pixels per Angstrom was found in the Fourier space. The relationship established using the oriented gold single crystal can be used to translate the $[d_1, d_2]$ range of interest, specified for pattern repetition, into an $[r_1, r_2]$ region in Fourier space. The FT of the original image is then masked for $r < r_1$ and $r > r_2$ ($r_2 > r_1$). The remaining annulus is then reverse transformed^c. The gray scale filtered is then transformed to a two color 'extracted structure' by establishing an intensity threshold value for the intensity of the pixels, separating the two colors (here selected as black and white). This extracted structure is the basis of analysis most of the previous chapter, and complete details on the image properties tested may be found there or in Palotás63. A complete write up of the SEMPER6P analysis code is found in Appendix B.

SOFTWARE PARAMETERS

The software parameters chosen were based on the early work of Palotás63 and experience, and should be valid for most carbons. However, an examination of the software parameters used in the analysis is warranted.

^c Theoretically the center peak (corresponding to infinite distance on the original image) in the Fourier space is always needed for the reverse Fourier Transformation, therefore an annulus would be insufficient. Our image analysis software retains the information content of the center peak, and even if the center is manually masked out the reverse transform can be performed.

Minimum Fringe Area

This is filtering parameter for the fringe size that will be considered in the extracted structure. The minimum area used to define a fringe was determined by multiplying the width of one of the thinner fringes (approximately 1 Å) by the length of two aromatic units (approx. 5 Å). The width (1 Å) is much smaller than the characteristic spacing (3-4 Å) due to the fact that the microscope will only provide contrast where atoms exist to provide contrast, and thus is much smaller than the characteristic spacing (in practical terms, roughly ½ of the space between planes will be excluded from the fringe due to contrast differences, resulting in thickness of 1-2 Å. Using the conversion ratio of 0.4336 Angstrom/nm, this corresponds to a size of approximately 25 pixels. The elimination of noise to the maximum possible extent is vital, since it can falsify describing parameters, e.g., orientation or elongation distributions.

As the minimum area is of critical importance, a distribution of the lattice fringe length was obtained by varying the minimum size parameter, as shown in Figure A-6. The absolute number of lattice fringes is seen to increase in size as the minimum area is increased without altering the distribution of larger fringes significantly. The width assumption is confirmed by comparing the maximum fringe hits for minimum areas of 20 and 60 pixels. For the 20 pixel minimum area, the maximum number of fringes is located near at 4 Å, corresponding to a mean thickness of 0.94 Å. The 60 pixel length is maximum is located at 10 Å, corresponding to a fringe thickness of 1.1 Å. For the basis of this analyses described in this report, a minimum area of 20 pixels was assumed,

although the lengths of less than 5 Å were measured but not used, as 5 Å corresponds to the minimum length that can be reasonably be expected to appear for symmetric aromatic molecules.

Figure A- 1. Comparison of Sphercarb particles and the subsequent analysis obtained by using two different powder preparation methods. Hand grinding in a mortar and pestle for 10 minutes or ball and mill grinding for 5 minutes. No statistical change is evident.

Figure A- 2. Comparison of Sphercarb particles and the subsequent analysis obtained by using two different methods to digitize the samples, a) VITEK scanner and b) UMAXS Powerlook II. No difference is evident except for those to be expected as the digitized regions samples are not exactly the same. The high degree of conformity also illustrates that the methodology provides for reproducibility.

Figure A- 3. Sample power spectrum of Spherocarb(a) depicted in Figure 5 . The cloud like character(a) is due to the random distribution of different lattice lengths in the sample. The power spectrum is also a good check for any long range ordering in the structure, as this will skew the power spectrum. Errors in microscopy techniques are also evident in the power spectrum in the same manner as a flattening, as in (b), a power spectrum from an astigmatic TEM image..

Figure A- 4. Effect of software parameters on the extracted pattern (carbon black). The horizontal axis shows the frequency window for the repeated pattern while the vertical

axis is I_t , the intensity threshold value for the filtered image. From Palotas.
 defined.

Figure A- 5. Effect of the intensity threshold value on the fractional coverage and on the number of lattice fringes found. As the minimum intensity accepted as part of a fringe increases the fractional coverage decreases since fewer pixels satisfy the condition of having sufficiently high intensity. At low intensity threshold value the fringes are long and thick and they are merged. As the threshold value increases the fringes begin to separate and the total number of fringes increases. By increasing the threshold value even more the disappearance of the lower intensity group of pixels accelerates and the number of identified fringes levels off and begins to decrease.

Figure A- 6. Variation in the number of fringes measured as a function of length for different size parameters. As minimum length goes down, the number of fringes increase dramatically. The value of 4 Angstrom is not entirely credible due to the nature of the minimum number of atoms needed to provide contrast, and can thought to be a lower limit on the lattice length.

Appendix B: Extracting structural data from TEM images with Semper 6P

This is a sample program needed to run Semper 6P to extract structural data, based on the program of Palotas^{Error! Bookmark not defined.}.

```
copy 6800 3:1; cd=3; 1
```

↑ This is the TEM image.

```
fourier 1 to 3; fullplane;
```

```
mask 3 radius 118; mask 3 inside radius 39;
```

↑ $r = \frac{235.62}{\text{distance in } \text{\AA}}$ ↑

```
halfplane; image; mask 3 radius 256
```

↑

Masks out possible computational errors outside image after
reverse Fourier.

```
analyse 3 5 1e -3.0 area 30,10000 segment 4
```

↑ The extracted pattern
("segmented image").

↑ Maximum area to be considered as "particle"
[pixels].

Minimum area for a "particle".

Intensity threshold: intensities above correspond to structure,
pixels with intensities below this value are not element of the
"structure" (do not form a "particle").

The Particle Parameter List (variable value: *ppl*=5).

pset count; TotalArea=0

↑ Count the particles, and the result is stored in variable *n*.

for index=1,n; pset area;

↑ The area of the actual "particle" (in pixels) is stored in
variable *a*.

TotalArea=a+TotalArea; loop;

Closes the loop "for" started in the previous line.

Calculates Total Area of all the particles (if it is done more than once, it is important to annul it before the next loop).

type TotalArea

Types the numerical value onto the screen.

copy 4 to 6737 byte; copy 5 to 6738;

Saves the Particle Parameter List. If you need to analyze it later, don't forget to define the variable *ppl* (i.e. give value to it, before using any command related to the *ppl*:

ppl=6738; pset count;...).

Saves the extracted pattern in byte format (byte requires less space on the hard drive).

calculate :4 >0 to 4;4 to 1

Makes the segmented image ("extracted structure") black and white (originally it is multi gray level, each "particle" has an intensity value equal to its sequential number.

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