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Evolution of Porosity and Thermal Conductivity during Char Oxidation
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ABSTRACT

Measurements of the natural convection drag and the photophoretic force have been conducted for Spherocarb char particles as a function of carbon conversion. These forces were obtained by measuring the balancing voltage with and without laser heating during the reaction of single particles in an electrodynamic balance. The photophoretic force was determined by subtraction of the calculated natural convection force, after an initial transient corresponding to about five percent carbon conversion during which the natural convection force was dominant. The particle conductivity inferred from the photophoretic force was found to increase by more than one order of magnitude as the reaction progressed, qualitatively in agreement with models of the dependence of conductivity on porosity. Confirmation of the temperature gradient across the particle was provided by the development of asphericity in the particles when heated from below but not when heated uniformly. The simultaneous measurements of the mass, diameter, and particle conductivity as a function of carbon conversion provides a critical test of pore evolution models since the reaction rate is dependent on the accessibility of the internal surface area to the reactant gas through the open pore structure and the thermal conductivity is dependent on the connectivity of the solid structure. Induction periods were observed before the reaction rate accelerated and the particle conductivity declined, confirming the influence of pore structure on both. Particles could be reacted to a high conversion of greater than 95 percent without any evidence of fragmentation providing further insight on the connectivity of the solid surfaces.

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INTRODUCTION

The effect of pore structure on the reactivity and fragmentation of char, although extensively studied, is still poorly understood. One incompletely resolved problem area is the accessibility of the interior of the porous volumes within the char to the reacting gas external to a particle which is one of the many factors determining reactivity. Another is the continuity of the connectivity of the char which determines fragmentation. The dependence of combustion properties of chars on the nature of the pore structure is evident from the calculated values of the critical porosity for fragmentation for chars which can vary, for simple assumed pore shapes and pore network structures, from 0.26 to 0.968 [1]. The problem is further complicated by the recent observations that the carbon structure undergoes rearrangement during reaction which results in a shrinkage of particles under chemically controlled reaction conditions [2] and a decrease in the intrinsic rate of reactivity at high carbon conversions [3].

The present study is directed at examining the size, shape, density, and fragmentation of char over its entire oxidation history using an electrodynamic balance (EDB). In the EDB, a single particle is levitated by electrodynamic forces and a DC voltage is applied across the top and bottom electrodes to balance the forces—gravitational, natural convection, photophoretic—acting on a particle. The particle can be heated and the changes in reaction rate and particle morphology followed over a wide range of conversions. Several advantages of the EDB over a conventional thermogravimetric apparatus had been previously recognized [4]: 1. An ability to follow the reaction of a single particle, avoiding the problems encountered in thermogravimetric analyzers of averaging over several thousand particles, 2. The continuous monitoring of the shape and size of the particle, which together with the measurement of mass, gives a continuous measurement of particle density, 3. The ability of determining fragmentation from the simultaneous observation of shape and weight changes, 4. The ability to follow reactions without the mass transfer problems resulting from multiple particles on a pan or from the boundary layer around the supporting pan. An additional advantage introduced in this paper is that of measuring the changes in thermal conductivity of the particle by measurement of the photophoretic force when the particle is heated from below. The conductivity can be measured continuously by interrupting the laser heating periodically during a run and determining the difference in balancing voltage, at a given weight, due to natural convection and photophoresis. After subtraction of the natural convection force the thermal conductivity can be inferred from the photophoretic force. It is therefore possible to follow the connectivity of the solid portions of a char, as inferred from its thermal conductivity, as well as the rate of reaction as a function of conversion. These

simultaneous measurements provide new insights on the evolution of the pore structure.

Experiments have been performed on synthetic char particles, Spherocarb, which have been extensively studied because they provide a reproducible material that can approximate a high surface area coal char. The Spherocarb particles have the further advantage of being spherical and being fairly uniform in size.

EXPERIMENTAL

The char oxidation studies were carried out in two different EDBs, one laser heated from below and one heated symmetrically from the sides, and a thermogravimetric analyzer (TGA). A schematic representation of the EDB is provided in Fig. 1. The electrodynamic field used to levitate the particle is produced by an AC voltage applied between the ring electrode and the top and bottom electrodes. Vertical forces on the particle are balanced by a DC voltage applied across the top and bottom electrodes. The particle position is maintained in the center of the balance with a vertical stability of better than 0.5% of the particle diameter by projecting an image on a photodiode array detector, which is used both to provide a signal to the feedback controller and a measure of the particle vertical diameter [5]. In addition a particle image is focused on a CCD camera and recorded at 24 frames per second. The particle is heated by a CO₂ laser either from below (Ben-Gurion) or opposed in a horizontal plane (MIT). When heating from below the laser is operated in the TEM₀₁-mode which provides a doughnut intensity profile which enhances the particle stability. The beam can be interrupted on command using a laser shutter controller. The temperature of the particle is measured by a two color infrared pyrometer [5]. During an experiment the size, shape, and radiation signals are collected continuously.

In the present study the initial particle diameter for the bottom heated experiment was 165 μm , the initial particle density was 726 Kg/m^3 , and the average reaction temperature was 790 K. For the side heated experiment the particle diameter was 171 μm , the particle density was 902 Kg/m^3 , and the average reaction temperature was 740 K. For the experiments in the thermogravimetric analyzer the particles were in the size range of 160 - 220 μm , the particle density was 400 to 900 kg/m^3 , and the surface area in the range of 950 to 1020 m^2/g . The composition of the Spherocarb is 96.9 % carbon, 2.4 % hydrogen, and 0.7% oxygen.

Measurement of Particle Charge and Density

The EDB provides a measure of the mass to charge ratio for a particle. The charge, q , can be obtained by imposing a flow of known velocity u across the particle and measuring the change in the balancing voltage. For a known gas

flow through the bottom of the chamber, the balance between the particle weight and the sum of the drag force and the balancing electrical voltage, for a particle of mass m and diameter d , is given by

$$mg = 3\pi d\mu u + \frac{qc}{z_0} V \quad (1)$$

where c is the instrument constant with a value of about 0.5, z_0 is the distance between electrodes, V is the balancing voltage, μ the gas viscosity. The charge on particle may be obtained from the change in balancing voltage with changes in velocity [e.g., $q = - (3\pi d\mu z_0 / c) / (dV/du)$]. This permits the determination of the particle mass m and, given the diameter d , the particle density ρ_p .

Measurement of Natural Convection and Photophoresis

The force balance on a particle that is suspended at the center of the EDB and is irradiated from the bottom is given by

$$mg = \frac{qc}{z_0} V + F_c + F_p \quad (2)$$

where the weight of the particle is balanced by a combination of the force generated by the DC voltage, the natural convection F_c , and the photophoresis F_p . The method of operation was to interrupt the laser heating at periodic intervals using the laser shutter. It had been previously determined that the time constant for cooling of particles was of the order of tens of milliseconds [4]. The voltage V_0 , once the particle is at ambient temperature, provides a measure of particle mass, $mg = qV_0 c / z_0$. Additional information is provided by the difference in balancing voltage $V_0 - V$ with and without laser heating. This difference provides a measure of the combined natural convection and photophoretic forces: $F_c + F_p = (V - V_0)mg / V_0$.

RESULTS

The balancing voltages V_0 and V with and without laser irradiation are shown in Fig. 2 for the case of heating from below. The temperature to which the particle is heated is 790 K. When the laser heating is interrupted at the start of a run, the balancing voltage is seen to drop by about 50 volts, or a little less than 20 percent of the voltage needed to balance a particle. For a period of about 1000 seconds the voltage is seen to change little with time. After this induction period, the balancing voltage is seen to drop and the difference in voltage with and without heating to increase to about 100 volts or about 80 percent of the voltage needed to balance a particle. Since the time of interest is that in which the particles are reacting, the data are replotted in Fig. 3 as a

function of only the time during which the particle were heated or reacted. The relevant induction time before the reaction rate begins to accelerate corresponds to a period during which the particles were heated for 350 seconds. During this initial period little seems to occur to the diameter, the particle shape, or the difference $V - V_0$ in balancing voltage.

From here on out, the results will be presented as a function of carbon conversion rather than time. The changes in density and diameter are shown in Fig. 4, for the cases of heating from both the bottom and from the side. The shrinkage in the particle diameter is consistent with the results obtained earlier for chemically induced ordering of the carbon structure [3]. The slight decrease in density shows that the shrinkage in particle volume does not quite compensate for the loss in mass. An additional observation made was that the particles heated from below developed into oblate ellipsoids over time. Examination of the progressive reaction frame by frame showed that the particles were consumed preferentially from the bottom but as they became top-heavy would flip over so that the preferential carbon consumption, although always occurring on the bottom heated surface was evened over the top and bottom of the particle as a result of the periodic flipping over of the particle. This periodic pancake flipping mode rather than continuous rotation results in a particle with a shape resembling more an oblate rather than a prolate ellipsoid. In order to confirm that the distortion of the particles was due to uneven heating, the Spherocarb particles were reacted on a pan in a thermogravimetric analyzer, periodically extracted, and examined under a microscope. Under these conditions no departure from symmetrical carbon consumption was observed. Silhouettes of particles reacted in the EDB heated from below, which showed the major change in shape, and from the TGA are shown in Fig. 5 for selected carbon conversions.

DISCUSSION

The major difference in this study from that of previous studies is the difference in balancing voltage with and without laser heating. This difference provides interesting new insights on the evolution of pore structure during reaction. The sum of the forces normalized by the actual (not initial) weight of the particle is shown as a function of carbon conversion in Fig 6 for both the heating from below (open diamonds) and heating from the side (closed diamonds). The large number of points up to 0.05 conversion reflects the long induction time before the reaction accelerated. It can be seen that the force is greater for the case of heating from below for which the sum of forces acting on the particle increase from about 0.15 times the weight near zero conversion (not visible because of overlap of data), rise rapidly up to 0.25 near 0.03 conversion, and increase approximately linearly with conversion up to 0.8 at a carbon conversion of 0.6. For the case of heating from the side the forces were fairly constant at about 0.15 times the weight up to about forty

percent conversion. In order to evaluate the photophoretic force it is necessary to first separate the drag force F_c due to natural convection.

Natural convection

The previous experimental and computational study of natural convection from spheres at the low Grashoff numbers encountered in the balance could be well fitted, for particle diameters of 50 to 250 μm and temperatures of 500 to 1500 K, with the following equation derived from the correlation of drag coefficient versus Grashoff number obtained by Dudek et al.[6]:

$$\frac{F_c}{mg} = \frac{0.62}{\rho_p} (a_0 + a_1 d + b_1 T + b_2 T^2 + c_0 T d + c_1 T d^2 + c_2 T^2 d) \quad (3)$$

where the particle density ρ_p is in g/cm^3 , $a_0 = -0.0442$, $a_1 = 0.0001 \mu\text{m}^{-1}$, $b_1 = 0.00027 \text{ K}^{-1}$, $b_2 = -6.3966 \times 10^{-8} \text{ K}^{-2}$, $c_0 = -2.3198 \times 10^{-7} \text{ K}^{-1} \mu\text{m}^{-1}$, $c_1 = -1.6806 \times 10^{-9} \text{ K}^{-1} \mu\text{m}^{-2}$, $c_2 = 2.9530 \times 10^{-10} \text{ K}^{-2} \mu\text{m}^{-1}$. The drag force calculated from this expression using the measured particle diameter and temperature is plotted in Figure 6 for the cases of both heating from below (open squares) and heating from the side (closed squares). For both cases, the natural convection accounts for most of the observed imposed force at zero conversion. The calculated natural convection force over the weight of the particle is approximately constant since the decrease in diameter just about compensates for the change in mass of the particle.

Photophoresis

The photophoretic force is determined from the difference of the total force measured by the interrupted heating and the calculated natural convection. The difference for the heating from the side (closed circles) is close to zero but is measurable and increases with increasing carbon conversion. The heating from the bottom provides a large difference (open circles) with the photophoretic force increasing up to a value equal to six tenths the weight of the particle at 60 percent carbon conversion.

The photophoretic force F_p on a particle of diameter d much greater than the gas mean free path, a particle density ρ_p , and irradiated from one side with a flux density I [with units of energy/(area)(time)], is given by [7]

$$F_p = \frac{3\pi\mu^2 d [-dT/dz]}{2T_p \rho_p k_s} \quad (4)$$

where the particle conductivity k_s is much greater than the gas conductivity, μ is the gas viscosity, ρ_g is the gas density evaluated at the particle

temperature T_p , and $(-dT/dz)$ is the temperature gradient across the particle and can be approximated by

$$-\frac{dT}{dz} \equiv \frac{I}{k_s} \quad (5)$$

In the analysis the particle is assumed to be black and opaque, although if needed the photophoresis may be calculated for any particle optical constants [8].

Particle conductivity

The photophoretic force can be used to obtain thermal conductivity. First an energy balance on the particle can be used to relate the temperature of the particle to the incident flux density, to give:

$$I = \frac{8k_s(T_p - T_g)}{d} \quad (6)$$

Equations 4, 5, and 6 can be combined to obtain the following relation between the photophoretic force and the ratio of gas to particle conductivities:

$$\frac{F_p}{mg} = \frac{72\mu^2(T_p - T_g)k_s}{T_p\rho_s\rho_p d^3 k_s} \quad (7)$$

The ratio of thermal conductivity to particle conductivity obtained using Eq. 7 is shown in Fig. 7. The dependence on conversion of the conductivity for the case of heating from below ($J = -0.5$) is similar to that from heating from the side ($J = -0.1$), with the temperature gradient for the latter being estimated from the small photophoretic force to be one fifth that for bottom heating. It is difficult to obtain a value of the solid conductivity close to zero percent conversion since the natural convection dominates. But the thermal conductivity falls rapidly and can be already estimated at five percent carbon conversion. Furthermore, the conductivity decreases by more than an order of magnitude as the carbon conversion increases from 0.05 to 0.5.

The thermal conductivity provides an interesting measure of the interconnectivity of the solid space in the char. The Spherocarb particles have much of their porosity in included bubbles. It is therefore instructive to compare the changes in conductivity obtained here with the models presented in the literature. One of the first is due to Maxwell which treated the conductance of regularly spaced spheres of one conductivity in a continuous matrix of a second conductivity [9], but this model is inadequate for handling high porosity solids where the voids are overlapping.

The case of random overlapping spherical spheres has been handled by Kim and Torquato [10]. For gaseous voids that are not conducting this model provides the ratio of the effective particle conductivity to the solid conductivity as a function of the void volume fraction ϕ . The Spherocarb particles are on average 70 percent void prior to reaction. Since the density decreases by a factor of up to 0.5 (at a conversion of 0.6), the void fraction ϕ will increase up to a value of 0.85. For this carbon conversion, the present study shows k_g/k_s to have values of about 0.043, corresponding to k_s values of 1.33 W/(m)(K). The analysis of Kim and Torquato give values of 0.05 for the ratio of the effective to solid conductivity at $\phi = 0.85$. The conductivity of the solid matrix would therefore be 27 W/(m)(K). This value can be compared to that of extruded polycrystalline graphitic carbon which mostly lie, at 790 K, in the range of 20 to 100 W/(m)(K) [11]. The extraction of conductivity at different conversions give slightly different values of the conductivity of the continuous matrix, showing that the overlapping void model gives a reasonable but imperfect approximation of the porosity in Spherocarb at different stages of conversion. This illustration, however, demonstrates how the ability to measure the thermal conductivity of individual particles provides an additional test of the models for pore evolution during oxidation.

Particle asphericity

The development of oblate ellipsoids provides a confirmation of the temperature gradient across a particle when heated from below. From Eqs. 5 and 6 it may be shown that the maximum temperature difference across a particle is about $8(T_p - T_g)(k_g/k_s)$. For the bottom heating experiments this can yield temperature differentials across a particle of greater than 50°C after ten percent conversion. Since the activation energy for the reaction of Spherocarb is about 36 kcal/mol this temperature differential would provide a factor of three difference in the rate of reaction between the top and bottom of the particle, sufficient to explain the preferential consumption of carbon at the bottom of a particle and the evolution of disk shaped particles [12]

Induction time

The induction for the chemical reaction has been observed previously in thermogravimetric studies of Spherocarb oxidation and is in part due to the transient build up of surface oxide complexes [13]. Clearly, the induction time for conduction is coupled to that in reaction, but it is not clear at this time why there is such a strong dependence of conductivity on conversion at the low conversions. The five percent of the carbon consumed must have been distributed in critical conduction paths as the fractional difference in total porosity between zero and five percent conversion is not large.

Fragmentation

A further check of porosity models is provided by the fragmentation behavior of particles. As particles approach complete conversion it is difficult to stabilize them in an EDB. Complementary experiments were therefore carried out in a conventional thermogravimetric analyzer. The particles were reacted to 95 percent conversion and the decrease in diameter was measured using an optical microscope. The mean and standard deviation of the diameter for a sample size of ten particles is shown in Fig. 8. The results show evidence of particle shrinkage, as had been observed previously [3]. However, the particles showed no evidence of fragmentation even at the highest conversions. Since the particle volume decreased by a factor of 0.32, for a particle with initial porosity of 0.7 the final porosity is 0.955. These results are supportive of the models such as the random spherical void model [14] which predict that percolation occurs only at high porosities (0.97).

CONCLUDING COMMENTS

The use of interrupted heating in the EDB provides a means of measuring the sum of the natural convection and photophoretic forces acting on a particle. For an unreacted char, the thermal conductivity is high enough that the natural convective drag force overwhelms the photophoretic force. However, as the porosity of a particle increases, the thermal conductivity decreases to the point that the photophoresis can be measured and used to calculate the thermal conductivity. The thermal conductivity, being a measure of the connectivity of the solid portions of the carbon, provides an additional test for models on the evolution of pore structure during oxidation. The results on the Spherocarb are qualitatively consistent with the predictions of models that treat the char as a matrix containing randomly distributed voids, with the exception of the behavior during the initial induction period.

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FIGURE CAPTIONS

- Fig. 1 Schematic of the electrodynamic balance with CO₂ laser heating from the bottom.
- Fig. 2 Spherocarb particle oxidation in an electrodynamic balance with CO₂ laser heating from the bottom. Raw data of the DC balancing voltage and the vertical particle diameter versus time.

- Fig. 3 Spherocarb particle oxidation in an electrodynamic balance with CO₂ laser heating from the bottom. DC balancing voltage versus actual reaction (laser-heated) time.
- Fig. 4 Spherocarb particle oxidation in an electrodynamic balance with CO₂ laser heating either from the bottom (hollow symbols) or from two opposing sides in the horizontal plane (filled symbols). Dimensionless particle diameter and particle density versus conversion.
- Fig. 5 Images of single Spherocarb particles at different conversions: zero conversion; 48 % conversion, CO₂ laser heating from the bottom in an EDB; 80 % conversion, CO₂ laser heating from the bottom in an EDB; 45% conversion, TGA experiment; 95% conversion, TGA experiment.
- Fig. 6 Spherocarb particle oxidation in an electrodynamic balance with CO₂ laser heating either from the bottom (hollow symbols) or from two opposing sides in the horizontal plane (filled symbols). The sum of the photophoretic force and the drag force, the drag force and the photophoretic force which are divided by the actual particle weight are plotted against conversion. The error bars give an estimated maximal contribution of the non sphericity on the drag force and the photophoretic force, respectively.
- Fig. 7 Spherocarb particle oxidation in an electrodynamic balance with CO₂ laser heating either from the bottom (hollow symbols) or from two opposing sides in the horizontal plane (filled symbols). The ratio of the gas conductivity to the particle conductivity is calculated from the photophoretic force and is plotted versus conversion.
- Fig. 8 The particle diameter of Spherocarb particles oxidized in a thermogravimetric analyser in pure oxygen is plotted against conversion. (One point represents the mean diameter of 10 measurements and the error bars represent the standard deviation.)

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