Fragmentation Behavior of Single Coal Particles in a Fluidized Bed

Cathryn A. Sundback, Jānos M. Beér, Adel F. Sarofim

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Abstract

The fragmentation behavior of single bituminous coal particles has been studied in a small scale fluidized bed. A typical coal particle fragments, and swells slightly during devolatilization, producing particles in two distinct size regimes. Although the fragmentation pattern varies from particle to particle, the bimodal weight-based char size distribution obtained for the pyrolysis of a collection of coal particles was found to be little influenced by changes in bed temperature (1023-1123K), oxygen concentration (0-10%), and coal particle size (2.2 - 6.2 mm).

The dramatic increases in burning rate following fragmentation made it possible to infer fragmentation during oxidation from the carbon dioxide concentration variation with time of the gas effluent from the burning of a single coal particle. The number and size of the coal fragments were determined by fitting the CO_2 data with the predictions of a char combustion model. The reduction in the average burning time due to swelling and fragmentation as determined at the experimental conditions of T=1073 K, O_2 = 5%, was about 60%, the overwhelming proportion of which was due to fragmentation during char oxidation.

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Introduction

Predictions of the carbon content in fluidized beds are important because carbon losses from the bed are proportional to the carbon loading, and because of carbon's role in the reduction of nitrogen oxides formed in the bed. The carbon load is proportional to the carbon particle burnout time and it is therefore important that processes which change the burning time be understood and quantitatively characterized. Since burning times are proportional to the particle diameter, raised to a power between one and two [1] even modest particle fragmentation will significantly decrease the burning time, and hence the bed carbon content.

Fragmentation of carbon particles under fluidized bed combustion conditions have been observed in several small scale studies [2,3,4,5,6]. The observations, with the exception of the work of Massimilla and coworkers have been qualitative. Chirone et. al.[3,7] inferred fragmentation from the size measurement of char particles retrieved from a fluidized bed fed with narrowly sized coal particles, providing evidence of the formation of many smaller particles. The objective of this study was to determine the impact of fragmentation on char burnout time and individual particle behavior by examining the rate of combustion of single particles fed to a bed. By use of single particles, the major increases in burning rate that occur during fragmentation can be measured and interpreted whereas these increases are masked in multiparticle studies.

Separate studies carried out on swelling and fragmentation during devolatilization provided information on the initial particle size distribution for the process of char oxidation.

Experimental Apparatus and Procedure

The fluidized bed consists of a 64 mm stainless tube with a 40μm sintered inconel distributor plate. The bed could be operated in two modes: for studies of swelling and fragmentation during pyrolysis a Nichrome wire mesh basket with 1.16mm spacings was immersed in the bed for retrieval of char particles during a run; for the time resolved oxidation studies a funnel for collecting the combustion products was bolted to the top of the bed (Fig. 1). Silica particles of 180 to 212μm, fine enough to pass through the wire mesh basket, were used for bed solids. The measured minimum fluidizing velocity was 31.8 mm/s at 1073K. All runs were made with a velocity five times minimum fluidization. The bed temperature, measured with a chromel-alumel thermocouple, was controlled by varying the input voltage to a three-zone furnace.

Devolatization

In order to quantify swelling and fragmentation during devolatization, single particles of a Kentucky bituminous coal (see Table I for properties) were fed to the bed and the char particles retrieved at predetermined times, selected to exceed the maximum volatile flame duration for the condition when particles were burned in air (the times varied from 6 seconds to 37 seconds, depending upon temperature and particle size). At the end of the run, the oxygen was replaced by nitrogen and the char particles extracted from the bed and quenched in a cold nitrogen stream. The resulting char particle dimensions (major and minor axes) were determined using an image analyzer and effective particle diameters calculated assuming the particles to be prolate ellipsoids.

Combustion

The progress of combustion of single coal particles was followed by continuously monitoring the CO_2 concentration in the exit gas. One percent water was added to the fluidizing gas to catalyze CO oxidation. The CO_2

measurements were made by nondispersive infrared (NDIR) detectors (ranges: 0-3000ppm, 0-5%CO_2) and the gas sample was filtered and dried to eliminate interference from water vapor with the CO_2 signal. Care was taken to maintain the sample pressure in the NDIR constant. Measurements of the CO concentration throughout a run were obtained by gas chromatography analysis of spot samples. The CO concentration was always less than 30 ppm.

The conditions used in the pyrolysis and combustion experiments are summarized in Table II.

Results and Discussion

Devolatilization

During the devolatization of individual coal particles, one to five char particles were produced for the 6.2 mm coal. The smaller 2.2 mm coal particles produced larger number of small fragments, but these particles did not contribute significantly to a mass-based distribution. The apparent volatile yield was a credible 47 percent indicating that particles too small to be collected by the wire mesh basket did not constitute a significant mass fraction of the total. The cumulative mass size distribution of the feed coal and the product char particles from 34 experiments are shown in Fig. 2 on a lognormal probability plot.

The straight line for the coal indicates that the particle size distribution is well represented by a unimodal lognormal distribution with a mean diameter of 8.63 mm. In contrast, the char shows a bimodal distribution. The smaller particles are the fragments produced during devolatilization with a mean diameter of 3.72mm. The size of the larger particles is influenced by both swelling and loss of mass by fragmentation. Their mean size is 9.38mm, showing that the net mean increase in their diameter is 8 percent. A statistical fit of the data was obtained in order to facilitate the calculation of burnout times. The equations developed using the methodology of Irani and Callis[8] are shown in Fig. 2.

Results obtained for the range of bed temperatures, oxygen concentrations, and coal particle sizes listed in Table 2 were very similar when normalized with the mean initial coal particle diameter, so that Fig. 1 may be used to characterize the fragmentation during devolatilization for all conditions studied.

Combustion

A representative CO_2 trace for the combustion of a single coal particle is shown in Fig. 3. In general, the CO_2 concentration rises during devolatilization to a level of about three percent. Towards the tail end of devolatilization, the CO_2 rapidly drops to a level of 400 to 1700ppm, the level being related to the number of fragments formed during devolatilization. For the 31 particles studied, the devolatilization time varied between 28.3 and 45.9 seconds as estimated from the time at which the steep devolatilization curve levelled off.

The area under the CO_2 curve beyond the devolatilization spike provides a measure of the mass of the initial char particles. The mass of the char was found to vary from 42 to 55 percent of the initial coal mass, consistent with an average volatile content of 47 percent. The ability to measure volatiles yield from the CO_2 suggests that mass loss of carbon in unreacted attrited particles was negligible for our conditions, although it is known to be significant at higher fluidization velocities[9].

One would normally expect the CO_2 profile to decrease monotonically during combustion. The high frequency fluctuations during combustion can be shown to be related to the circulation of char particles in the bed and are not of concern here; for the subsequent analysis the CO_2 curves were smoothed by averaging the signals over seven second intervals. There are, however, periodic step increases in the CO_2 level resulting from the acceleration in the burning rate following fragmentation. At least one and up to eleven such step increases have been observed for the different single particle experiments.

The char size distribution, including the effects of fragmentation, can be estimated from the shape of the smoothed CO_2 data.

Theoretical Considerations

The mass burning rate ρ is related to the CO_2 mole fraction, y_{CO_2}, by the simple mass balance equation

$$\rho = \frac{1}{12} \frac{P_o Q_o}{RT_o} \frac{y_{CO_2}}{\pi d^2} \qquad (1)$$

where Q_o is the volumetric flow rate through the bed evaluated at standard temperature (T_o) and pressure (P_o).

In turn, the combustion rate for a single particle can be related to its diameter by the conventional burning law (see Appendix).

$$\rho = \frac{C_g}{\frac{1}{R_c} + \frac{d}{3/8\ ShD}} \qquad (2)$$

where the first and second terms represent the terms for chemical and diffusion control. These simple equations may be used to infer information both on the kinetics and the fragmentation of the particles.

Determination of Kinetic Parameters

The CO_2 concentration obtained for a single char particle of known mass and size may be used to infer the chemical reaction rate, R_c by equating (1) and (2). From the devolatilization experiments it is known that a fraction of the coal particles do not fragment during pyrolysis. These particles can be identified from the CO_2 traces because (a) they yield a relatively low CO_2 level since their surface area is smaller than that of the pieces of a fragmented particle, and (b) the slope of the CO_2 curve is fairly flat in the absence of rapidly reacting small particles. The CO_2 traces for three particles, which satisfy these constraints, are shown in Fig. 4. The initial particle size d_o was estimated from the initial char mass obtained from the CO_2 trace, and found to be in good agreement with the coal size, adjusted for the small swelling factor. From the value of y_{CO_2} at the start of the char oxidation, values of R_c of 0.049, 0.039, and 0.047 (kgC) (m)/(kgO_2) (s) are found with an average of 0.045 (kgC) (m)/(kgO_2) (s). The value of R_c so determined is an intermediate to that of Field et. al.[10] and that inferred from Smith's[11] intrinsic rate using the BET area for the present char (see Appendix). For the present char, which has a relatively low surface area of 50m^2/gm, the kinetic resistance was half the total at the initial particle diameter ($d_o \cong$ 7mm).

Interpretation of CO_2 Profile For a Single Particle

In this section we wish to rationalize the observed CO_2 profiles. The step increases in burning rate on fragmentation can be deduced from the step increases in CO_2 but more information is needed to infer the number and size of the particles.

Additional information is provided by the shape of the CO_2 profiles which is strongly dependent upon particle size (in the limits of diffusion and kinetic control the y_{CO_2} - t curve are convex and concave respectively).

The size distribution is easiest to infer by starting at the time of burnout t_b. The time to burnout, $t_b - t_{f_1}$, from the time t_{f_1} at the last fragmentation point (step increase in CO_2) provides a measure of the largest particle size at t_{f_1}. This can be obtained using the integral form of the "shrinking sphere" burning law:

$$\int_{d_1}^{d_2} \left(\frac{1}{R_c} + \frac{d'}{3/8ShD} \right) dd' = \int_{t_1}^{t_2} \frac{2Cg}{\sigma_c} dt \qquad (3)$$

For particle 118, $t_2 = t_b$ = 31.3 min and $t_1 = t_{f_1}$ = 15.1 min. The difference in time corresponds to the burning time of a particle 2.2 mm in diameter.

The size of the next largest particle is obtained from the time at which the measured y_{CO_2} curve deviates significantly from that calculated from Eqs 1-3 for a 2.2 mm particle burning over the time interval t_{f_1} to t_b. A new y_{CO_2} curve can be calculated from t_{f_1} to the burnout time of the second particle and the process repeated to match the y_{CO_2} curve down to t_{f_1}. This procedure may be used to introduce more than one particle of a given size at a given time. This inversion procedure yielded 19 particles at t_{f_1}.

At a fragmentation point the constraints can be imposed that (a) mass is conserved, (b) the number and size of particles prior to fragmentation yield the correct lower value of y_{CO_2}, (c) the number and size are so selected as to match the y_{CO_2} - t curve to the next (prior) fragmentation point. It is difficult to obtain a unique solution. An approximate procedure was used here by making the simplifying assumption that only one particle fragments at each step increase in y_{CO_2}. The number and size of fragments recombined, stepping back in time, were determined by trial and error using the match of the measured and calculated y_{CO_2} curve between fragmentation times as a check. Particles which burn out between two fragmentation points are detected, as in the previous discussion, by a systematic positive deviation of the measured y_{CO_2} from the calculated values.

An illustration of the fragmentation behavior between the end of devolatilization, (t=0) and t_{f_1}, the last fragmentation point, is shown for particle 118 in Fig. 5. The time from the end of devolatization is shown along the top of the figure. The shrinkage of particles between points is shown by horizontal lines. For each time marked at the top of the figure, one fragmentation occurs; the sizes of the parent particles and fragments are shown interconnected. For example, at 13.3 min, a 2.9 mm particle fragments to yield four particles 2.0, 1.7, 1.7, and 1.8 mm in diameter.

The matches between the measured and calculated y_{CO_2} 's are shown in Fig. 4. The values of R_c used for each curve were those obtained for the individual particle (see previous section). The good match of the overall features of the CO_2 profile suggest that the fragmentation behavior postulated is roughly correct, although we recognize that slightly different combinations of particle number and size would give equally good results. No attempt was made to match the fine structure which we believed to be accounted for by very small fragments; the smaller the particle, the steeper the y_{CO_2} - t curve it produces.

The normalized mass of the char particles 106, 118 and 123 are shown as a function of time in Fig. 6. Fragmentation appear as small changes in the slope of these curves showing the difficulty that would be encountered in trying to detect fragmentation from time resolved weight loss measurements made on particles retrieved periodically from a fluidized bed.

CO_2 Profiles for a Collection of Particles

With a number of particles the inflection points are no longer evident as seen in the composite normalized mass curve in Fig. 7 obtained by summing the data on 31 individual particles. Also shown on the figure are the normalized mass of particles, having the shortest and longest burning time (119 and 130). These results underline the importance of using single particle studies for determing the effect of fragmentation.

Implications

The impact of fragmentation on the burning time is examined by comparing in Fig. 8 the measured normalized char mass of the 31 particles studied with those calculated assuming that the initial char particles (a) have the same dimensions as the parent coal particles - an assumption often made in modeling studies - and (b) undergo swelling and fragmentation during devolatilization only, using as input the empirical data from Fig. 2.

The results show how the burnout time, and therefore carbon loading, would be greatly overestimated using the two approximate formulations. The times required to achieve 99 percent burnout are 27.5, 63.3, and 70.6 minutes determined respectively from CO_2 measurements, calculation using the devolatized char size distribution, and calculation using the initial coal size distribution. Fragmentation of char during combustion, often overlooked in calculations, is of major importance for the set of conditions studied. Further studies, with different coals, particle sizes, and combustion conditions are needed to fully establish its significance.

Nomenclature

C	concentration of oxygen, kgO_2/m^3
d	particle diameter, mm
D	bulk diffusivity of oxygen, m^2/s
h_m	mass transfer coefficient (kgC)(m)/(kgO_2)(s)
m	true reaction order
n	apparent reaction order
P	pressure, pascal or cumulative probability
Q	volumetric florate, m^3/s
R_c	chemical rate coefficient based on external surface area, (kgC)(m)/kgO_2)(s)
R_i	intrinsic reaction rate coefficient based on internal surface area, (kgC)(m)/(kgO_2)(s)
Re	Reynolds number ($d\ U_{mf}\ \sigma_g/\mu$)
Sc	Schmidt number ($\mu/\sigma_g\ D$)
Sh	Sherwood number
T	temperature, K
t	time, s
U	gas velocity, m/s
y	molefraction

Greek Symbols

σ	density, kg/m^3
μ	viscosity (kg)/(m) (s)
ρ	reaction rate based on external surface area, (kgC)/(m^2)(sec)

Subscripts

b	burnout
f	fragmentation point
g	in bulk gas
mf	minimum fluidization
o	standard conditions or initial
p	particle
s	at particle surface