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Proceedings of the Combustion Institute 32 (2009) 2021–2027

Proceedings of the Combustion Institute

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A new technique for the measurement of the product CO/CO_2 ratio at the surface of char particles burning in a fluidized bed

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Abstract

A new experimental technique is proposed to measure the product CO/CO_2 ratio at the surface of spherical char particles during fluidized bed combustion. It is based on the measurement of the burning rate of a single char particle under low oxygen concentration conditions and on the use of an accurate prediction of the particle Sherwood number. This technique was applied to spherical char particles obtained from a bituminous coal which is characterized by a low attrition and fragmentation propensity. The product CO/CO_2 ratio was measured at a bed temperature of 850 °C and at a fluidization velocity of 0.3 m/s in a lab-scale apparatus operated with a bed of 0.5–0.6 mm sand. The char particle size was varied between 2 and 7 mm and the inlet oxygen concentration between 0.1% and 2.0%. Results showed that under the experimental conditions investigated carbon was mostly oxidized to CO_2 within the particle boundary layer, with a maximum fraction of carbon escaping as CO of 10–20% at the lowest oxygen concentrations and largest particle sizes.

Keywords: Fluidized bed combustion; CO/CO_2 ratio; Coal char; Sherwood number; Boundary layer

1. Introduction

Large coal char particles burn at typical fluidized bed (FB) conditions under the external (or boundary layer) diffusion control combustion regime. In these conditions the particle burning rate is controlled by the rate of oxygen transfer through the particle boundary layer and by the size and shape of the particles, i.e. by the external surface. Another quantity that influences the particle burning rate is the stoichiometry of the carbon oxidation. In fact carbon can be oxidized either to carbon monoxide or to carbon dioxide. The proportion to which carbon converts to either of the two products on the particle surface (the so-called primary CO/CO_2 ratio) has been the subject of an extensive number of research papers and it is still open to debate [1]. A further complication to the problem derives from the possibility of CO to be oxidized to CO_2 in the gas phase at or near the carbon surface. From a practical point of view, the critical quantity to be known is the CO/CO_2 ratio at the exit of the particle boundary layer, since any CO oxidized within this layer can be effectively considered to be equivalent to the primary CO_2 product. This is because both the

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doi:10.1016/j.proci.2008.06.047

oxygen transfer rate and the heating rate of the particle depend on the relative proportion of CO and CO_2 that are produced close to the particle surface. Measurement of this product CO/CO_2 ratio is very difficult since carbon monoxide can be further oxidized in the reactor far from the burning particle, even if the sand bed in a fluidized combustor is reported to provide a CO oxidation quenching effect [2].

The result of the above complexities is that very few works attempted to measure the product CO/CO_2 ratio for large char particles burning in a fluidized bed. In a pioneering work, Basu et al. [3] burnt anthracite coal particles in a fluidized bed at 850 °C and suppressed gas phase CO oxidation by injecting phosphorous oxychloride. They found a CO/CO_2 ratio value of about 0.4. Prins [4] measured the CO/CO_2 ratio during the FB combustion of single graphite spheres by measuring the CO and CO_2 concentrations at the reactor outlet and estimating the contribution of the homogeneous oxidation of CO within the reactor. The values obtained for CO/CO_2 were in the range 0.17–0.5 with an average of about 0.3 at 837 °C. Guedes de Carvalho and co-workers [5,6] compared results of combustion of coke and char particles in fixed and fluidized beds of either sand or Pt catalyst beads at 950 °C. Basing on the experimental data, they supported a mechanisms of carbon oxidation to CO at the particle surface followed by CO oxidation outside the particle boundary layer. Linjewile and Agarwal [7] measured the product CO/CO_2 ratio near the surface of fixed petroleum coke spheres burning either in a fluidized bed or in a convective flow using a specially designed water-cooled suction probe. The measurements for CO/CO_2 were in the range 0.1–0.55 at temperatures between 700 and 900 °C. Hayhurst and co-workers [8,9] estimated the CO/CO_2 ratio for large spheres of graphite or sewage sludge char burning in an air fluidized bed by measuring the carbon burning rate (following the CO and CO_2 concentrations at the reactor outlet) and the particle temperature. The heat balance around the burning particle was then solved with a heat transfer coefficient estimated according to literature data, and the CO/CO_2 ratio was extracted. Results at bed temperatures in the range 750–900 °C were consistent with CO being the main combustion product for graphite and CO_2 for the sludge char. Mathias et al. [10] burned large char particles from a bituminous coal in a controlled-profile reactor with a cantilever balance attachment at temperatures between 552 and 927 °C. The product CO/CO_2 ratio was estimated by matching a detailed reaction model with the mass loss and particle temperature data. For most of the experimental conditions investigated the analysis indicated full conversion of CO to CO_2 at the particle surface.

Most of the techniques reported before are based on a number of assumptions and approximations and produce results with a considerable degree of uncertainty. In this work a new technique is proposed which is relatively simple and accurate. It is based on the measurement of the burning rate (following the CO and CO_2 concentrations at the reactor outlet) of a single char particle under low oxygen concentration conditions ($[O_2] < 2\%$) in a lab-scale fluidized bed. In these conditions two advantages are obtained: the boundary layer mass transfer coefficient can be calculated without the need to account for high-mass-transfer-rate and/or possible non-equimolar-counterdiffusion corrections (the maximum error is below 1% as estimated according to Hayhurst [11] in the conservative case that the only reaction product is CO); heat effects are very limited and the char particle temperature can be assumed to be approximately equal to the bed one (this point will be discussed later). Comparison of the measured particle burning rate with an independently estimated particle Sherwood number, with the aid of a simple fluidized bed combustor model, allows us to find the product CO/CO_2 ratio, without the need of estimating the homogeneous CO oxidation rate in the reactor. The relevant particle Sherwood number is calculated by means of an accurate correlation recently reported in the literature and based on experimental data gathered in the same experimental apparatus and under similar operating conditions [12]. In this work the mass transfer coefficient around few freely moving Pt catalyst spheres in the bed was measured by following the CO oxidation reaction at 450 °C at different fluidization velocities, catalyst sphere sizes and inert bed particle sizes. Experimental data were excellently fitted by the following correlation:

$$Sh = 2.0 \cdot \varepsilon_{mf} + 0.70 \cdot (Re_{mf}/\varepsilon_{mf})^{1/2} \cdot Sc^{1/3} \qquad (1)$$

where Sh is the particle Sherwood number, ε_{mf} the bed voidage at minimum fluidization conditions, Re_{mf} the particle Reynolds number calculated at the minimum fluidization velocity, and Sc the Schmidt number.

In the present experiments spherical char particles obtained from a Snibston bituminous coal were burnt at 850 °C in a fluidized bed. Char from this coal has been reported to have the lowest propensity to attrition and fragmentation among the coals studied in previous investigations [13]. It is important to minimize these phenomena as they increase the carbon consumption rate and modify the size, shape and exposed surface of the char particle in a manner that is difficult to be accounted for.