SAND2013-3236C

Measurement of Pulverized Coal Char Combustion Rates in Different Diluent Gases: The Influence of Gas Diffusivity

Christopher R. Shaddix [1,*] and Cristina Gonzalo-Tirado [2]

[1] Combustion Research Facility, Sandia National Laboratories, Livermore, CA 94550 USA
[2]LITEC/Univ. of Zaragoza, María de Luna 10, 50018 Zaragoza, Spain

Abstract
One of the characteristics of CO_2 that influences the oxy-fuel combustion of pulverized coal char is its low diffusivity, in comparison to N_2. To explore how the gas diffusivity influences the apparent rate of pulverized char combustion, experiments were conducted in a laminar, optical flow reactor using helium, nitrogen, and CO_2 diluent gases. The char particle combustion temperatures were highest for combustion in N_2 environments, with combustion in CO_2 and He environments producing nearly identical char combustion temperatures, despite more rapid particle burnout in helium. Preliminary analysis of the apparent char kinetic burning rate in He yields a rate that is approximately three times greater than that in N_2.

Introduction

Oxy-fuel combustion of coal with recycled flue gas is a promising approach for continued use of coal for electric power production, while producing near-zero emissions of gases [1-3]. The nearly pure CO_2 product stream produced from this process is suitable for use in Enhanced Oil Recovery (EOR), Coal Bed Methane (CBM) production, or geologic sequestration. In contrast to coal gasification, oxy-combustion of coal allows carbon capture and sequestration as a retrofit technology for conventional pulverized coal boilers, taking advantage of the enormous capital investment represented by existing boilers. Also, oxy-fuel recycle combustion represents a modest modification of the existing pulverized coal combustion technology that has well-proven reliability and industrial acceptance.

Successful implementation of oxy-fuel combustion requires a detailed understanding of changes associated with replacing first in the oxidizer stream and with using enhanced levels of oxygen (as required to maintain similar temperature profiles when recycling CO_2). During coal char combustion, one of the important influences of CO_2 is through the reduced diffusivity of oxygen through a CO_2-rich gas. As shown in Fig. 1, oxygen diffuses 20% slower through CO_2 than through N_2. The impact of this reduced diffusivity of oxygen on particle burning rates and on derived char kinetic rates is complicated by the Zone II combustion behavior of pulverized char particles, wherein both oxygen diffusion and fundamental heterogeneous reaction rates contribute to the observed behavior. For application of apparent kinetic rate expressions, as are typically utilized in CFD modeling of burners and boilers, the influence of a reduced diffusion rate on the applicable kinetic rate is unclear, because the apparent rate implicitly accounts for (and is dependent on) the extent of oxygen penetration into the char particle.

To improve the understanding of the influence of oxygen diffusivity on derived char kinetic rates, we conducted char combustion experiments with three different diluent gases: nitrogen, carbon dioxide, and helium. The diffusivity of oxygen through helium is 3.5 times as large as its diffusivity through nitrogen. Furthermore, helium has the useful property that its thermal conductivity is also much higher than that of the other diluent gases tested (i.e., higher by a factor of approximately 5), such that the char particle combustion temperature remains similar to those in the other gases, despite the higher char oxidation rate in helium. For this reason, comparing the char reaction rates in nitrogen and helium can give good insight into the effect of O_2 diffusivity on the apparent char burning rate.

Experimental Methods

Sandia's combustion-driven optical entrained flow reactor was utilized for this study. This reactor has been well characterized and the details of its operation have been previously reported [4]. The particle-sizing pyrometer performs measurements of the char particle size, temperature, and velocity for individual entrained char particles. Char particle temperature measurements provide critical information on the actual char combustion rate temperature and, in the absence of competing gasification reactions, can be used to directly derive apparent char combustion rates [4].

To assure a common char starting material for the particles in the different reactor environments, high heating rate char particles were first generated from a Powder River Basin low-sulfur subbituminous coal by feeding pre-sieved pulverized coal particles at a low feed rate into a turbulent entrained flow reactor operating at 1200 °C and 1 atm with a nitrogen flow with 1.5% O_2 (to prevent tar formation and condensation) The particles were exposed to the high-temperature environment for 250 ms to assure complete devolatilization, before being quenched by means of room-temperature N_2 flow at the inlet of a water cooled collection probe. To ensure at least partial oxygen penetration, even for the cases of N_2 and CO_2 diluents, the 63-75 µm size cut was utilized in this study.

The choice of optical furnace operating conditions involved a complex balance of assuring ready char ignition and combustion, even in the presence of CO_2, while attempting to keep the char combustion temperatures low enough to minimize or eliminate contributions from boundary layer conversion of CO [5]

* corresponding author

and/or heterogeneous char gasification from CO_2 and steam [5,6]. For this reason, a nominal furnace gas temperature of 1300 K was chosen, produced by operating the Hencken burner that drives the furnace flow at an adiabatic flame temperature of approximately 1400 K. A total furnace flow of 40 slpm was used, with oxygen concentrations of 12 vol-%, 18 vol-%, and 24 vol-%. The dry (unheated) diluent gas that was used to deliver the char particles to the furnace was limited to 0.12 slpm for N_2 and CO_2 and to 0.20 slpm for He. It was observed that the helium diluent flows suffered substantially larger heat losses in the (upflow) reactor as a function of vertical position, presumably as a consequence of increased thermal conduction to the unheated reactor walls. Consequently, the burner adiabatic flame temperatures were fine-tuned such that the measured gas temperature at a height of 5 cm in the reactor was the same for all three diluents. The actual gas temperature profiles (shown in Fig. 1) were measured with a very fine wire (25 μm dia.) type-R thermocouple, corrected for radiant loss [7], and were utilized in the char kinetic analysis.

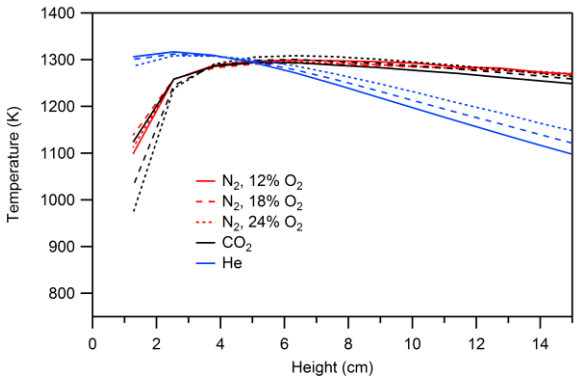

Fig. 1. Centerline gas temperature profiles in the optical entrained flow reactor for the investigated flow conditions.

Results and Discussion

To assure good sampling statistics, between 100 and 150 good quality single-particle optical signal traces were collected for each chosen sampling height for a given reactor condition. The particle residence time in the laminar flow furnace was deduced for each of the investigated flow conditions based on the optically measured mean char particle velocities (slight differences in velocity were evident for different flow conditions). Figure 2 shows the mean particle temperatures measured in the three different N_2 diluent environments as a function of residence time. For reference purposes, a height of 5 cm in the reactor corresponds to a residence time of 38 ms. Fig. 2 shows the expected dependence of char combustion temperature on the oxygen concentration of the furnace gas, for all three diluent gases. It is also apparent that the char particles ignite much more rapidly in the helium environment than in either the N_2 or CO_2 diluent environment. This would be expected, based on both the higher O_2 diffusivity through He as well as the high thermal conductivity of helium. These two factors act to rapidly heat the char particles while rapidly delivering oxygen to the particles to initiate exothermic oxidation reactions [8]. The steady burning char combustion temperature in CO_2 is consistently lower than in N_2, by 100–150 K, as has been observed previously [8-11]. Interestingly, the steady burning char combustion temperature in helium is almost exactly the same as that in CO_2. This presumably reflects the somewhat larger relative value of thermal conductivity of helium (helping to keep the particle temperature close to the ambient gas temperature) in comparison to its diffusivity (helping transport oxygen to the surface for reaction).

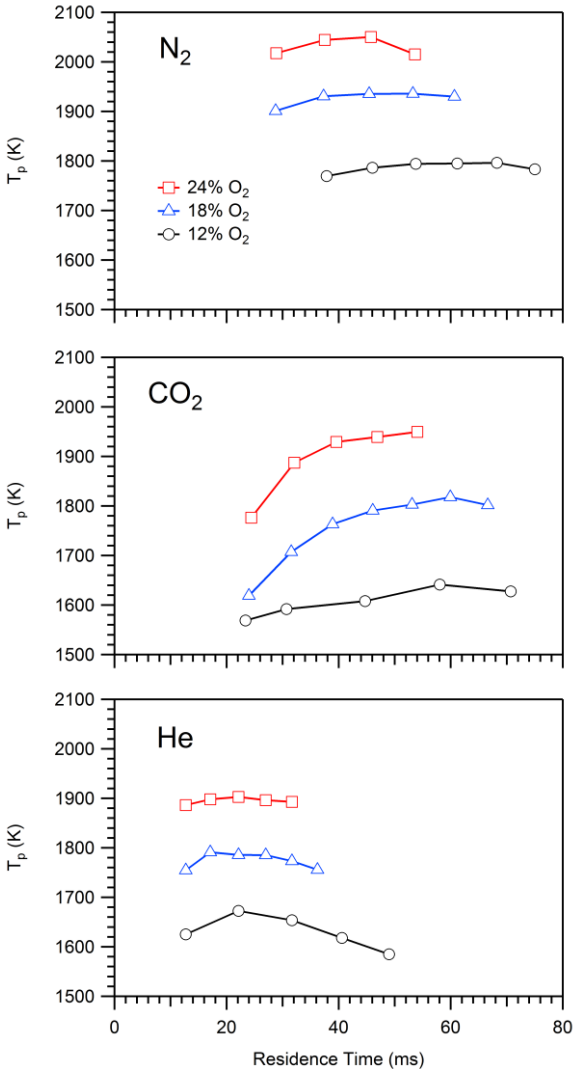

Fig. 2. Measured mean char particle temperatures as a function of residence time in the entrained flow reactor for N_2, CO_2, and He diluents.

A preliminary apparent kinetics analysis has been performed of the N_2 and He optical data by employing a single-film apparent kinetics reaction model for char oxidation [11] (including the Tognotti relationship for the CO_2/CO production ratio [12]) and deriving rms deviation values for the model predictions versus the

measured char particle temperatures as a function of position in the reactor. The best-fit results are achieved when employing a low activation energy for the oxidation reaction (40 kJ/mol), as well as a low value (0.15) of the reaction order for oxygen. Using these values, the model is able to predict the measured mean particle temperatures quite well. With these common values for the remainder of the kinetic parameters, the pre-exponentials for reaction in N_2 and reaction in He have the ratio of 1:2.9 – i.e. the apparent kinetic rate in helium is nearly three times that in N_2.

As mentioned in the introduction, the diffusivity of O_2 through He is approximately 3.5 times faster than its diffusivity through N_2. Consequently, we would expect the oxygen that is present at the char surface in a helium environment to be able to diffuse much more rapidly *into* the char particle, thereby accessing more surface area to react with. In fact, the diffusivity in porous catalysts and porous particles is typically modeled as being equal to the product of the molecular diffusivity and the porosity, divided by the tortuosity, i.e. $D = D_0 \, \theta/\tau$. Therefore, the diffusivity of oxygen into the char should be nearly 3.5 times faster for char particles burning in He than in N_2. As the only way for an apparent kinetics reaction model to account for differences in particle penetration is through the kinetic rate parameters themselves, it is perhaps not surprising that the apparent kinetic rate for char combustion in helium is so much larger than that for combustion in N_2.

This result highlights the inherent limitation of apparent kinetics approaches when the gas diffusivity varies, and suggest a similar, though much smaller, effect is probably apparent when deriving apparent kinetic rate constants for describing char combustion in CO_2. We are in the process of conducting a kinetic analysis with intrinsic kinetic models to better understand the data and therefore the role of gas diffusivity on apparent kinetic rates of char combustion.

Conclusions

Char combustion experiments were performed in a laminar, optical entrained flow reactor for N_2, CO_2, and He diluent gases. The char particle combustion temperatures were highest for combustion in N_2 environments, whereas combustion in CO_2 and He environments produced nearly identical char combustion temperatures. Preliminary analysis of the apparent char kinetic burning rate in He yields a rate that is 2.9 times greater than the rate in N_2, likely reflecting the greater internal penetration of oxygen into char particles burning in helium. Analysis with intrinsic kinetic models is currently being applied to better understand the role of gas diffusivity on apparent kinetic rates of char combustion.

Acknowledgements

This research was sponsored by the U.S. Department of Energy through the National Energy Technology Laboratory's Cross-Cutting Research Program, managed by Dr. Robert Romanosky. Sandia National Laboratories is a multiprogram laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

References

[1] B.J.P. Buhre, L.K. Elliott, C.D. Sheng, R.P. Gupta, T.F. Wall, *Prog. Energy Combust. Sci.* 31 (4) (2005) 283-307.

[2] M.B. Toftegaard, J. Brix, P.A. Jensen, P. Glarborg, A.D. Jensen, *Prog. Energy Combust. Sci.* 36 (2010) 581–625.

[3] L. Chen, S.Z. Yong, A.F. Ghoniem, *Prog. Energy Combust. Sci.* 38 (2012) 156-214.

[4] J.J. Murphy, C.R. Shaddix, *Combust. Flame* 144 (2006) 710–729.

[5] E. Hecht, C.R. Shaddix, A. Molina, B.S. Haynes, *Proc. Combust. Instit.* 33 (2011) 1699-1706.

[6] E.S. Hecht, C.R. Shaddix, M. Geier, A. Molina, B.S. Haynes, *Combust. Flame*, 159 (2012) 3437-3447.

[7] C.R. Shaddix, Proc. 33rd National Heat Transfer Conference, HTD99-282, ASME, New York, NY, 1999.

[8] C.R. Shaddix, A. Molina, *Proc. Combust. Instit.* 32:2091-2098 (2009).

[9] P.A. Bejarano, Y.A. Levendis, *Combust. Flame* 153 (2008) 270–287.

[10] M. Geier, C.R. Shaddix, K.A. Davis, H.-S. Shim, *Appl. Energy* 93 (2012) 675-679.

[11] M. Geier, C.R. Shaddix, Proc. 28th Annual International Pittsburgh Coal Conference, Pittsburgh, PA, September 12–15, 2011.

[12] L. Tognotti, J.P. Longwell, A.F.Sarofim, *Proc. Combust. Inst.* 23 (1990) 1207-1213.