One of the characteristics of CO\textsubscript{2} that influences the oxy-fuel combustion of pulverized coal char is its low diffusivity, in comparison to N\textsubscript{2}. To further explore how the gas diffusivity influences the apparent rate of pulverized char combustion, experiments were conducted in a laminar, optical flow reactor that has been extensively used to quantify char particle combustion rates. Helium, nitrogen, and CO\textsubscript{2} diluent gases were employed as diluent gases. The diffusivity of oxygen through helium is 3.5 times higher than through nitrogen, tending to supply more oxygen to the particle and accelerating the particle combustion rate and heat release. However, the thermal conductivity of helium is 5 times larger than that of nitrogen, tending to keep the burning char particle temperature close to that of the surrounding gas. The combination of these two factors makes char combustion in helium atmospheres significantly more kinetically controlled than combustion of char particles in nitrogen atmospheres. The char particle combustion temperatures were highest for combustion in N\textsubscript{2} environments, with combustion in CO\textsubscript{2} and He environments producing nearly identical char combustion temperatures, despite much 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 the rate in N\textsubscript{2}, likely reflecting the greater internal penetration of oxygen into char particles burning in helium. Analysis with intrinsic kinetic models is being applied to better understand the data and therefore the role of gas diffusivity on apparent kinetic rates of char combustion.

1. 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\textsubscript{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\textsubscript{2}). During coal char combustion, one of the important influences of CO\textsubscript{2} is through the reduced diffusivity of oxygen through a CO\textsubscript{2}-rich gas. As shown in Fig. 1, oxygen diffuses 20\% slower through CO\textsubscript{2} than through N\textsubscript{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 in which three different diluent gases are used: nitrogen, carbon dioxide, and helium. The diffusivity of oxygen through these three gases is significantly different, as shown in Fig. 1. In fact, the diffusivity of
oxygen through helium is 3.5 times as large as its diffusivity through nitrogen. Furthermore, as shown in Fig. 2, 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 differences in apparent and actual reactivity in oxy-fuel combustion environments, because of the reduced diffusivity of oxygen through carbon dioxide.

![Binary diffusion coefficient of oxygen in He, N\textsubscript{2}, and CO\textsubscript{2} as a function of temperature, computed using correlations from Marrero and Mason [4].](image1)

![Thermal conductivity of He, N\textsubscript{2}, and CO\textsubscript{2} as a function of temperature, according to the correlations published by Kestin et al. [5] for He and by Uribe et al. [6] for the polyatomic gases.](image2)

2. 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 and its utility for char kinetic determinations have been previously reported [7]. 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 [7].

A He-quench water-cooled isokinetic sampling probe was also used during, to collect char samples at selected reactor heights for subsequent determination of char burnout. The char samples were analyzed to determine their total ash content, according to the ASTM procedure, through utilization of a Mettler-Toledo thermogravimetric analyzer (TGA). A typical sample weighed 3 mg and the TGA balance has a resolution of 1 μg. The total ash tracer approach was used to determine the unburned mass fraction remaining at each sampling height.

To assure a common char material for the particles in the different reactor environments, high heating rate char particles were first generated 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% O₂ (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 ambient-temperature N₂ flow at the inlet of a water cooled collection probe. The collected char was sieve-classified to 53-63 μm, 63-75 μm, 75-90 μm, 90-106 μm, 106-125 μm, 125-150 μm size fractions. To ensure at least partial oxygen penetration, even for the cases of N₂ and CO₂ diluents, the 63-75 μm size cut was utilized in this study. The collected particles in this size cut were resieved, to assure negligible fines content. To achieve relatively strong optical signals for these small particles, a Powder River Basin low-sulfur subbituminous coal (Black Thunder) was utilized.

The choice of optical furnace operating conditions involved a complex balance of assuring ready char ignition and combustion, even in the presence of CO₂ [8], while attempting to keep the char combustion temperatures low enough to minimize or eliminate contributions from boundary layer conversion of CO [9] and/or heterogeneous char gasification from CO₂ and steam [9,10]. 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. Three different oxygen concentrations were utilized: 12 vol-%, 18 vol-%, and 24 vol-% O₂. A total furnace flow of 40 slpm was used. The dry (unheated) diluent gas that was used to deliver the char particles to the furnace was limited to 0.12 slpm for N₂ and CO₂ 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. 3) were measured with a very fine wire (25 μm dia.) type-R thermocouple, corrected for radiant loss, and were utilized in the char kinetic analysis.
3. 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 4 shows the mean particle temperatures measured in the three different N₂ 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.

![Graph](image)

**Figure 4.** Measured mean char particle temperatures as a function of residence time in the entrained flow reactor for N₂, CO₂, and He diluents.
Figure 4 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 from Fig. 4 that the char particles ignite much more quickly in the helium environment than in either the N₂ or CO₂ diluent environment. This would be expected, based on both the improved O₂ diffusivity through helium as well as the high thermal conductivity of helium. These two factors act to rapidly heat the diluent gas surrounding the particles (and the particles themselves) while also rapidly transporting oxygen to the particles to initiate exothermic oxidation reactions [8]. The steady burning char combustion temperature in CO₂ is consistently lower than in N₂, by 100–150 K, as has been observed previously [8,11-13]. Interestingly, the steady burning char combustion temperature in helium is almost exactly the same as that in CO₂. 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).

Figure 5. Measured fraction of char mass remaining as a function of residence time in the entrained flow reactor for N₂, CO₂, and He diluents.
The measured unburned char fraction, as a function of residence time, is shown in Fig. 5, for all three diluent gases. Linear fits have been performed on the data, to deduce effective burning rates, which are given in Table 1. Interestingly, in some cases the expected dependence of mass burning rate on the oxygen content of the bulk gas is not apparent in the burnout data, perhaps because of uncertainties and errors in the burnout analysis which can cloud such trends. Similarly, reactions in the CO\textsubscript{2} diluent show both the slowest rates (at 12\% O\textsubscript{2}) and the highest rates (at 24\% O\textsubscript{2}) of all the investigated conditions. The expected dominance of burning rates in the helium atmospheres is not apparent, except at 12\% O\textsubscript{2}.

### Table 1. Deduced Mass Burning Rates

<table>
<thead>
<tr>
<th>Diluent Gas</th>
<th>Oxygen Concentration</th>
<th>Burning Rate (1/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N\textsubscript{2}</td>
<td>12 vol-%</td>
<td>15.1</td>
</tr>
<tr>
<td></td>
<td>18 vol-%</td>
<td>26.9</td>
</tr>
<tr>
<td></td>
<td>24 vol-%</td>
<td>24.4</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>12 vol-%</td>
<td>6.8</td>
</tr>
<tr>
<td></td>
<td>18 vol-%</td>
<td>24.8</td>
</tr>
<tr>
<td></td>
<td>24 vol-%</td>
<td>40.4</td>
</tr>
<tr>
<td>He</td>
<td>12 vol-%</td>
<td>23.0</td>
</tr>
<tr>
<td></td>
<td>18 vol-%</td>
<td>25.3</td>
</tr>
<tr>
<td></td>
<td>24 vol-%</td>
<td>26.9</td>
</tr>
</tbody>
</table>

A preliminary apparent kinetics analysis has been performed of the N\textsubscript{2} and He optical data by employing a single-film apparent kinetics reaction model for char oxidation [13] (including the Tognotti relationship for the CO\textsubscript{2}/CO production ratio [14]) 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, as shown in Fig. 6. With these common values for the remainder of the kinetic parameters, the pre-exponentials for reaction in N\textsubscript{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\textsubscript{2}.

As shown in the introduction, the diffusivity of oxygen through helium is approximately 3.5 times faster than its diffusivity through N\textsubscript{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. Therefore, the diffusivity of oxygen into the char should be nearly 3 times faster for char particles burning in He than in N\textsubscript{2}. As the only way for an apparent kinetics reaction model to account for differences in particle penetration is through the apparent kinetic rates 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\textsubscript{2}. These results do point out 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\textsubscript{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.

### 4. Conclusions

Char combustion experiments were performed in a laminar, optical entrained flow reactor for N\textsubscript{2}, CO\textsubscript{2}, and He diluent gases. The char particle combustion temperatures were highest for combustion in N\textsubscript{2} environments, whereas combustion in CO\textsubscript{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\textsubscript{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.
Figure 6. Measured and modeled char particle temperatures as a function of residence time in the entrained flow reactor for N\textsubscript{2} and He diluents.

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.

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