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Direct Measurement of High-Temperature CO_2 Gasification Rate of Pulverized Coal Chars at 1 atm

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For oxy-fuel combustion with substantial flue gas recirculation, as is commonly employed, pulverized coal combustion occurs in the presence of elevated CO_2 levels. Our previous investigations of pulverized coal char combustion in such atmospheres have suggested, through computational modeling of the experimental results, that CO_2 gasification rates are sufficiently high under oxy-fuel combustion conditions to significantly influence the char combustion process. Experimental measurements of such rates under the relevant conditions (1 atm, T > 1700 K) are lacking. To address this, we have measured both the char particle temperature statistics and the char mass loss when a high volatile bituminous coal char and a subbituminous coal char are introduced into a high-temperature optical flow reactor with nearly 100% CO_2. The experimental measurements show a temperature decrease from the gasifying particles (consistent with the strong endothermicity of the char gasification reaction) and show increasing mass loss with increasing residence time and temperature, as expected.

1. Introduction

In response to the growing concern regarding the impact of continued CO_2 emissions on the environment, research and development is being actively performed on oxy-fuel combustion of coal, which can result in significant CO_2 emission reductions when combined with flue gas compression, purification, and ultimately carbon sequestration [1-3]. To moderate flame temperatures within the boiler and to prevent excessive slagging of furnace walls and steam tubes, this technology typically employs substantial flue gas recirculation. As the flue gas in this approach is primarily composed of CO_2, the coal devolatilization and combustion processes necessarily occur in the presence of a CO_2 bath gas.

Previous research has demonstrated that the higher molar heat capacity of CO_2 and its lower molecular diffusivity, relative to the usual N_2 bath gas, results in retarded coal ignition [4-11], a reduced rate of volatile consumption [8], and a reduced rate of char combustion [8,12-14], for a given furnace temperature and oxygen concentration. However, some researchers have proposed that overall char consumption rates in oxyfuel combustion may be enhanced through the action of the classic CO_2 gasification reaction with char (sometimes referred to as the Boudouard Reaction) [15-17]: $C(s)+ CO_2 => 2CO$. Under air-fired conditions, this reaction is too slow to

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compete with oxidation of the coal. However, with CO_2 concentrations in the boiler on the order of 60-70 vol-% during oxy-firing with flue gas recirculation, this reaction may begin to contribute to the overall consumption of coal char. Unfortunately, accurate rate information on the CO_2 gasification reaction is not readily available for coal chars at high temperatures. What measurements exist show a wide range of rates and activation energies [18-21], making it difficult to predict the relative influence of this reaction for any particular coal char. However, pulverized char combustion simulations under oxy-fuel combustion conditions suggest that the CO_2 gasification reaction has a strong influence on the char combustion temperature (because the strong endothermicity of the reaction decreases the particle temperature) and thereby on the radiant emission from burning char particles [22]. The lower char particle temperatures reduce the rate of char oxidation, but the net effect of combined oxidation and gasification reactions is to nearly offset each other with respect to the overall char consumption rate (i.e. the char consumption rate is almost unaffected by the actions of the gasification reaction) [22].

To clarify the importance of the char gasification reaction during oxy-fuel combustion, there is a strong need for new experimental measurements of this reaction rate for practical coal chars under the appropriate char combustion conditions – i.e. for high temperature (> 1700 K) char particles reacting with CO_2 at an overall pressure of 1 atm. With the high activation energy of the char gasification reaction (~ 250 kJ/mol [22]), there is reason to believe that it may be more important under oxygen-enriched combustion conditions, in which the char particle temperatures can reach > 2000 K [12,13]. Recently, Gonzalo-Tirado et al. [23] investigated the CO_2 gasification reaction with a subbituminous pulverized coal char at 1 atm, for application to oxy-fuel combustion. Burnout profiles were measured in a drop tube for wall temperatures between 1310 K and 1570 K. When compared to the measured char oxidation rates for the same coal char, the gasification reaction was found to be large enough to influence char conversion rates during oxy-fuel combustion, even under these moderate temperature conditions.

2. Method

Sandia's laminar entrained flow reactor facility was employed for this study. Char particle size-temperature statistics were measured using a particle-sizing pyrometer, as shown in Fig. 1, and a He-quench water-cooled sampling probe was used to collect partially reacted particles for determination of char burnout. This reactor and diagnostic setup have been used for over 25 years to provide char particle population-based data for determining char combustion rates at high temperatures. A detailed description of the experimental setup has been given in the literature [24]. The reactor operates at one atmosphere and uses a diffusion-flamelet-based Hencken burner to provide a high-speed, high temperature gas flow. Solid fuel particles are injected at the furnace centerline through a 0.75 mm stainless-steel tube. For the experiments reported here, the char feed rate was kept very low (< 1 g/hr), assuring that the injected particles burned in isolation from one another. A 5 cm × 5 cm quartz chimney isolates the reacting particles and burner products from the surrounding air and allows optical measurements to be performed on the particles injected into the flow.

Measurement of the gasification rate was attempted in two independent ways. First, optical pyrometry measurements of the reacting char particle temperatures give a measure of the highly endothermic gasification reaction by calculating the particle energy balance at a given location of the flow based on knowledge of the flow composition and the local gas temperature (and radiant boundary conditions). This is essentially the same approach that we have traditionally used

optical pyrometry measurements during char combustion to deduce the instantaneous char combustion rate, except now the gasification rate is deduced based on the temperature deficit of the particle. Hampartsoumian et al. [25] also used optical pyrometry to measure the char particle temperatures during gasification in CO_2-containing gas mixtures from 1400-1800 K and found char temperatures that were as much as 250 K lower than the surrounding gas temperature.

The other means of deducing the gasification rate is to collect char samples at different axial locations within the furnace and to calculate the char burnout (based on the ash tracer technique). In order to alleviate uncertainties in char burnout associated with volatiles loss from raw coal, preformed char particles were injected into the optical furnace. The char particles were formed by introducing 75-105 um size-classified coal particles into an electrically heated entrained flow reactor operating with a gas temperature of 1473 K. The coal particles were introduced into a flow of 3 vol-% O_2 in N_2, with the O_2 being used to prevent secondary reactions of tar and the formation of soot. After 250 ms of exposure to the high temperature flow, the particles were collected in a gas-quench, water-cooled probe and collected in a cyclone. After collection, the chars were sieved to a 75-106 um size cut. Black Thunder subbituminous coal (from the Powder River Basin – PRB) and Pittsburgh bituminous coal (a well-studied and common eastern U.S. medium-sulfur bituminous coal) were studied. In addition, particle temperature measurements were conducted for commercial graphite particles that had nominal diameters of 50 um or 100 um for one of the two furnace operating conditions.

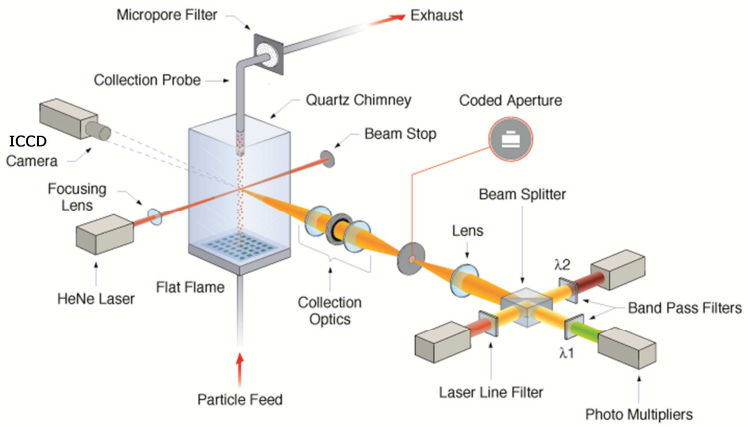

Figure 1: Schematic illustration of Sandia's laminar entrained flow reactor for coal combustion studies. The particle-sizing pyrometry diagnostic is shown to the right of the flow reactor. Data collection is triggered whenever a particle passes through the focus of the HeNe laser beam at the center of the reactor.

In this study, the Hencken burner was operated with CO as fuel, with a small quantity of H_2 added for flame stability, yielding a furnace flow that was nearly pure CO_2. To avoid fouling the quartz-walled furnace with Fe_2O_3 deposits, CO from aluminum cylinders was used [26]. Two different Hencken burner flame conditions were utilized at overall furnace gas flow rates of 70 SLPM, corresponding to adiabatic flame temperatures of 2408 K and 2580 K. Operation of the Hencken burner at these very high flame temperatures required switching the usual flow positions of fuel gases and oxidizer gases into the burner. Furthermore, air-jet cooling was installed along the outer wall of the furnace and protective thermal shielding was employed around the furnace to limit radiant heating of the associated optical systems. Measurement of the

furnace gas temperature also becomes problematic at these high temperatures, as they exceed the melting point of the fine-wire type-R and type-S thermocouples we typical employ to measure the furnace gas temperature profile. Type-B thermocouples are available which extend the applicable temperature range slightly, but the available thermocouple wire sizes are larger than those available for type-R or type-S, and radiant loss correction to thermocouple measurements in this furnace environment are significant for larger size wire [27]. Fig. 2 shows the temperature profiles measured with a type-R thermocouple constructed with 25 um wire and a type-B thermocouple constructed with 127 um wire, after correction for radiant loss [27]. The profiles show that the two thermocouples give good agreement for moderate temperatures, but at higher temperatures the deduced temperature from the larger thermocouple is higher. This discrepancy could result from uncertainties in thermocouple emissivity as a function of temperature, or uncertainties in estimated gas conduction heat transfer at these high temperatures, or could reflect increasing furnace gas radiant transport to the thermocouple, which isn't currently accounted for in the overall thermocouple energy balance that is used to compute the correction for thermocouple radiant loss. At any rate, it is clear from the thermocouple measurements that the actual furnace flow temperatures through the bulk of the furnace were significantly lower than these adiabatic flame temperatures, though the initial temperatures near the base of the furnace may in fact be close to the adiabatic values.

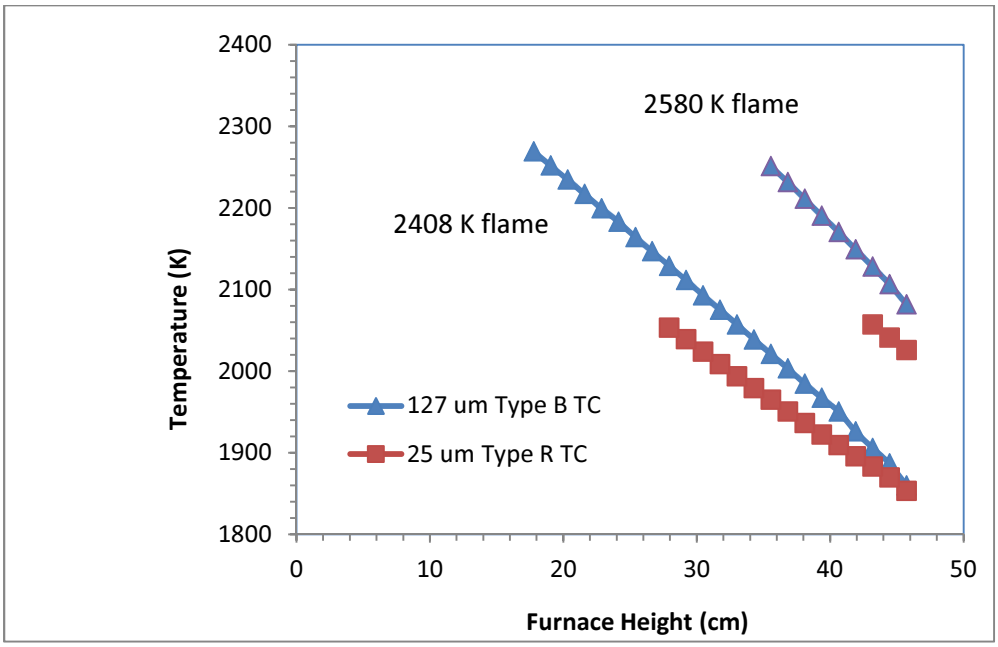

Figure 2: Radiation-corrected thermocouple measurements of the gas temperature profile through the optical furnace for two different CO_2 flow conditions corresponding to adiabatic flame temperatures of 2408 K and 2580 K. The thermocouples were used up to their respective temperature limits of operation.

A further complication of furnace operation at these high temperatures is molecular dissociation, which can generate non-negligible concentrations of O_2 and oxidative radicals (O and OH) from CO_2 that will react much more quickly with the coal char than CO_2. To minimize this, flame conditions were chosen that were somewhat fuel-rich (with equivalence ratios between 1.06 and 1.08). Under these conditions, the concentrations of these oxidative species decreased rapidly

once the furnace temperature dropped to 2200 K, as shown in Figs. 3 and 4. Examining the equilibrium concentrations in Figs. 3 and 4, together with the temperature profiles shown in Fig. 2, it is apparent that molecular oxygen and oxidative radicals are probably not important over most of the furnace height for the 2408 K flame condition. However, for the 2580 K flame condition, some contribution to char removal from oxygen or oxidative radicals cannot be ruled out.

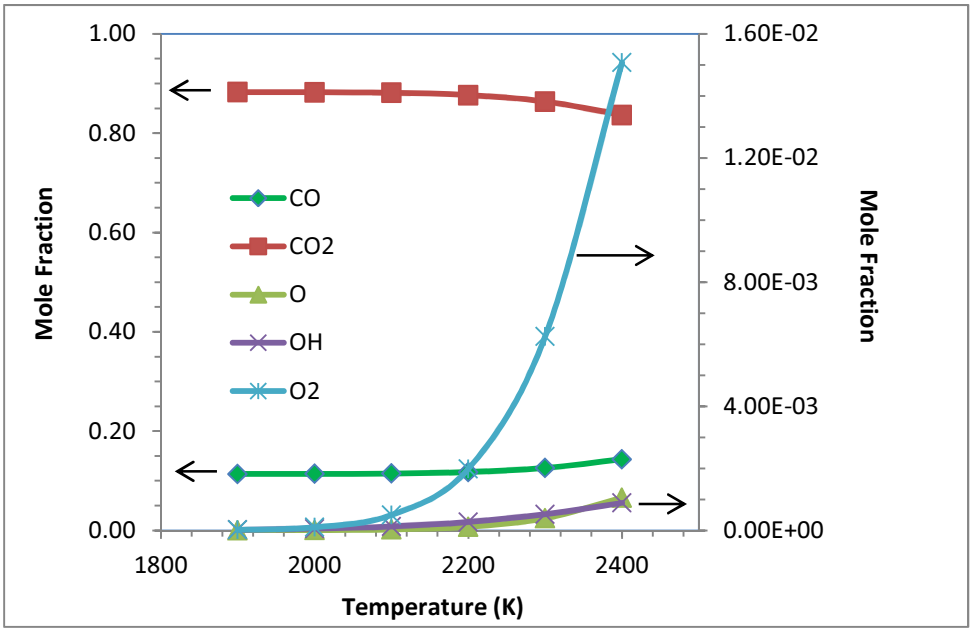

Figure 3: NASA CEA equilibrium code calculation of molecular composition of flow reactor gases under T_{ad} = 2408 K conditions, as a function of gas temperature.

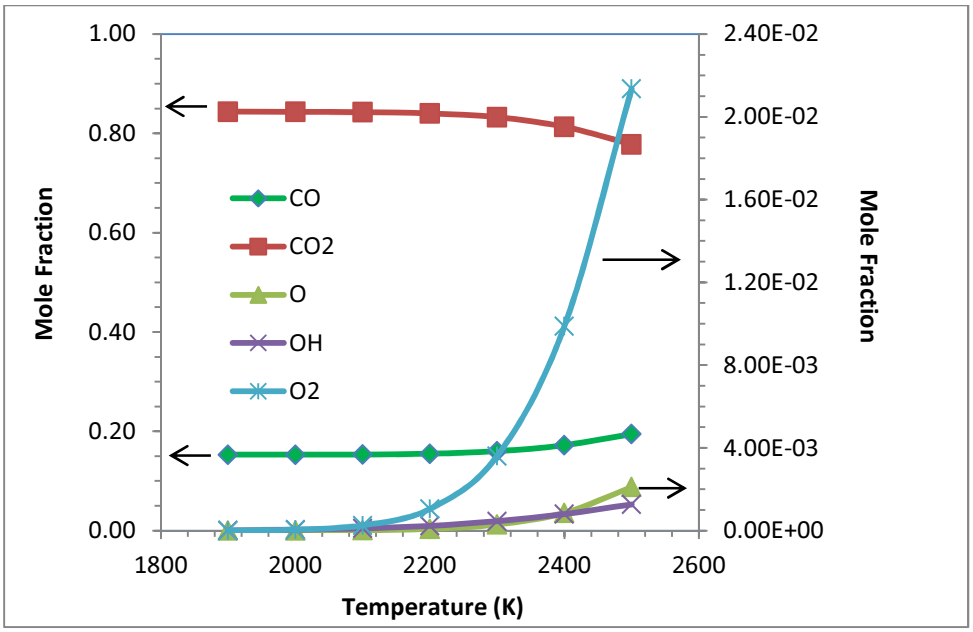

Figure 4: NASA CEA equilibrium code calculation of molecular composition of flow reactor gases under T_{ad} = 2580 K conditions, as a function of gas temperature.

3. Results and Discussion

The mean measured temperatures of the char particles and graphite particles are plotted as a function of height in the furnace for the two furnace conditions, in Figs. 5 and 6. Also shown for reference is the best estimate of the gas temperature profile, deduced by adjusting the radiation correction of the 127 um type-B thermocouple to match the corrected 25 um type-R thermocouple readings, since the amount of radiation correction for the smaller type-R thermocouple is many times less than that for the type-B thermocouple [27]. It is immediately evident that all of the fed particles have significantly lower temperatures than the gas temperature. Some decrement in particle temperature is expected simply on the basis of radiant loss. However, the amount of particle temperature decrement found here, an over 300 K temperature drop from the gas temperature, is clearly suggestive of the action of gasification reaction.

Fig. 5 shows that the larger graphite particles suffer from a heating lag, associated with the high density (2.1 g/cm^3) of these particles. The lower particle temperatures seen for the larger graphite particles at later times (once the particles have come up to their equilibrium temperature), presumably results from the increased radiant loss associated with larger particles. The overlap of the temperature profiles of the larger size graphite particles and Pittsburgh coal char particles at later reaction times seems to suggest that these particles have similar gasification reactivities, though the much higher density of the graphite particle may also be contributing to an overall reduction in temperature because of persistent thermal inertia effects. The Black Thunder subbituminous coal char particles are 200 K lower in temperature than the Pittsburgh coal char particles at early reaction times, clearly implying a higher gasification reactivity, as expected. Note that two different sets of data points for the Black Thunder coal char particles, reflecting

the results of experiments performed months apart. The agreement in measured particle temperatures verifies the reproducibility of the furnace gas control system and the precision of the two-color pyrometry diagnostic that measures the particle temperatures.

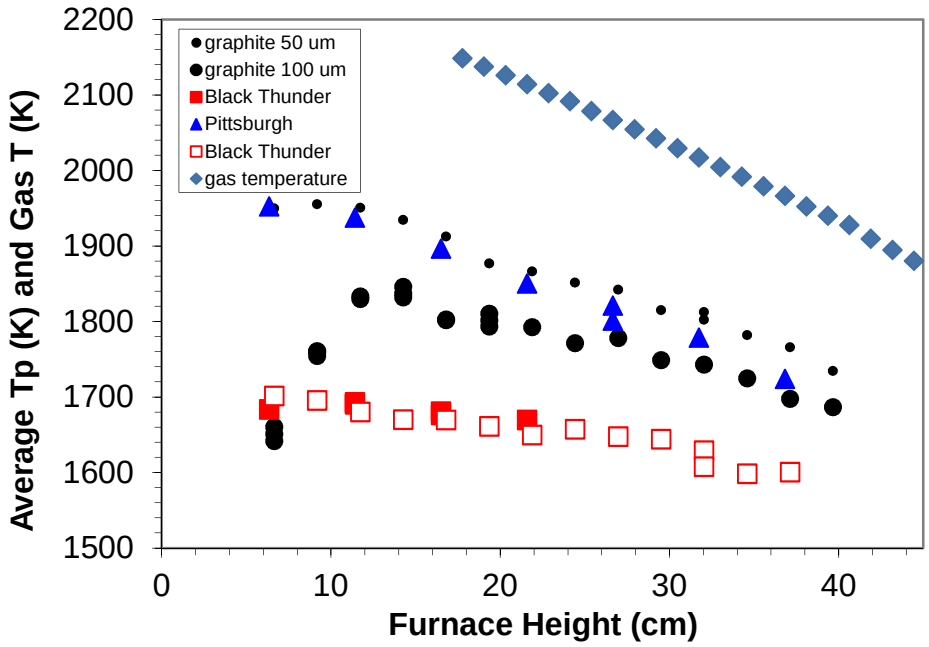

Figure 5: Mean particle temperature measurements and corrected thermocouple gas temperature measurements under the T_{ad} = 2408 K furnace condition.

Fig. 6 shows particle temperatures are between 150 K and 200 K hotter for the higher temperature 2580 K furnace condition. Once again, the Black Thunder coal char particles are significantly cooler than the less reactive Pittsburgh coal char particles.

Fig. 7 shows char burnout, calculated from the proximate analysis of the collected chars, relative to the chars that were collected at a height of 7.6 cm in the flow. As expected, the subbituminous Black Thunder char particles burn out more quickly than the bituminous Pittsburgh char particles. Furthermore, for both coals, the higher temperature furnace condition results in substantially faster burnout. In all cases, there is at least 30% burnout by the upper sampling point (at a height of 35.6 cm), and the burnout approaches 80% for the subbituminous coal in the high temperature environment.

The char burnout data indicate that there is active removal of char material through gasification at the examined furnace conditions. Quantification of the relevant CO_2 gasification rates will be performed in the future, by comparing candidate rates against both the measured char particle temperatures and the measured char burnout rates.

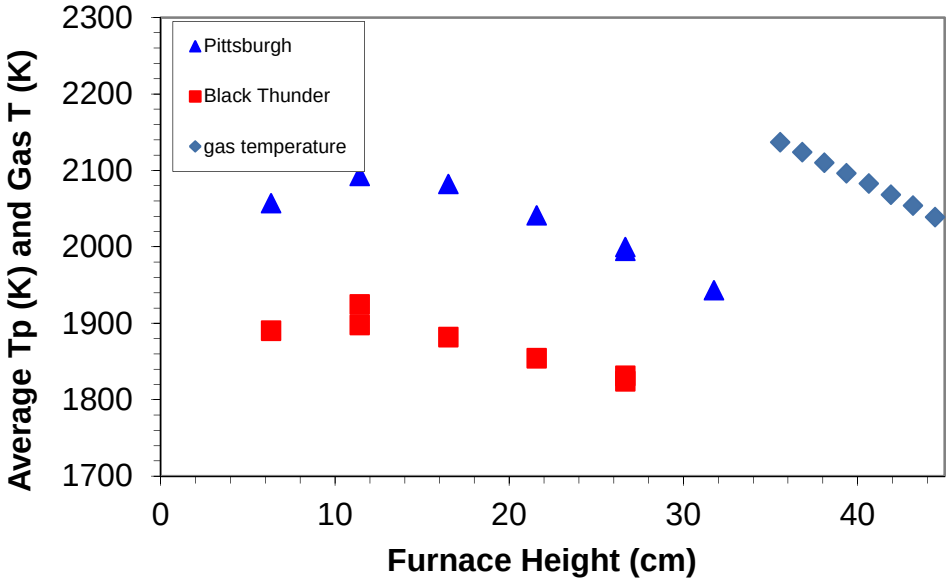

Figure 6: **Mean particle temperature measurements and corrected thermocouple gas temperature measurements under the T_{ad} = 2580 K furnace condition.**

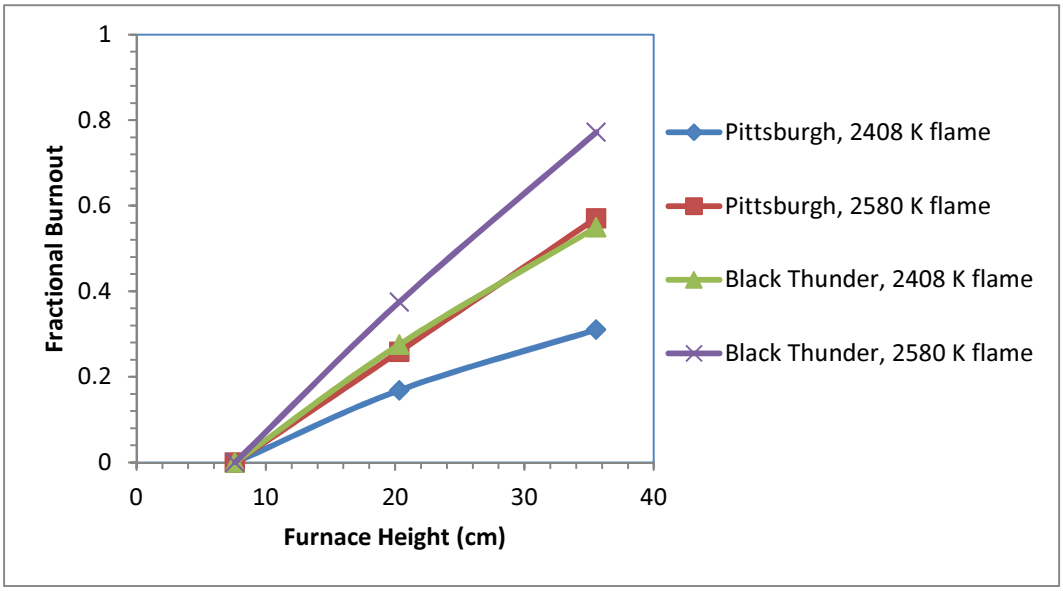

Figure 7: **Fractional burnout of collected chars, relative to the chars collected at a height of 7.6 cm.**

4. Conclusions

An attempt has been made to determine char gasification rates in CO_2 at 1 atm and high temperatures, applicable to oxy-fuel combustion of coal char. Particle temperatures and char burnout were both measured for Pittsburgh high-volatile bituminous coal and Black Thunder

subbituminous coal. The subbituminous coal showed a stronger gasification rate, as expected. Furthermore, experiments at two different temperatures showed stronger gasification at the hotter temperature. Analysis is continuing in order to deduce the char gasification rate, for use in oxy-fuel combustion CFD models.

Acknowledgements

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