



### 3rd Oxyfuel Combustion Conference

## The influence of CO<sub>2</sub> on oxy-fuel combustion of pulverized coal

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### 1. Introduction

For pulverized coal (pc) oxy-fuel combustion with significant flue gas recycle, as is currently employed, the coal burns in a gas mixture primarily consisting of CO<sub>2</sub>, oxygen, and steam. Naturally, the question arises whether the elevated CO<sub>2</sub> content in the surrounding gases influences the coal combustion process, and, if so, precisely what is the nature of this influence. The first studies of oxy-fuel combustion noted the lower flame temperatures resulting from the high molar heat capacity of CO<sub>2</sub> and therefore the need to use elevated concentrations of oxygen to achieve flame temperatures similar to combustion in air [1,2]. In addition to this obvious effect, a number of subsequent experimental observations have pointed towards additional effects from CO<sub>2</sub> on the coal combustion process, relating to thermal radiation, gas diffusion, heterogeneous reactions, and gas-phase reactions.

The interplay of these various effects from CO<sub>2</sub> on the combustion of pulverized coal is complex, and has resulted in the assertion of confusing and often incorrect explanations of CO<sub>2</sub> effects in various papers on oxy-fuel combustion. Indeed, some of the confusion has arisen from the unrecognized influence of CO<sub>2</sub> on the operation of experimental devices used to investigate coal combustion. To clarify the understanding of the influence of CO<sub>2</sub> during pc combustion, we discuss what influences can be expected during the different stages of pc combustion and what the research results have revealed about these effects.

### 2. Heat Capacity

The additional vibrational and rotational degrees of freedom for atomic motions within the triatomic, nonlinear CO<sub>2</sub> molecule, in comparison to the diatomic N<sub>2</sub> molecule, result in a higher heat capacity for CO<sub>2</sub> on a molar basis. The ratio of the molar heat capacity of CO<sub>2</sub> to that of N<sub>2</sub> is 1.28 at 300 K and rapidly rises to 1.57 at 600 K. By 1000 K this ratio has risen to 1.66 and then very slowly rises with further increases in temperature. Interestingly, the molecular weight of CO<sub>2</sub> is 1.57 times that of N<sub>2</sub>, such that at elevated temperatures the specific heat of CO<sub>2</sub> is nearly identical to that of N<sub>2</sub>. However, for a gas-phase process such as combustion, the relevant factor is the heat capacity per volume of gas, and since the volume of gas is proportional to the molar concentration, the difference in

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*molar* heat capacity is the relevant consideration. What the high molar heat capacity of  $\text{CO}_2$  affects, most directly, is the temperature rise that accompanies exothermic gas-phase chemical reactions. This means that coal volatiles burning in a  $\text{CO}_2$  environment will produce lower temperature flame products, for a given initial oxygen concentration. Adiabatic flame calculations demonstrate that for a typical coal volatile composition, combustion in 33 vol-%  $\text{O}_2$  in  $\text{CO}_2$  produces the same flame temperature as combustion in air. Similarly, the oxidation of CO (the primary product of char oxidation) to  $\text{CO}_2$  needs to occur in an oxy-fuel environment containing 32 vol-%  $\text{O}_2$  to produce the same flame temperature as combustion in air.

In addition to the influence of  $\text{CO}_2$ 's high heat capacity on flame temperature, it can also strongly influence the coal ignition and flame stabilization process. In most burner arrangements, the coal flame is anchored where hot flame products recirculate heat back to mix with injected coal streams. In this case, a lower temperature flame product stream will tend to inhibit coal jet ignition and therefore flame holding. Furthermore, in most oxy-fuel applications the coal is transported to the burner in a  $\text{CO}_2$ -rich gas stream, whose high heat capacity inhibits the heating of the coal and thus coal ignition. In addition, even if coal particles are heated at the same rate in an oxy-fuel application, the dampening effect of  $\text{CO}_2$  on local temperature rise will delay homogeneous ignition [3-5].

The high molar heat capacity of  $\text{CO}_2$  has no direct impact on the char oxidation rate. That is, if one surrounds a char particle with  $\text{CO}_2$ -containing gases at the same temperature and with the same oxygen content as in a  $\text{N}_2$  environment, and if one further assumes or demonstrates that the  $\text{CO}_2$  is not reacting with the char, then the char combustion process is governed by the transport of oxygen to the particle, the heterogeneous reaction rate, and the transport of oxidation products and heat away from the particle, but is independent of the heat capacity of the gases. As will be discussed later, the presence of  $\text{CO}_2$  does impact gas diffusion, as well as the char particle combustion temperature and extent of CO oxidation in the boundary layer, but these aspects are not directly associated with the high heat capacity of  $\text{CO}_2$ .

The high heat capacity of  $\text{CO}_2$  often affects the operation of bench-scale experiments. In several cases, rather extreme apparent effects from  $\text{CO}_2$  have been reported in bench-scale experiments, due to the unforeseen influence of  $\text{CO}_2$  on heat transfer within the experiment. For example, injection of coal particles in a flow of cool  $\text{CO}_2$  will necessarily delay ignition, particularly in laminar flow devices with slow mixing, because of the high heat capacity of  $\text{CO}_2$ . This fact motivates the use of as little particle carrier flow as possible when performing such experiments. Furthermore, many experimental results have been reported using drop tube furnaces, most often controlled and monitored by thermocouples associated with the furnace walls rather than the actual flow temperature. In this case, the high heat capacity of  $\text{CO}_2$  will often result in a significantly lower gas temperature in the drop tube for the same nominal temperature setting as used for experiments in  $\text{N}_2$  environments [6,7]. This will have a dramatic influence on apparent ignition properties and a somewhat more moderated influence on measured char combustion rates.

### 3. Thermal Radiation

Thermal radiation plays an important role in heat transfer within medium- to large-scale furnaces, so the contribution of radiantly-active  $\text{CO}_2$  to the total heat transfer can be significant. The lower gas velocities in the furnace during oxy-fuel combustion (~ 15% lower) also enhance the radiant heat transfer from the combustion products, because of the correspondingly longer residence time for flame products to radiate. For these reasons, pilot-scale furnaces are observed to produce similar overall heat flux profiles when operating in oxy-fuel mode with an overall oxygen concentration of approximately 27 – 28% [8,9], rather than the 32 – 33%  $\text{O}_2$  that would be required to produce the same flame temperatures in the absence of radiation effects. The influence of gas-phase radiation is strongly dependent on the physical scale of the flow, so bench-scale experiments generally experience a minor influence from gas-phase radiation.

### 4. Gas Diffusion

The binary diffusion coefficient of  $\text{O}_2$  is 20% lower in  $\text{CO}_2$  than in  $\text{N}_2$  for temperatures higher than 500 K. Consequently, during active pc char particle combustion, the transport of oxygen to the char surface and within the char particle is inhibited. This effect is particularly true for larger and more reactive particles that are burning in the diffusion-limit, but is also true for most pc combustion conditions, wherein the particles are burning in so-called "Zone II" combustion, with the burning rate determined by combined diffusional and kinetic resistances. For 100

$\mu\text{m}$  diameter particles, the additional diffusional resistance from  $\text{CO}_2$  has been calculated to reduce the char combustion temperature of subbituminous and high-volatile bituminous coal chars by approximately 50 K, with a corresponding 5 – 10% reduction in the burning rate [10]. In addition to reducing the flow of  $\text{O}_2$  (and other gasifying agents) to the reacting particle, the presence of  $\text{CO}_2$  reduces the diffusion rate of CO away from the reacting char particle and thereby may influence the thermal feedback of CO conversion in the reacting particle boundary layer (for sufficiently large particles) [11]. For coal particles igniting in laminar flow, the reduced diffusivity of oxygen towards the particle might delay ignition, and for particles or groups of particles with volatiles burning in an envelope flame, the reduced diffusion rate of volatiles to the flame reduces their burning rate [12].

## 5. Heterogeneous Reactions

One of the poorest understood aspects of  $\text{CO}_2$  during oxy-fuel combustion is with respect to its role in heterogeneous char gasification reactions. At low temperatures ( $\sim 800^\circ\text{C}$ ), where the preponderance of relevant kinetic measurements have been made, the gasification of coal chars by  $\text{CO}_2$  proceeds at a rate that is 4 – 5 orders of magnitude slower than char oxidation [13] and is clearly irrelevant over the timescales of interest for combustion. However, the activation energy for  $\text{CO}_2$  gasification of char is about 250 kJ/mol, compared to 160 kJ/mol for char oxidation, such that  $\text{CO}_2$  gasification becomes increasingly important for higher char temperatures. At 2000 K, which is a typical pc char particle combustion temperature, the kinetic rate coefficient for  $\text{CO}_2$  gasification is still about 100 times slower than the kinetic rate coefficient for oxidation. On the other hand, considering the higher concentration of  $\text{CO}_2$  than  $\text{O}_2$  in the bulk gas and the greater char particle penetration achieved by  $\text{CO}_2$  than  $\text{O}_2$  during combustion, it is clear that  $\text{CO}_2$  gasification needs to be considered during oxy-fuel char combustion. In fact, particle simulations show that the highly endothermic  $\text{CO}_2$  gasification reaction strongly reduces the char particle combustion temperature during oxy-fuel combustion while slightly augmenting the overall char conversion rate [13–15]. Simulations also demonstrate that the effect of  $\text{CO}_2$  gasification is greater for higher gas temperatures and for higher  $\text{O}_2$  concentrations, because of the higher char combustion temperatures under these conditions and because of the high activation energy of  $\text{CO}_2$  gasification. Conversely, during coal particle devolatilization and lower temperature combustion conditions,  $\text{CO}_2$  gasification reactions are not important over the timescales of interest.

## 6. Gas-Phase Reactions

The strong influence of  $\text{CO}_2$  on gas-phase combustion chemistry is often not appreciated.  $\text{CO}_2$  promotes radical recombination reactions. However, its largest effect occurs from reaction with H atoms in the flame zone to produce CO. Conversely, thermal dissociation of  $\text{CO}_2$  is generally not a significant source of CO.

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