# The Influence of $CO_2$ on Oxy-fuel Combustion of Pulverized Coal


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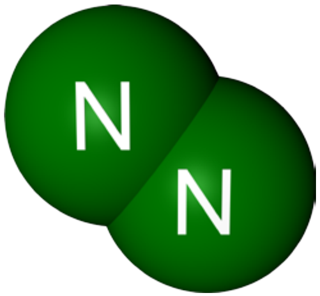
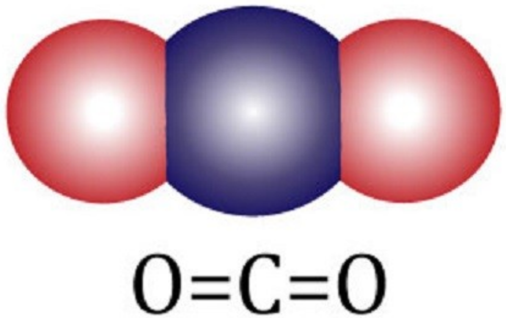
# Motivation for this talk: Confusion over Effects of $CO_2$ in Oxy-fuel Combustion

- How does replacing this   with this  

  affect PC combustion?

- Important to understand differences in **fundamental properties** and then *propagate* understanding to **observed effects**

  . . . else risk possible improper interpretation of observations

# $CO_2$ vs $N_2$, on molecular scale

- $CO_2$ has much higher mass (44 amu vs. 28 amu)
- $CO_2$ is slightly larger (collisional diameter of 390 vs. 375 x $10^{-12}$ m)
- $CO_2$ is heteronuclear, triatomic molecule (IR-active rotational-vibrational energy states)
- $CO_2$ is more reactive (BDE of 532 kJ/mol vs. 945 kJ/mol)

# Effect #1: $C_p$

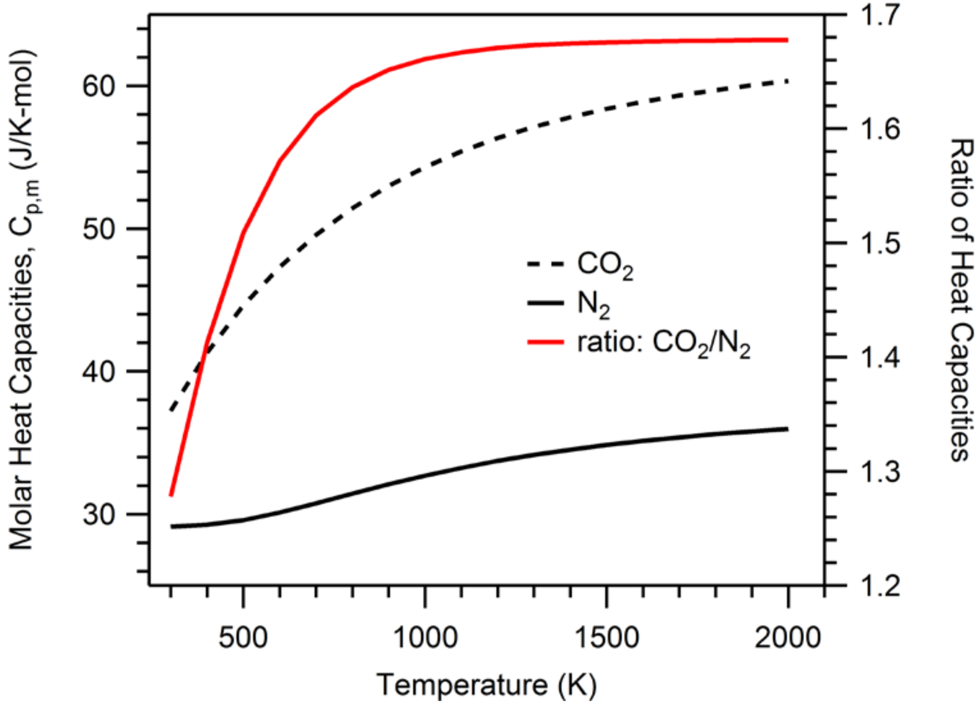
- Heat capacity *on a molar basis* is the relevant factor for gas-phase processes (gas number density is independent of molecular mass)

- Additional vibrational and rotational degrees of freedom for atomic motion result in greater heat capacity for $CO_2$, on molar basis

$$C_{p,m} = C_{v,m} + R = \frac{(f+2)}{2} R$$ , where f = # deg of freedom

- As temperature increases, more degrees of freedom are activated in $CO_2$, giving an increasing heat capacity, relative to $N_2$, until all 13 dof are activated (vs. 7 for $N_2$)

# Effect #1: $C_p$



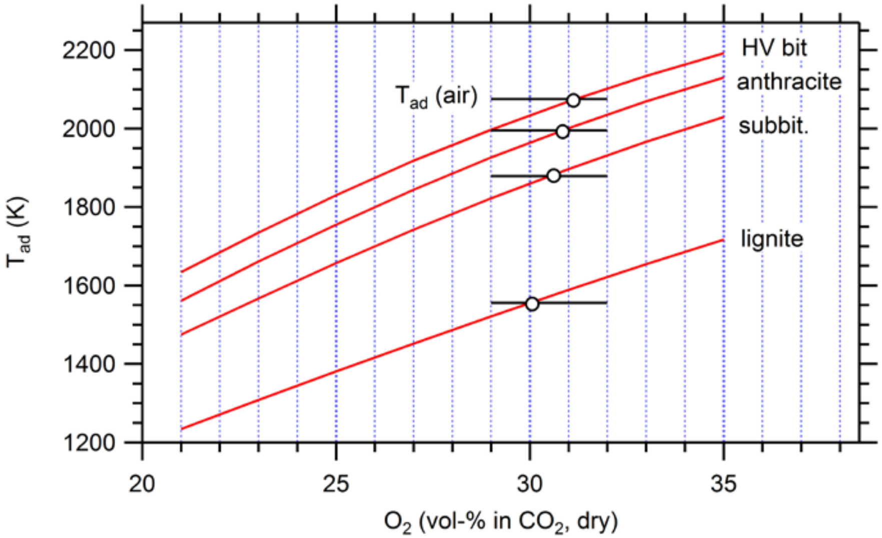

At high temperatures (> 1000 K), molar $C_p$ of $CO_2$ is ≈ **1.67x** that of $N_2$

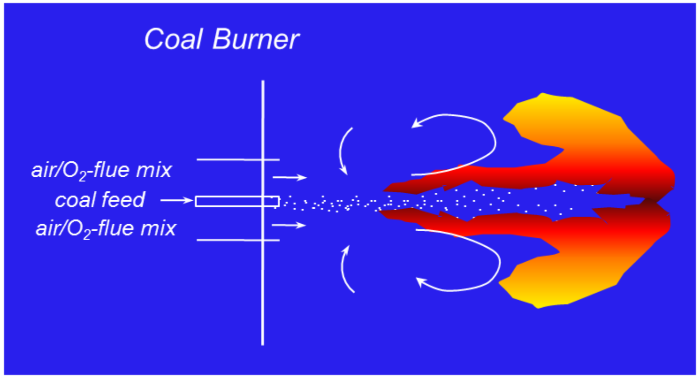
Note: because the $MW_{CO2}$ is 1.56x $MW_{N2}$, at high T the *specific* heat of $CO_2$ is just slightly higher than specific heat of $N_2$

# Effects of a higher molar $C_p$ for $CO_2$

High $C_p$ means a given amount of energy release or energy transfer results in a smaller temperature rise, so . . .

- With oxy-fuel combustion, burners/boilers need to be operated with less diluent to achieve similar temperatures as combustion in air



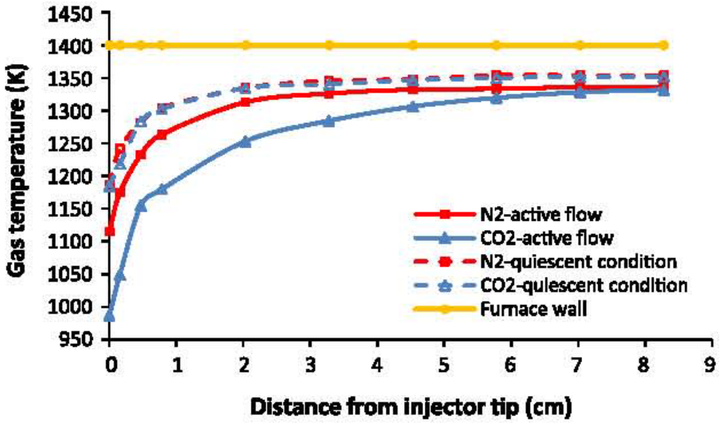

  - flame holding (i.e. burner stability) is very sensitive to combustion product temperature

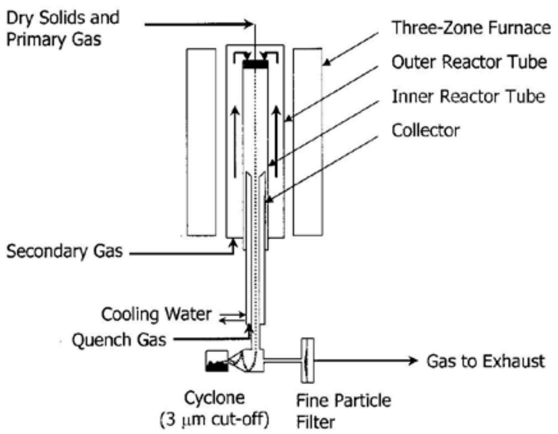
# Effects of a higher molar $C_p$ for $CO_2$

High $C_p$ means a given amount of energy release or energy transfer results in a smaller temperature rise, so . . .

- Lower diluent flow means lower gas velocities (increasing residence time, altering distribution of radiant vs convective heat transfer, affecting turbulent flow characteristics)
- Delivering coal to a furnace with cool $CO_2$ has strong impact on coal stream heat-up and ignition (particularly in laminar flow)

Measured temperatures for drop tube ignition experiments
(Khatami, Stivers, and Levendis, CNF 159:3554-3568, 2012)



# *Not* an effect of the higher molar $C_p$ of $CO_2$

For most pc particles (< 70 μm in diameter), char oxidation rate is governed by a balance of oxygen diffusion to the particle, chemical reaction, and radiant and convective heat transfer from the particle (single-film model)

$$\underbrace{\frac{d_p \rho_p C_{p_p}}{6}\frac{dT_p}{dz}}_{\text{thermal inertia}} = \underbrace{-\varepsilon\sigma\left(T_p^4 - T_w^4\right)}_{\text{radiant loss}} \underbrace{- \frac{2\lambda}{d_p}\left[\frac{\kappa/2}{e^{\kappa/2}-1}\right]\left(T_p - T_g\right)}_{\text{convective loss}} + \underbrace{q\Delta h}_{\text{heat release}}$$

– no dependence of $C_p$ for these processes (during steady state)
– thermal conductivity (λ) of surrounding gas is only thermal property that is important
– only for cases where CO oxidation in boundary layer is important (larger particles and high gas T or high $O_2$ concentration) should $C_p$ play a role

# Effect #2: Thermal Radiation

- $N_2$ has negligible thermal radiation, because only highly excited molecules can radiate, mostly at blue-violet or UV wavelengths (no lower energy rotational-vibrational transitions in IR)

- $CO_2$ thermal radiation (and radiation absorption) is significant at boiler length scales

- Combined influence of lower gas velocities (≈ 15% lower) and contribution of radiation from $CO_2$ results in pilot-scale and demo-scale furnaces operating with 27 – 28 % $O_2$ to match radiant heat transfer with air-fired combustion, rather than 30 – 31% $O_2$ needed to match actual flame temperatures

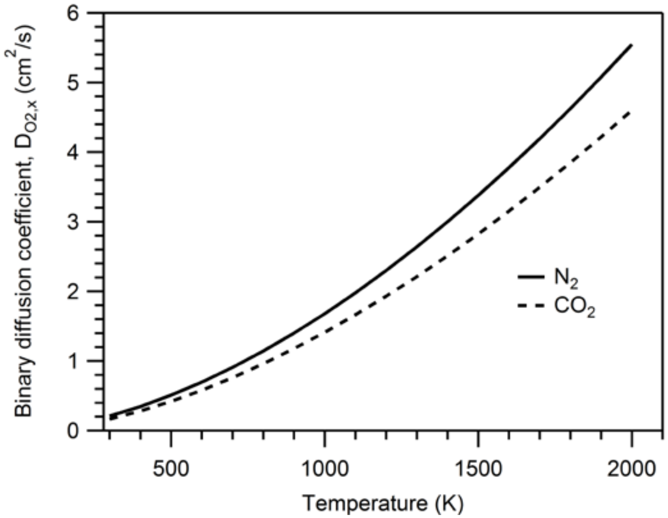
# Effect #3: Gas Diffusion

- From dilute gas theory, bimolecular gas diffusivity follows

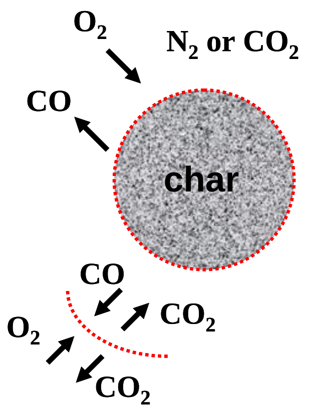
$$D_{a,b} \propto \sqrt{\frac{1}{m_a} + \frac{1}{m_b}} \cdot \frac{T^{3/2}}{P(d_a + d_b)^2}$$

- Larger collision diameter and mass (especially), decreases diffusion of molecules through $CO_2$

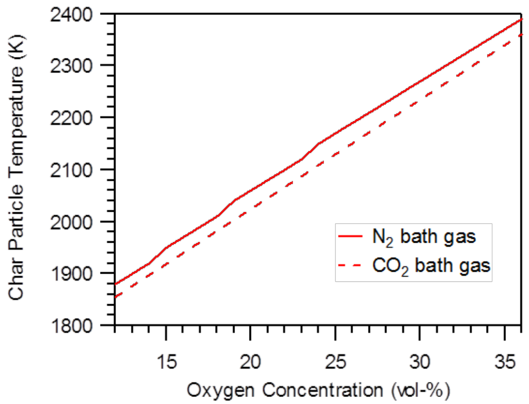
- For most molecules of interest (including $O_2$) diffusivity in $CO_2$ is ≈ 17% lower than diffusivity in $N_2$

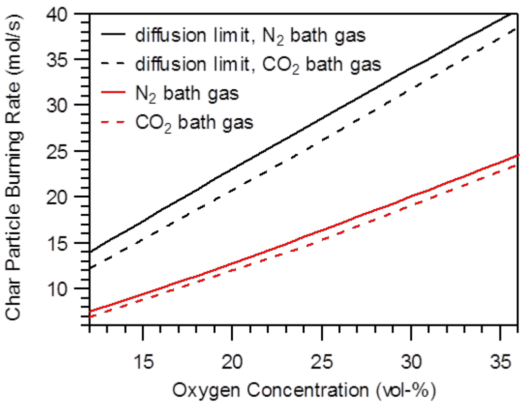


# Effects of a lower diffusivity in $CO_2$



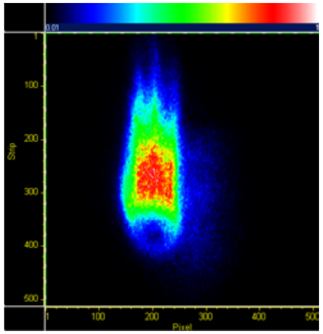

- For all but zone I (kinetically controlled) combustion, the char oxidation rate depends on $O_2$ diffusivity
  - for a 100 μm dia. hv bit. char particle, calculated effect of reduced diffusivity is to reduce char T by 40 K and burning rate by 7%




- Diffusion rate of CO away from char particle also affected, impacting boundary layer oxidation of CO

- For particle(s) burning with an envelope flame, reduced $O_2$ and volatile diffusivity reduces burning rate



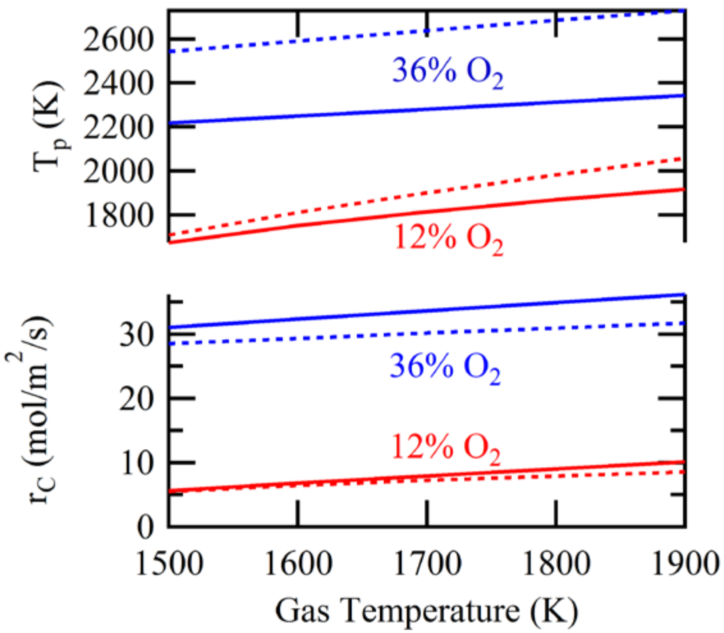
# Effect #4: Heterogeneous Reactions

- Much confusion over role of $CO_2$ gasification reaction, and its effect on devolatilization and char conversion
- At low to intermediate temperatures, where char devolatilization occurs, gasification rate is extremely slow – irrelevant over timescales of interest for combustion
- Because the activation energy of $CO_2$ gasification reaction is large (≈ 250 kJ/mol), it becomes increasingly important at high T
- At 2000 K, the kinetic rate coefficient for $CO_2$ gasification is still ≈ 100x slower than oxidation, but larger $CO_2$ concentration, greater penetration of particle, and large *endo*thermicity of reaction make it important $CO_2 + C(s) \rightarrow 2CO \quad (\Delta H_{rxn} = +172\, kJ/mol_C)$

# Effects of Char Gasification Reaction

- Endothermicity of reaction decreases char temperature substantially (at high temperatures, where gasification is active)
- Reduction in char temperature reduces char oxidation rate – almost completely offsetting the added char consumption from gasification

Simulation results: 100 μm subbit. char particle burning in $O_2/CO_2$ mixtures
(Hecht et al., CNF 159:3437-3447, 2012)




dashed lines: ignoring gasification rxns
solid lines: including gasification rxns

# Effect #5: Gas-Phase Reactions

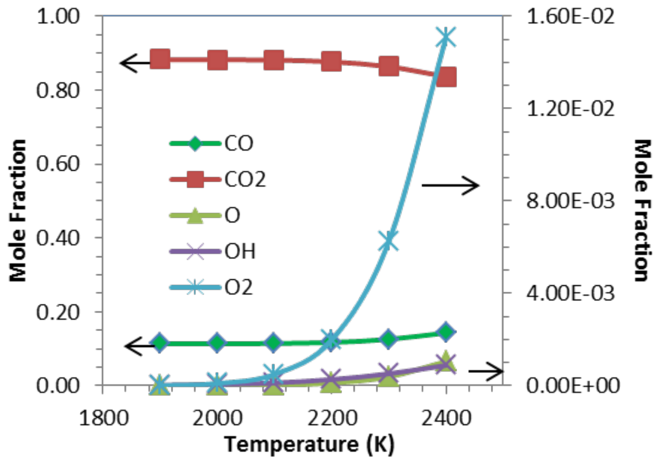
- Gas-phase reactions with $CO_2$ are often forgotten, but are significant in the flame zone

- Several kinetic studies have demonstrated that

$$H + CO_2 \rightarrow CO + OH$$

is important during oxy-fuel combustion, resulting in elevated CO concentrations in the flame zone and redistribution of radical pool from H to OH

- Conversely, some papers mistakenly attribute elevated CO concentrations to char gasification reaction or to thermal dissociation of $CO_2$ (unimportant until gas T > 2200 K)



# Summary

An attempt has been made to clarify the (important) role of $CO_2$ in oxy-fuel combustion of pulverized coal:

- Most far-reaching impact is due to the much higher molar heat capacity of $CO_2$ (relative to $N_2$)
- The impact of radiantly active $CO_2$ on boiler-scale heat transfer is important
- Reduced gas diffusivity through $CO_2$ primarily influences pc char combustion
- $CO_2$ gasification reaction reduces char combustion T and slightly increases char consumption rate
- Reaction of H atom with $CO_2$ generates substantial quantities of CO in the flame zone

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# Questions?