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# Oxyfuel Combustion: Basic Principles and Results from Small-Scale Investigations

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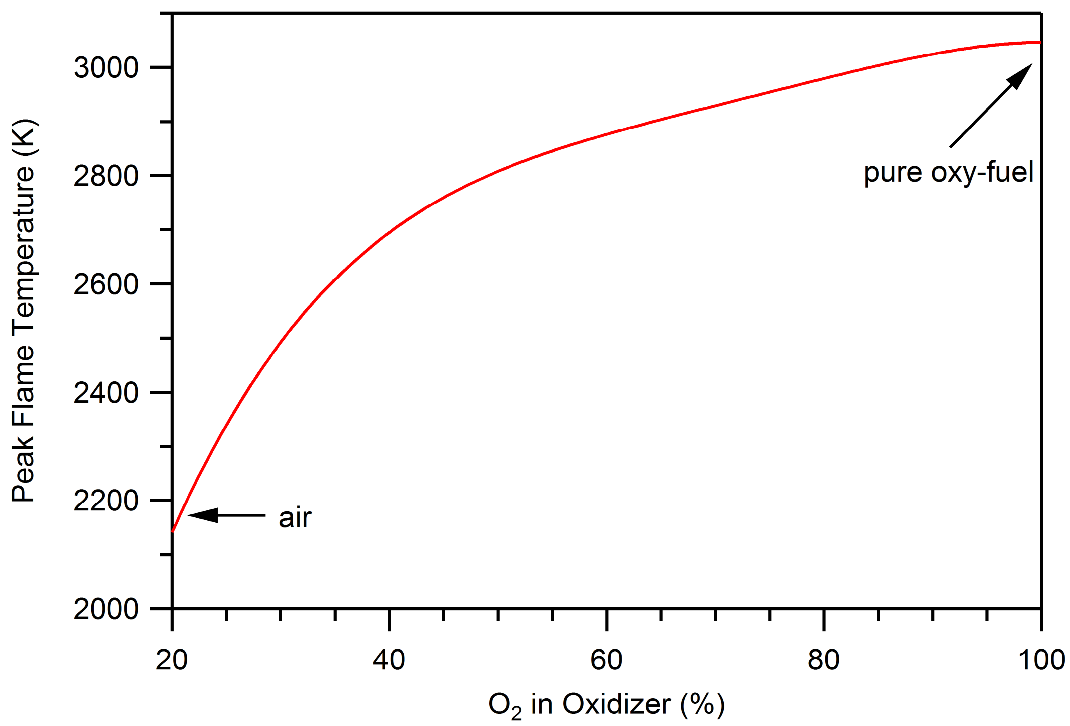
# Outline

- Fundamental Properties of Oxyfuel Combustion
- Oxyfuel Combustion of Gaseous Fuels (mostly Sandia work)
- Oxyfuel Combustion of Pulverized Coal (only Sandia work)
- Conclusions

# Fundamentals of Oxyfuel Combustion – I

- **$O_2$ concentration in oxidizer can be tailored**
  - through global or local exhaust gas recirculation (EGR), effective $O_2$ concentration can be tuned
  - flame structure, heat release rate, and size, as well as product gas temperature can be adjusted based on the ***oxidizer*** composition

# Effect of $O_2$ Content on Flame Temperature (methane fuel, $N_2$ as diluent)



# Fundamentals of Oxyfuel Combustion – I

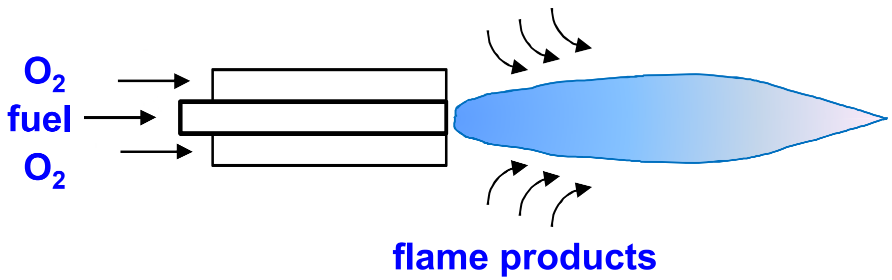
- **$O_2$ concentration in oxidizer can be tailored**
  - through global or local exhaust gas recirculation (EGR), effective $O_2$ concentration can be tuned
  - flame structure, heat release rate, size, and product temperature can be adjusted based on the ***oxidizer*** composition
  - highly enriched (or even pure) $O_2$ jets can be used to aid flame attachment

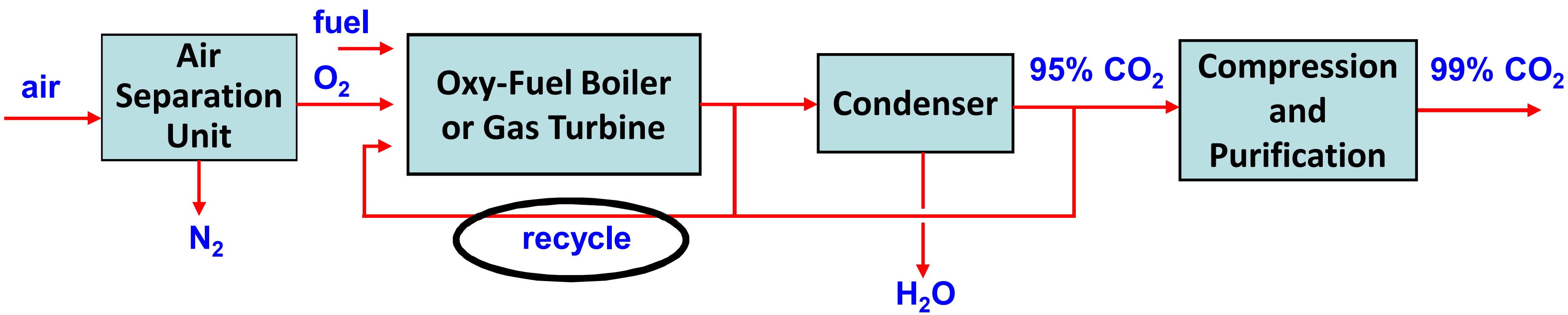
*As combustion engineers, with oxyfuel combustion we now have significantly more freedom to design the combustion process!*

# Fundamentals of Oxyfuel Combustion – II

- Combustion generally takes place in high $CO_2$ and possibly high $H_2O$ environment

# Two Practical Oxyfuel Combustion Configurations



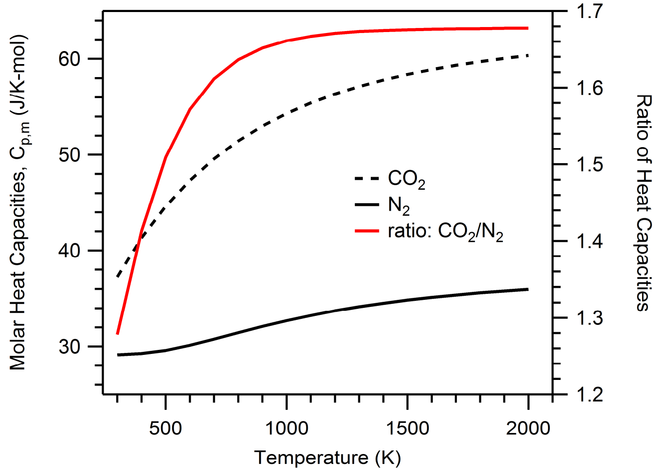



# Fundamentals of Oxyfuel Combustion – II

- Combustion generally takes place in high $CO_2$ and possibly high $H_2O$ environment
  - **gas transport properties** are different from air-fuel combustion
  - some **chemical reaction fluxes** are different from air-fuel combustion
  - **flame structure** is different from air-fuel combustion
    - for solid fuels, both volatiles flame structure and char combustion reaction structure differs

# Fundamentals of Oxyfuel Combustion – III

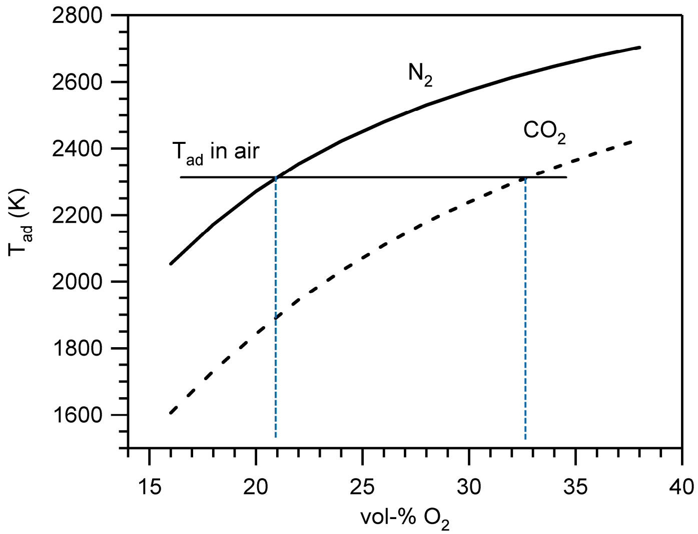
- Primary effect of enhanced $CO_2$ and $H_2O$ concentrations is through their high molar heat capacities




$C_{p,m} = C_{v,m} + R = [(f+2)/2]*R$ ,
where f = # deg of freedom

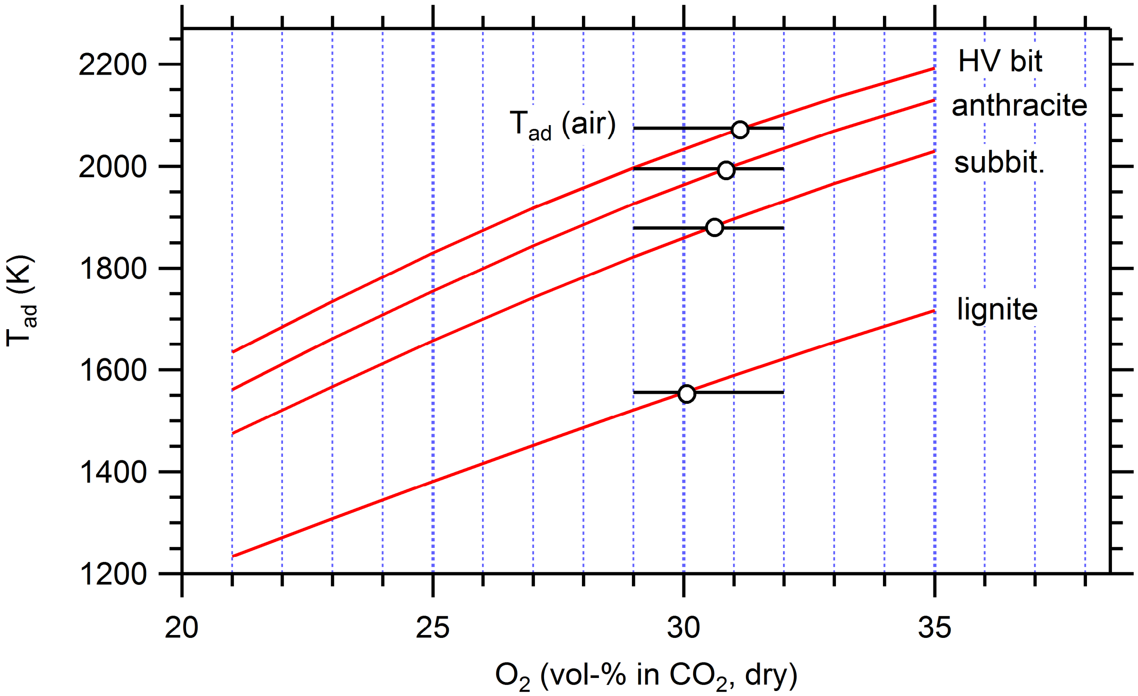
13 DOF for $CO_2$ and 10 DOF for $H_2O$ vs. 7 for $N_2$

Methane adiabatic flame temperature




- To reach the same temperature as air-fuel firing, higher $O_2$ concentrations are needed in oxyfuel EGR applications (i.e. need to use less diluent)

# $T_{ad}$ for Oxyfuel Combustion of Dry Coals



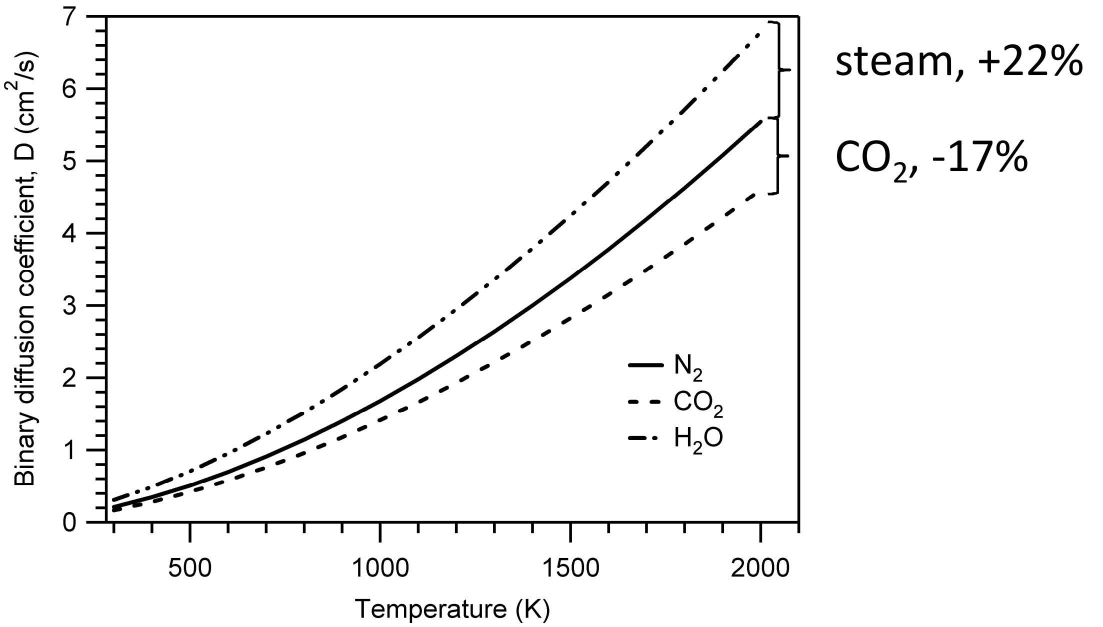
# Fundamentals of Oxyfuel Combustion – IV

- Radiant heat transfer is stronger in oxyfuel flames
  - for applications with high-$O_2$ firing, flame products are hotter
  - **concentration of radiant flame products** ($H_2O$ and $CO_2$) **is greater** (i.e. effective gas emissivity is larger)
  - with reduced flow of diluent, **gas residence time increases** (by factor of 3.5 for pure oxyfuel combustion)

# Fundamentals of Oxyfuel Combustion – V

- Mass diffusion rates *can* be different in oxyfuel environments (by up to ~ 20%)

Diffusion coefficient of $O_2$ in diluent




  – for non-premixed, gaseous combustion, diffusivity effects burning rate
  – for solid fuel combustion, diffusivity effects burning rate of chars (except in kinetic limit)

# Fundamentals of Oxyfuel Combustion – VI

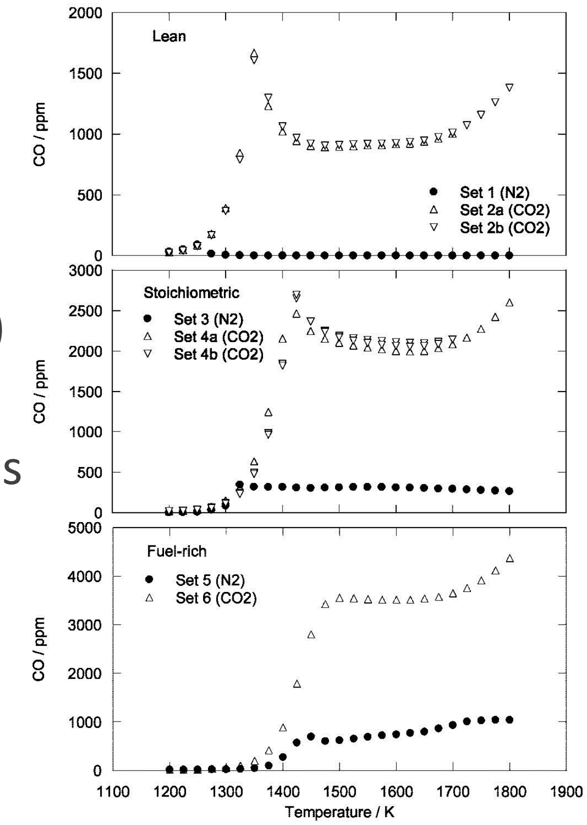
- Pure oxyfuel flames utilize high injection velocities (up to 180 m/s) and usually do not use swirl
  - higher reactivity (flame speed) of fuel-$O_2$ mixture promotes flame attachment to burner
  - very high flame temperature will destroy burners if flame attaches

# Oxyfuel Combustion of Gaseous Fuels – Investigations on Effects on Flame Chemistry

- Beginning in 1990's chemical effect of $CO_2$ on flame structure was investigated after observation that adding $CO_2$ to flame reduced soot formation
- Zhang, Atreya, and Lee (PCI 1992)
  - species measurements and chemical kinetic analysis of counterflow flames of $CH_4/N_2$ and $CH_4/CO_2/He$ and $CH_4/H_2O/He$ with same fuel conc. and $T_{ad}$
  - suggested reduction in soot formation with $CO_2$ or $H_2O$ addition is due to **$H + CO_2 \rightarrow OH + CO$** and **$H + H_2O \rightarrow OH + H_2$** in fuel-rich regions (reverse of normal oxidation reactions)

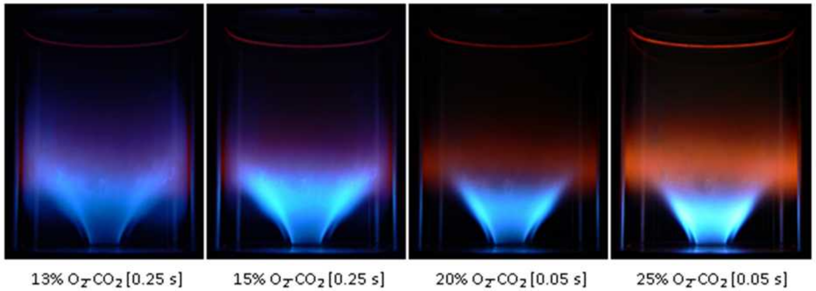
# Oxyfuel Combustion Flame Chemistry – I

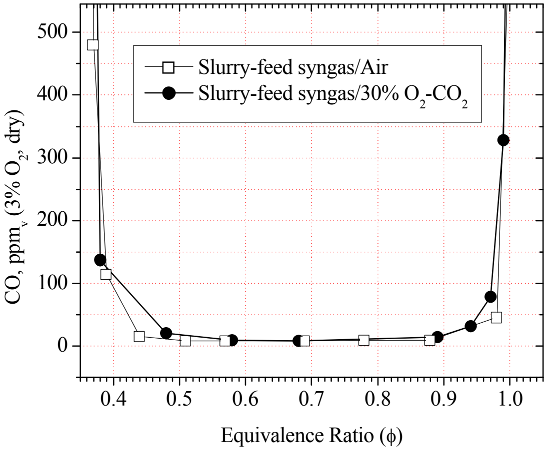
- Beginning in mid-2000's have been several studies of oxyfuel combustion chemistry of methane and syngas
- Glarborg and Bentzen (ENF 2008)
  - flow reactor study of highly diluted $CH_4$ and $O_2$ in $N_2$ or $CO_2$
  - wide range of T (1200 – 1800 K) and $\phi$ (0.5 – 4.0)
  - starting at 1300 K, CO produced at all stoichiometries, but especially for rich conditions
  - kinetic analysis shows H + $CO_2$ is dominant $CO_2$ reaction, with some contribution from $^{1,3}CH_2 + CO_2 \rightarrow CH_2O + CO$
  - at T > 1700 K, some CO production from direct dissociation of $CO_2$



# Oxyfuel Combustion Flame Chemistry – II

- Williams, Shaddix, and Schefer (CST 2008)
  - measured stability limits and emissions for $CH_4$ and various syngas compositions burning in air and $O_2/CO_2$
  - premixed dump combustor (Re = 22000)



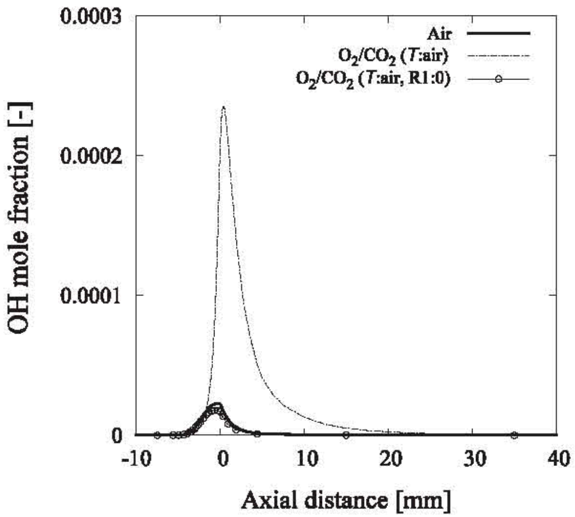




  - CO emissions inconsequential in stable combustion regime
  - CO emissions increase similarly for oxyfuel combustion and air-fuel combustion for $\phi > 0.95$
  - at lean instability limit, CO emissions also increase similarly
  - *verified Glarborg conjecture that H + $CO_2$ reaction in flame zone merely displaces region where most of CO gets oxidized in combustor*

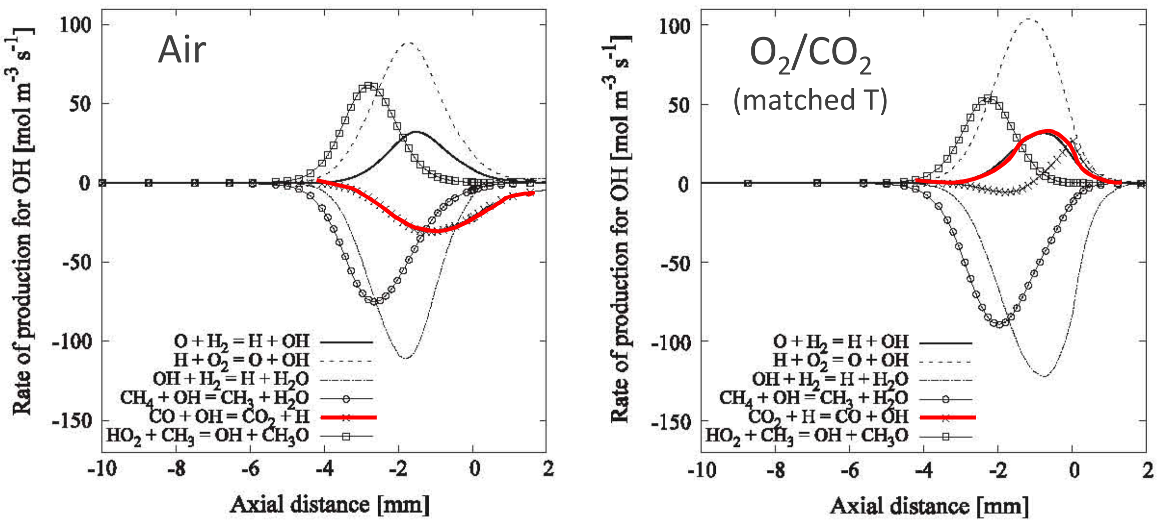
# Oxyfuel Combustion Flame Chemistry – III

- Watanabe, Arai, and Okazaki (CNF 2013)
  - fuel-rich flat flame experiments and modeling
  - demonstrated that H + $CO_2$ reaction leads to faster consumption of hydrocarbons in fuel-rich regions through abstraction reactions with OH

Calculated OH profiles




Calculated OH reaction fluxes



# Other Important Areas of Research in Oxyfuel Combustion of Gaseous Fuels

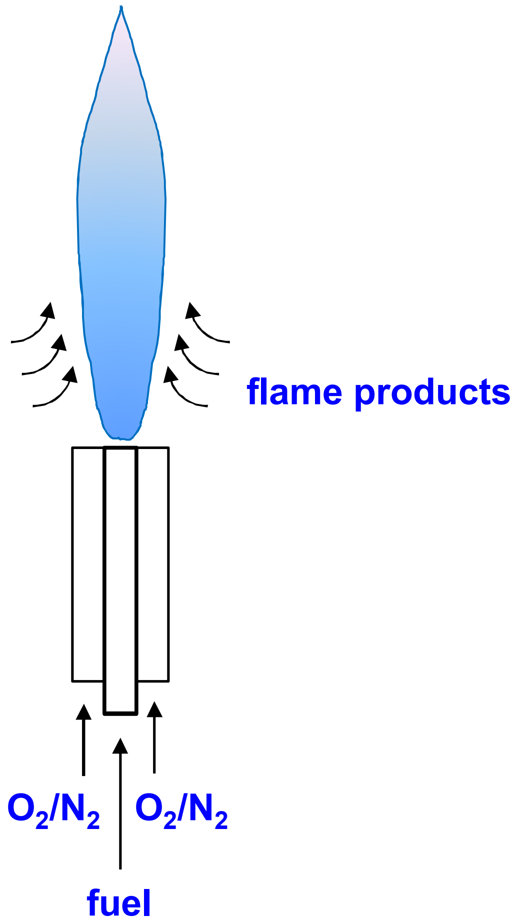
- Flame radiation
- Flame shape and size
  - e.g. Kim et al., *Energy & Fuels* 2007 (collaboration between Hanyang Univ. and KIMM)
- Flame stability
  - e.g. Oh and Noh, *Fuel* 2013 and 2014 (KIER)
- Soot formation
- Emissions (esp. NOx)
  - e.g. Kim et al., *Energy & Fuels* 2006 and 2009, *PCI* 2007 (collaboration between Hanyang Univ. and KIMM)

# Recent Study at Sandia – Effect of Oxygen Purity on Soot Formation and Flame Radiation

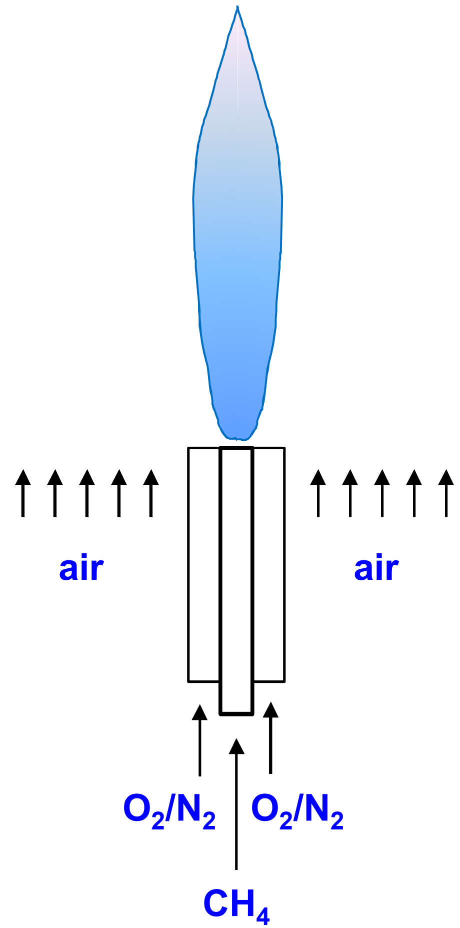
- Paper in press, Proceedings of the Combustion Institute, to be presented at Combustion Symposium (next week)
- Idea: try to separate effects of turbulence intensity (mixing) from flame effects of oxygen purity of oxidizer
  - investigated 2 series of methane-air non-premixed flames
  - one in which the oxidizer concentration varied but its flow rate stayed the same
  - one in which pure oxygen was used, but its flow rate was varied

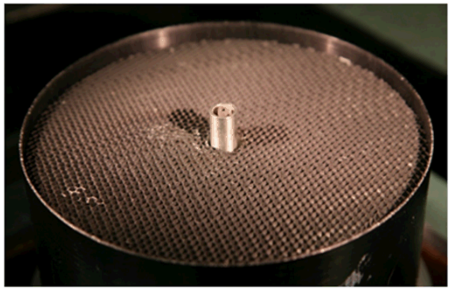
# Burner Geometry

**Practical Oxy-fuel Jet Flame Configuration**




**Investigated Oxy-fuel Jet Flame Configuration**

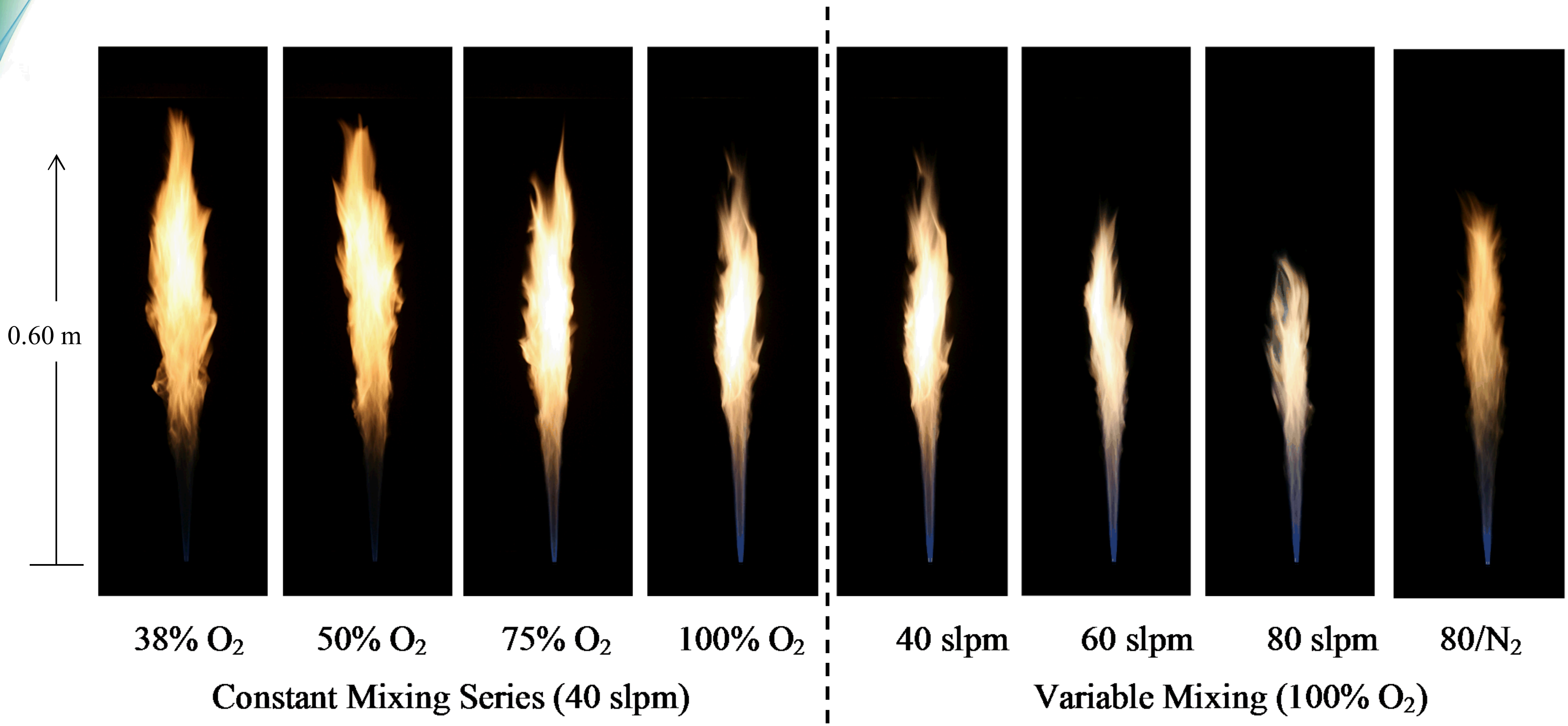


**Fuel Tube: 3.3 mm ID**

**Oxidizer Tube: 11.7 mm ID**

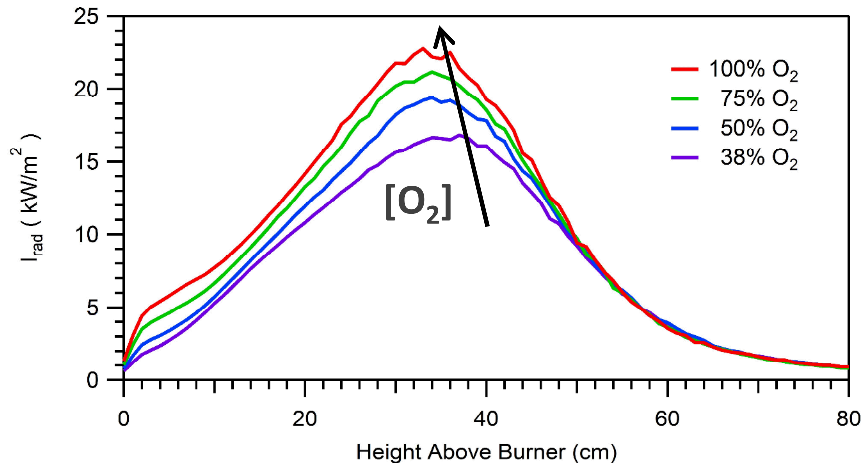
# Photographs of Investigated Flames

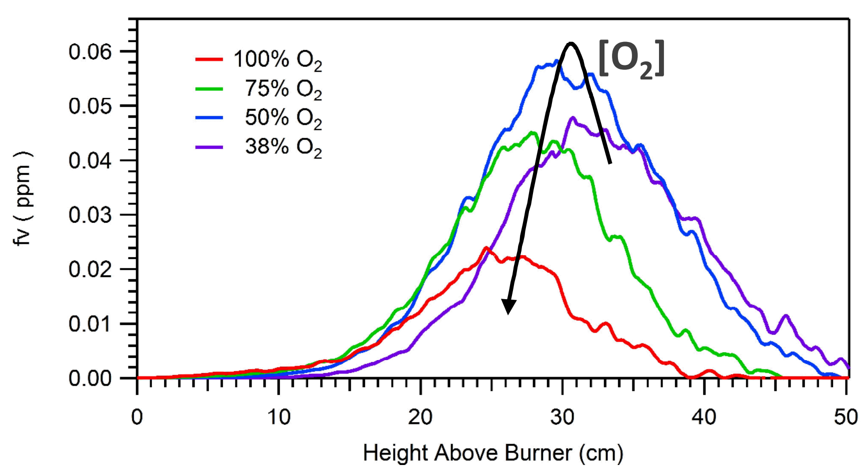


# Principal Results

## Effect of $O_2$ Purity

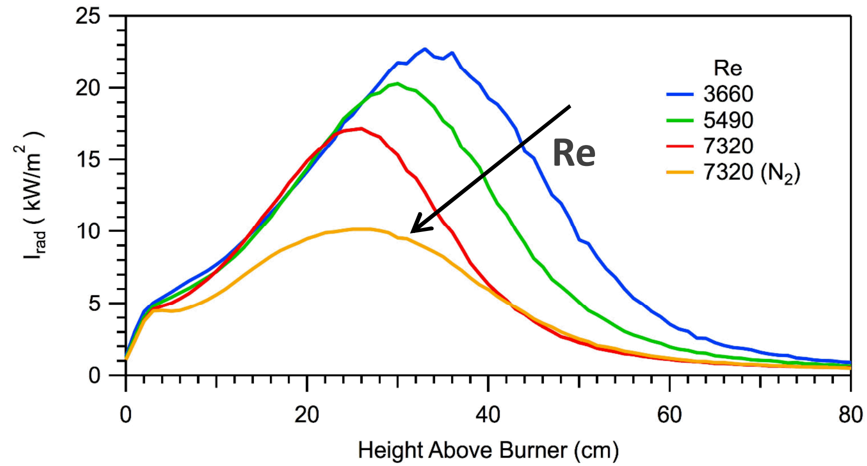
Oxidizer Re= 3660

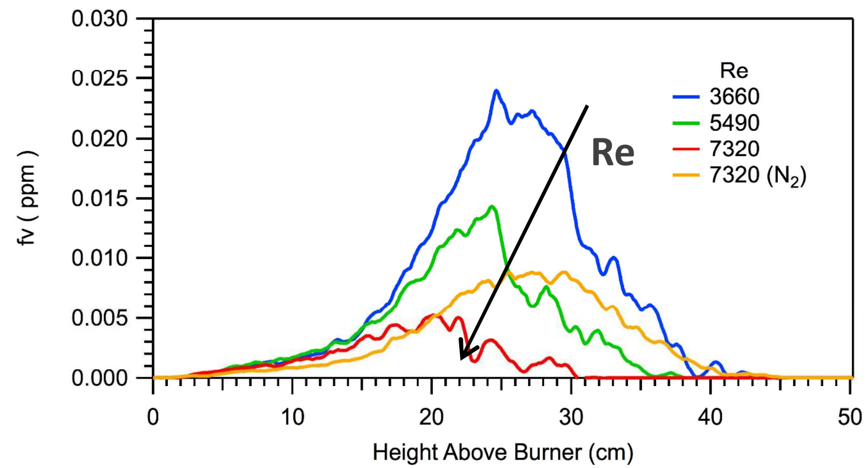


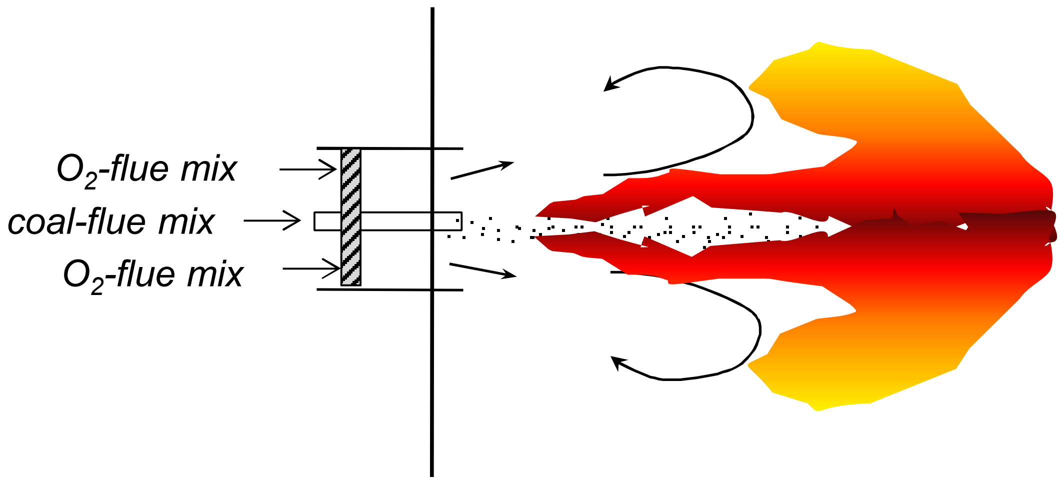

## Effect of Turbulent Mixing

100% $O_2$ , Oxidizer Re= 3660 – 7320



# Additional Considerations in Oxyfuel Combustion of Pulverized Coal (relative to gaseous fuels)




- Coal jet heat-up and ignition
- Volatiles burning rate
- Char particle combustion
- Radiant heat transfer
- Pollutant formation (and capture in $CO_2$ CPU)
- Ash particle formation and deposition, influence of S recycle, etc.

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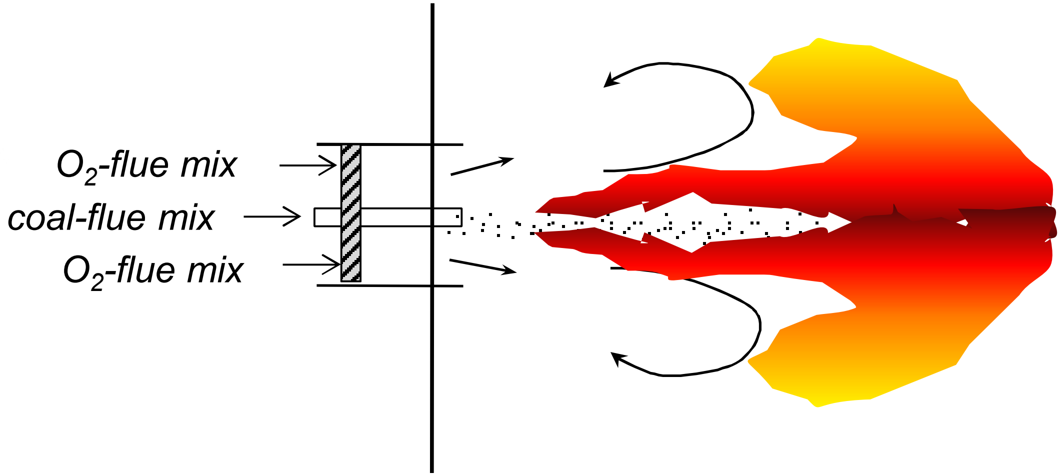
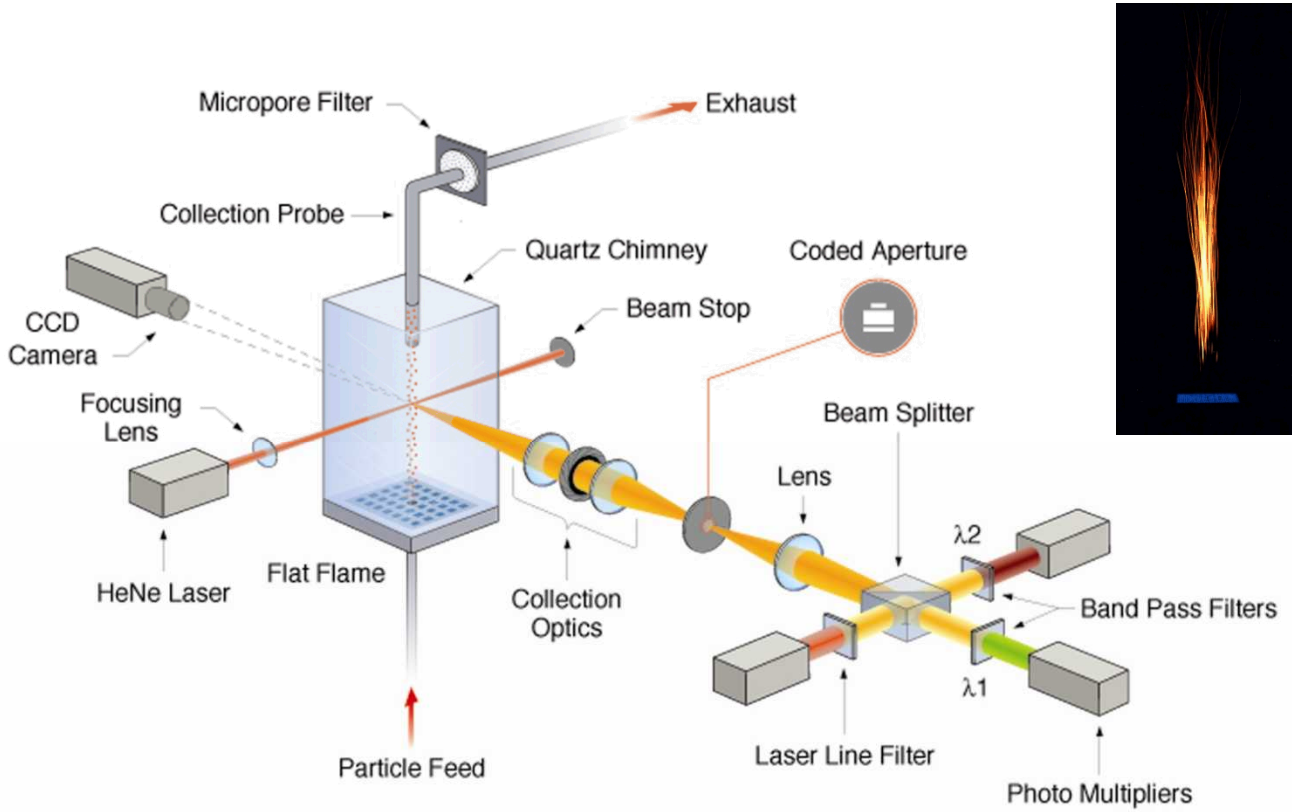



**Sandia studies**

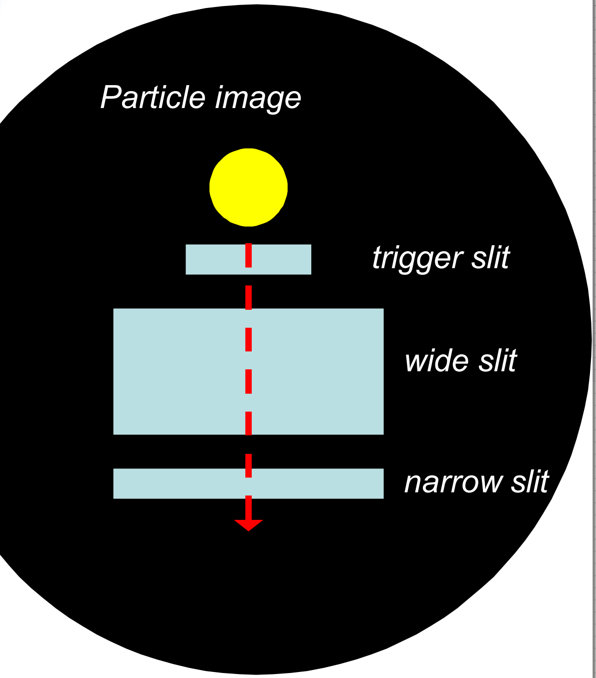
- **Coal jet heat-up and ignition**
- Volatiles burning rate
- **Char particle combustion**
- Radiant heat transfer
- **Pollutant formation** (and capture in $CO_2$ CPU)
- Ash particle formation and deposition, influence of S recycle, etc.

# Sandia Optical Entrained (Laminar) Flow Reactor

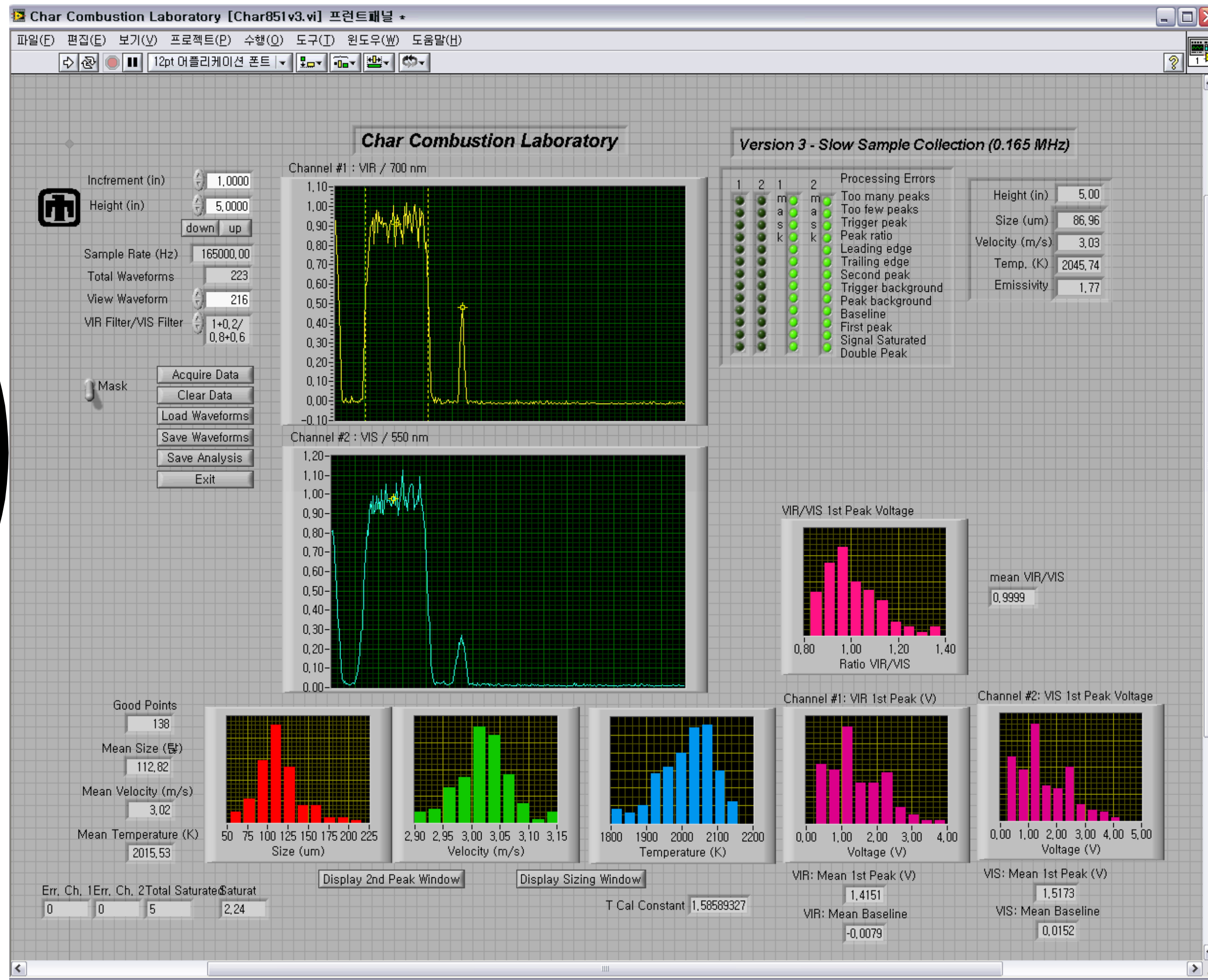



- 1 atm
- 5 cm X 5 cm X 46 cm quartz chimney
- furnace flow from compact, diffusion-flamelet burner
  - T from 1100–2300 K
  - $O_2$ from 0–60%
  - $CO_2$ from 4–98%
- coal/biomass/char particles introduced along centerline
- particle-sizing pyrometry for temperature, velocity, and size of individual char particles
- CCD/ICCD imaging of one or more particles (ignition studies)

# Oxy-Fuel Char Combustion – Key Diagnostic: Particle-Sizing Pyrometry




schematic of coded aperture

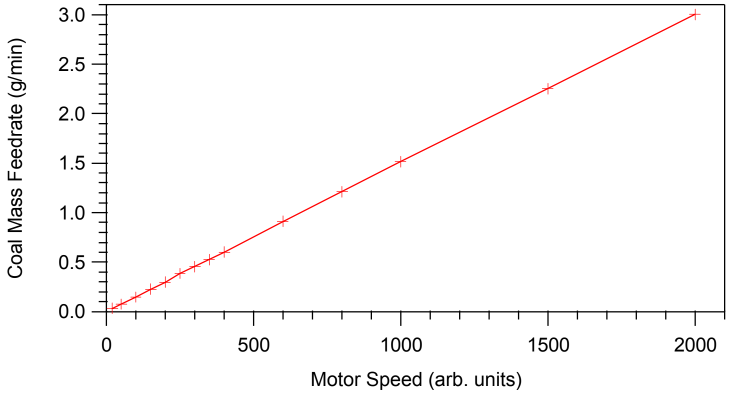


# Coal Feeder: Key to Accurately Measuring Combustion Ignition Delay

Maintaining steady coal feed is difficult, especially at small scales

- custom coal feeder developed from design originated by Sarofim at MIT
- test tube with vibrator
- outflow is through fixed hypodermic needle
- feed rate determined by rate of displacement of coal-containing test tube (electric motor drive)
- coal entrained by as little as 0.033 slpm feed gas

Coal feed calibration plot




Photograph of pulverized coal feeder

# Motivations for Study of PC Combustion Ignition Delay

- No previous detailed study on ignition delay of pulverized coal streams in well-controlled laminar flows
- Conflicting reports in literature on magnitude of effect of $CO_2$ on particle ignition
- Conjecture (by modelers) that ignition delay in laminar systems should correlate with particle group number (in analogy to liquid droplets)

# PC Combustion Ignition Delay Study

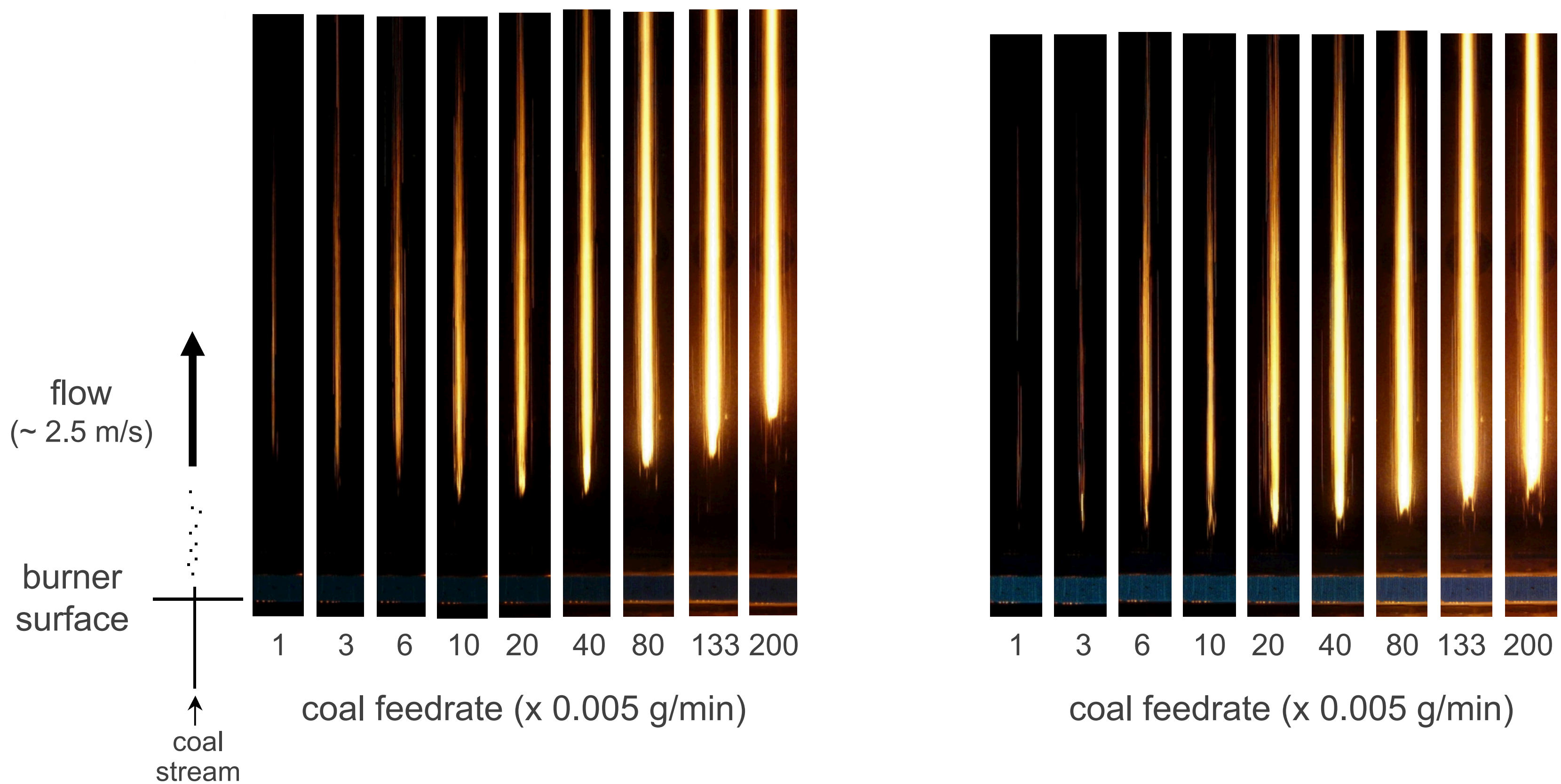
- Pittsburgh hvbit, Black Thunder subbit, Shenmu hvbit, and Guizhou hvbit coal
- variable coal feed rates
  - particle size cuts from 54–125 μm
  - 12, 16, and 20 vol% $O_2$ in $N_2$ at 1230–1320 K
  - 20 vol% $O_2$ in $CO_2$ at 1280 K
- fixed coal feed rate
  - 20 vol% $O_2$ in $N_2$ and in $CO_2$ at 1200 K, 1340 K, and 1670 K
- 80.0 slpm bulk gas flow
- 0.033 slpm $N_2$ or $CO_2$ flow to deliver particles
- ignition based on CCD camera image of 10 cm height in furnace through CH* filter (431 nm, 10 nm FWHM)

# Combustion Ignition Delay – Photographs

Black Thunder (subbituminous) coal, 12 vol-% $O_2$ in $N_2$

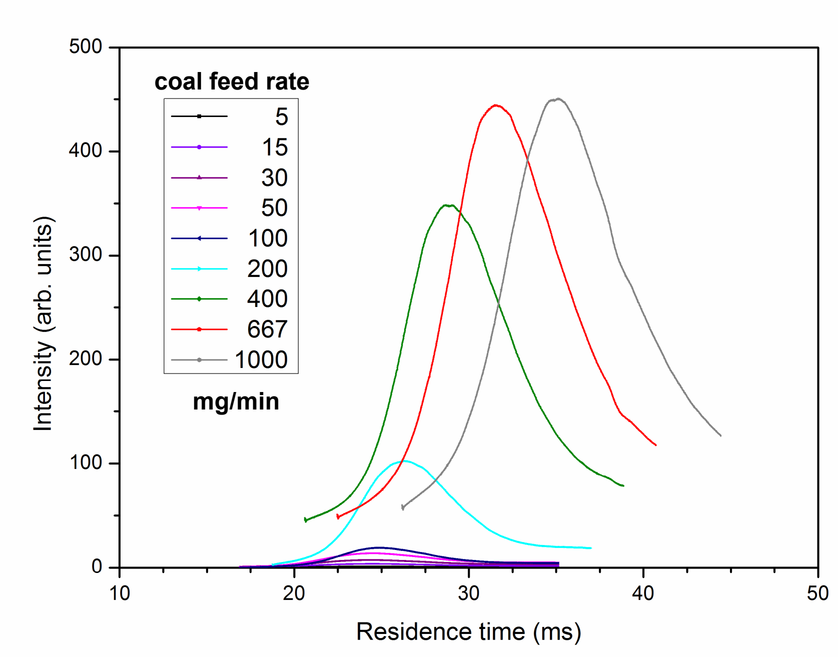
1230 K

1320 K

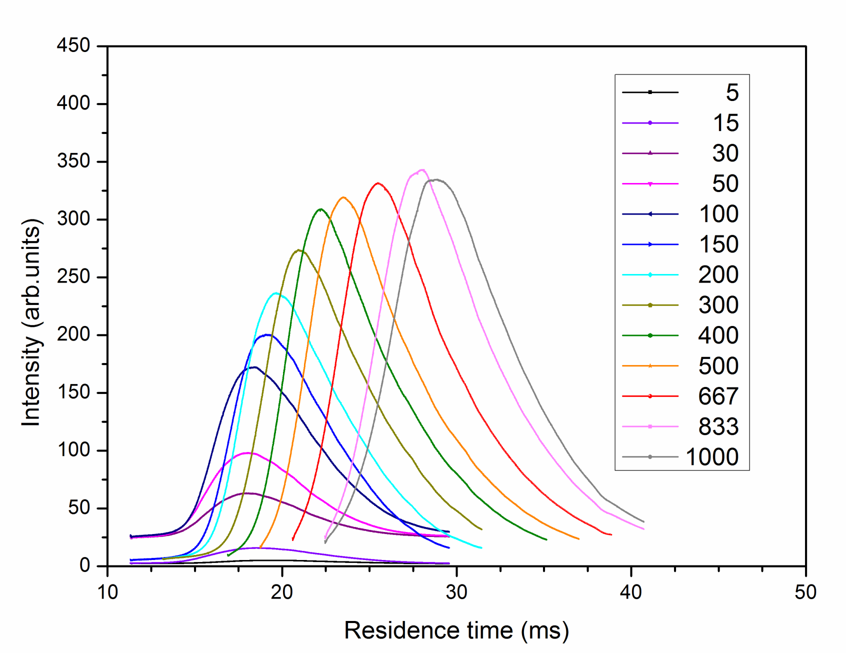


# Radially Binned, Background Corrected CCD Image Profiles

Shenmu coal, 20% $O_2$ in $CO_2$, 1280 K



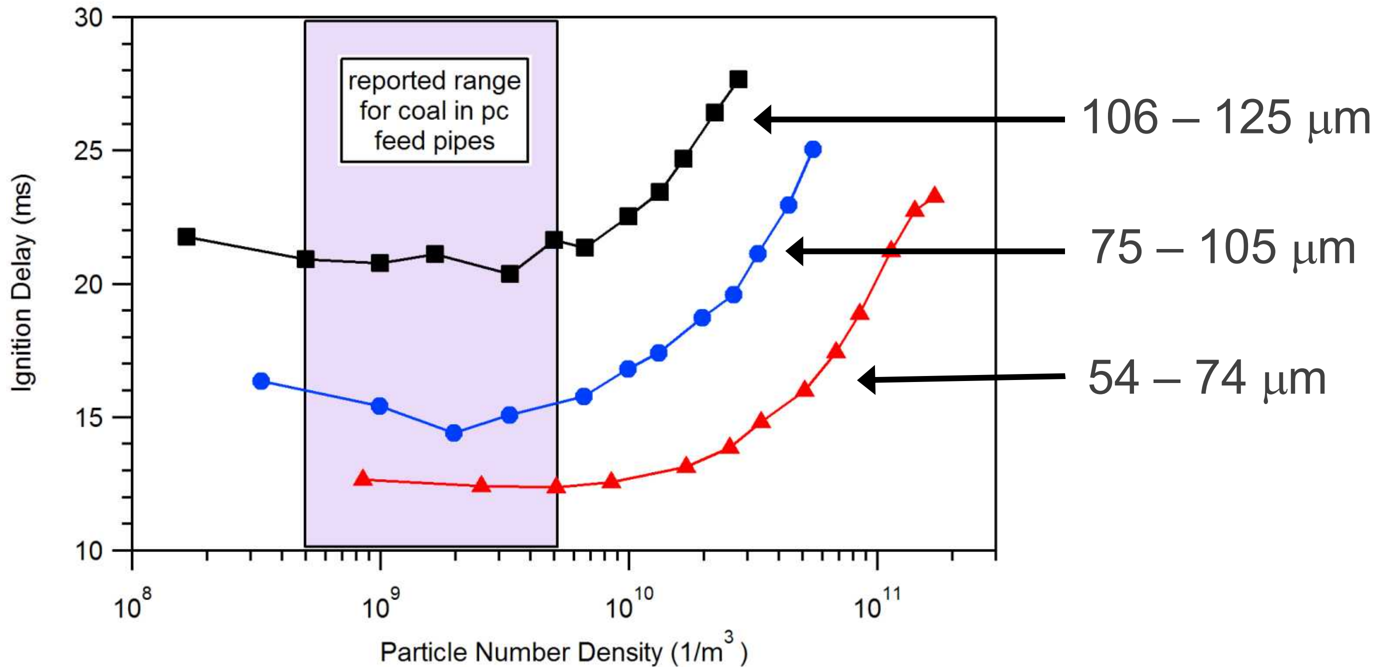

Pittsburgh coal, 12% $O_2$ in $N_2$, 1320 K




- ignition criteria: location where signal equals $0.5*I_{max}$

# Major Findings of Ignition Delay Study – I

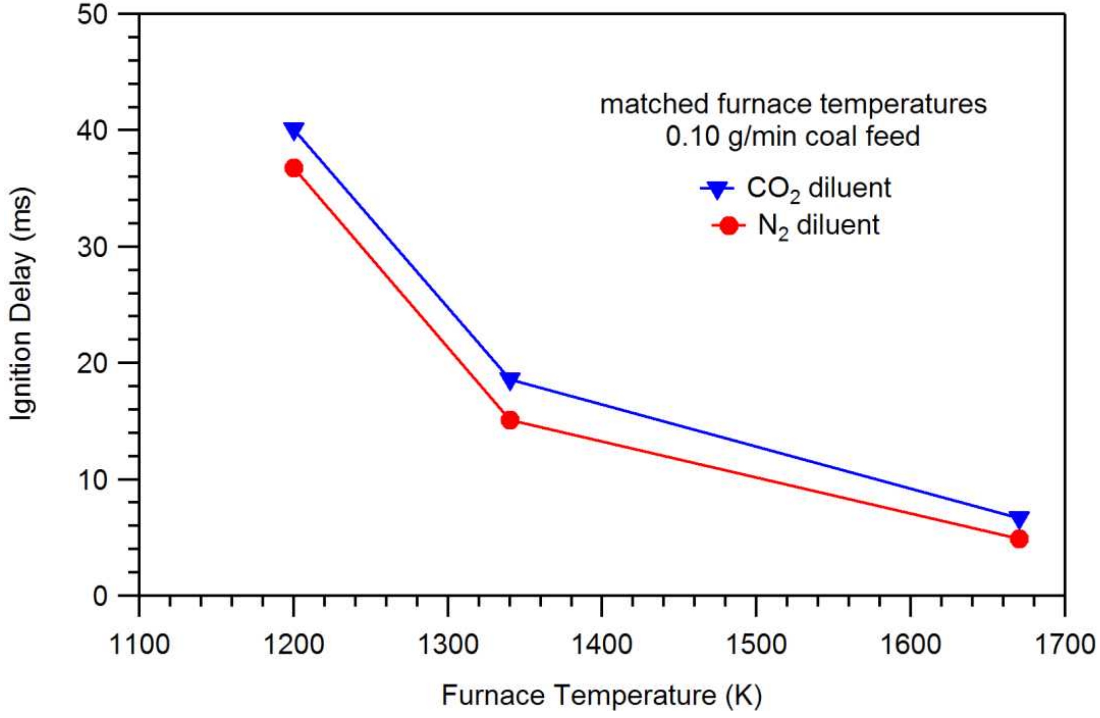
Pittsburgh coal
12% $O_2$ in $N_2$
1320 K




- ignition delay is very sensitive to particle size (implications for lab studies)
- minimum ignition delay correlates with **particle number density** (across range of particle sizes) – does not correlate as well with G

# Major Findings of Ignition Delay Study – II

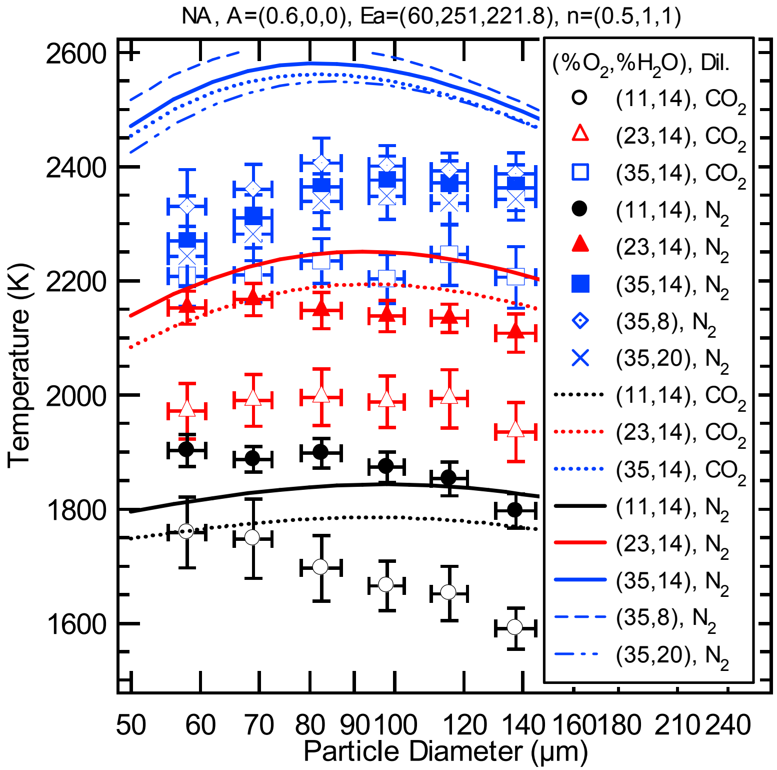
Pittsburgh coal, 20% $O_2$

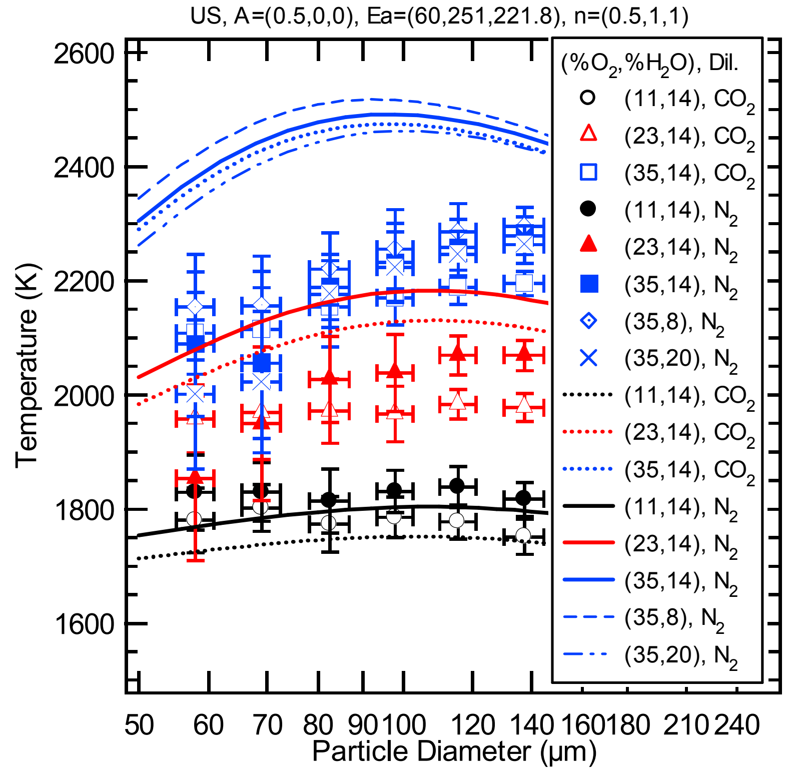



- ignition delay is very sensitive to ambient temperature
- ignition delay is *slightly* delayed in $CO_2$ environments, *when injecting diluent gas/particle mix*

# A Funny Thing Happened on the Way to Measuring Oxy-Fuel Combustion Kinetics

- Comparisons of char combustion models (simplified and detailed) to data over range of $O_2$ concentrations showed oxidation-only models overpredict char particle T rise as $[O_2]$ increases



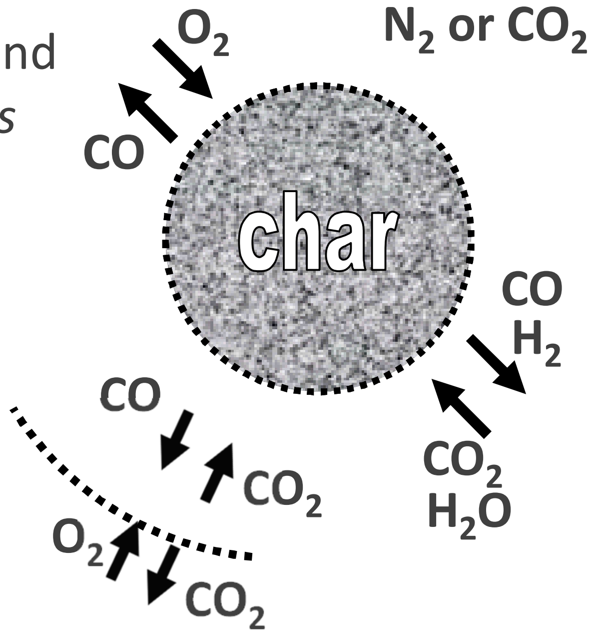



# Tool to Explore This: Detailed Particle Modeling

**SKIPPY** (Surface Kinetics in Porous Particles) – Brian Haynes, U. Sydney

- 1D steady-state model of spherical *porous* char particle
- *Detailed surface kinetics and gas-phase kinetics* provided through links to CHEMKIN II
- Heterogeneous mechanism, char properties and combustion environment specified by user
- Allows evaluation of *boundary layer reactions* and *different kinetic mechanisms or rate parameters*

| Reaction | *A* (g/cm$^2$ s) | *E* (kJ/mol) |
|---|---|---|
| **Heterogeneous oxidation:** | | |
| (R1) C_s + $O_2$ => CO + O_s | 3.3E+15 | 167.4 |
| (R2) O_s + 2C(b) => CO + C_s | 1.0E+08 | 0. |
| (R3) C_s + $O_2$ => $O_2$_s+ C(b) | 9.5E+13 | 142.3 |
| (R4) $O_2$_s + 2C(b) => C_s + $CO_2$ | 1.0E+08 | 0. |
| **$CO_2$ gasification reaction:** | | |
| (R5) C_s + $CO_2$ => CO + O_s + C(b) | variable | 251.0 |
| **Steam gasification reaction:** | | |
| (R6) C_s + $H_2O$ => $H_2$ + O_s + C(b) | variable | 222.8 |

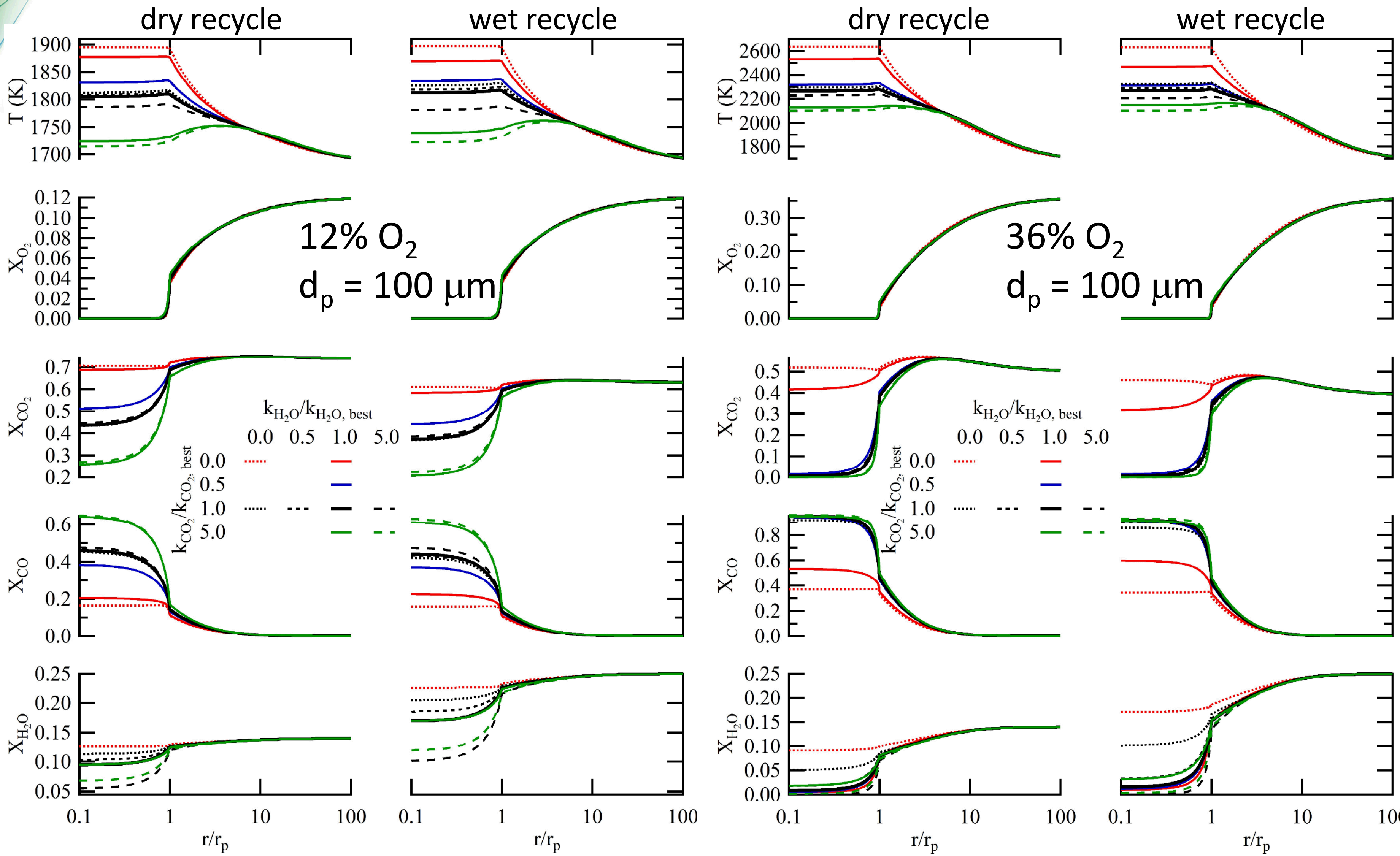


# Oxyfuel Char Combustion – The Role of Gasification Reactions

- The combination of experimental measurements of char combustion temperatures and modeling indicates gasification reactions **are** important during oxyfuel combustion, particularly because of their reaction endothermicity

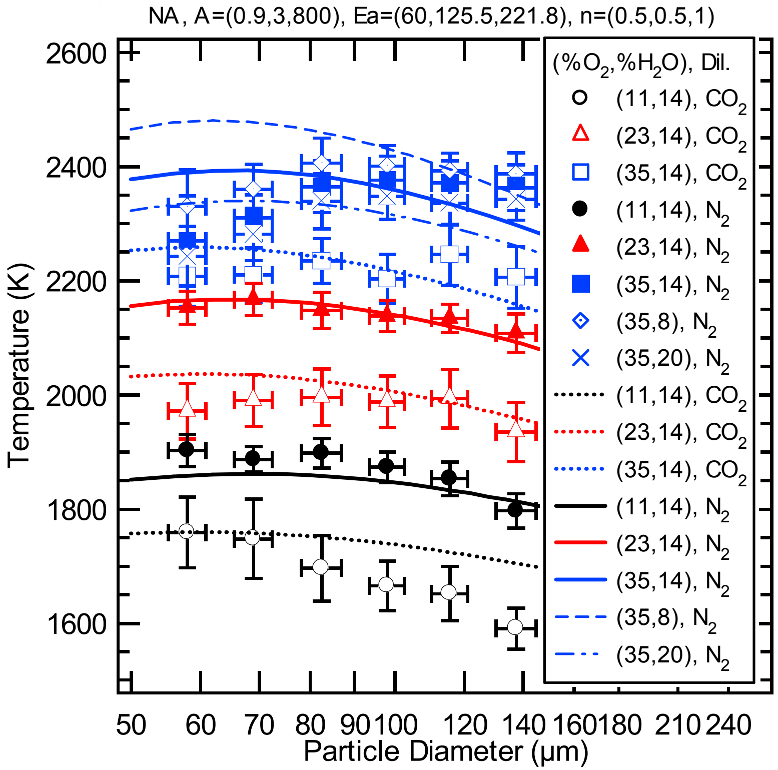
| Reaction | $\Delta H_{rxn}$ (kJ/mole-$C_s$) |
|---|---|
| $2C(s) + O_2 \rightarrow 2CO$ | -110.5 |
| $C(s) + CO_2 \rightarrow 2CO$ | 172.5 |
| $C(s) + H_2O \rightarrow CO + H_2$ | 131.3 |

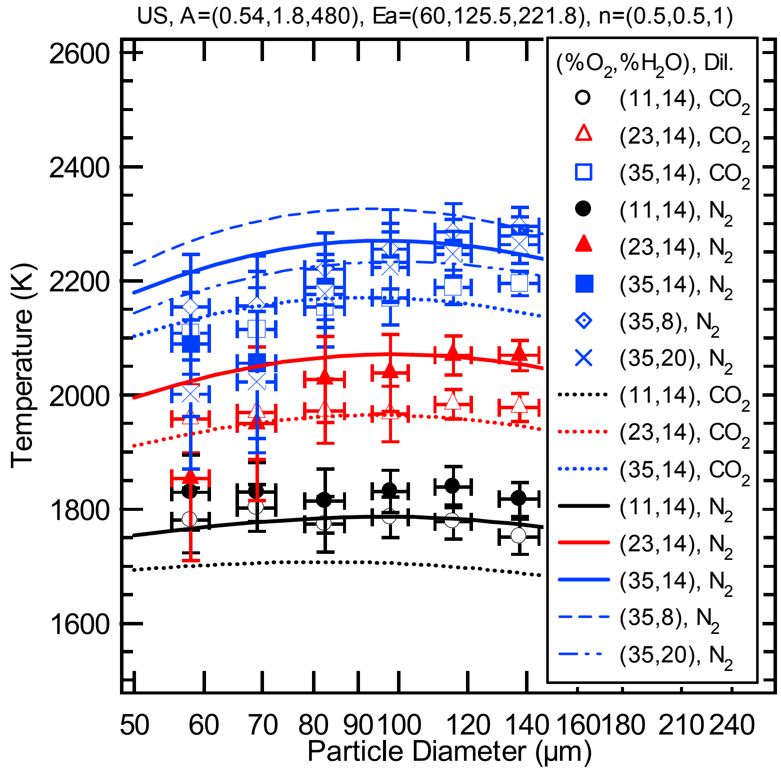
# SKIPPY Modeling of Oxy-Fuel Char Combustion – Effect of Gasification Reactions



# Combined Oxidation-Gasification of Coal Char

- Incorporation of gasification reactions, at rates supported by kinetic studies in the literature, gives much better agreement with optical pyrometry data



# Competition Amongst Heterogeneous Reactions

- Because the activation energies of gasification reactions are large, they become increasingly important *at high particle T*

$$CO_2 + C(s) \rightarrow 2CO \qquad (E_a \cong 250\ kJ)$$

$$H_2O + C(s) \rightarrow H_2 + CO \qquad (E_a \cong 220\ kJ)$$

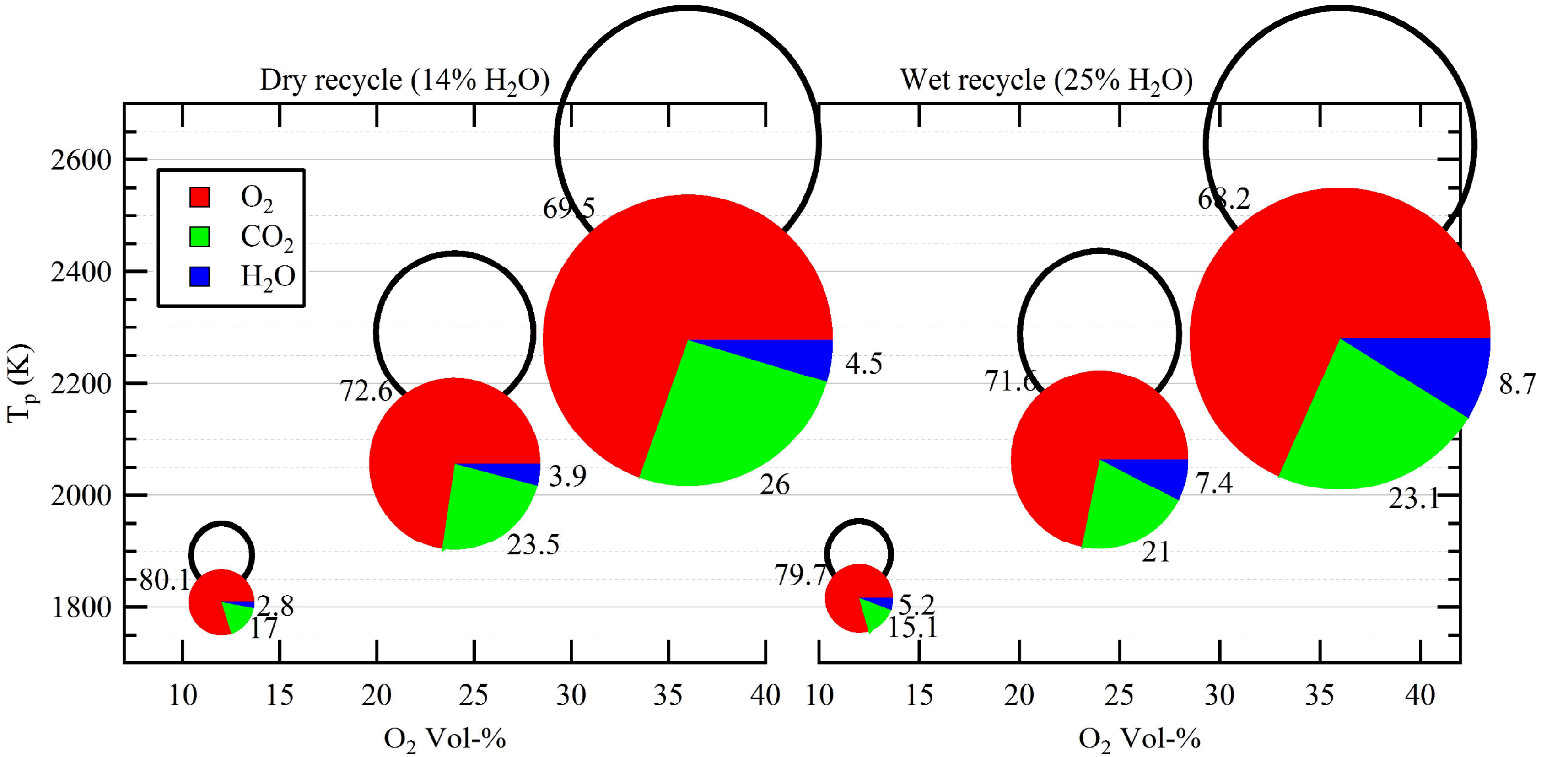
$$O_2 + 2C(s) \rightarrow 2CO \qquad (E_a \cong 160\ kJ)$$

- At the low to intermediate temperatures where coal devolatilization occurs, gasification rate is extremely slow – irrelevant over timescales of interest for combustion

- At 2000 K, the kinetic rate coefficient for $CO_2$ gasification is still ≈ 100x slower than oxidation, but is still important
  - large $CO_2$ concentration
  - deep penetration of particle (accessible surface area)
  - large *endo*thermicity of reaction

# SKIPPY Evaluation of Effects of Char Gasification Reaction

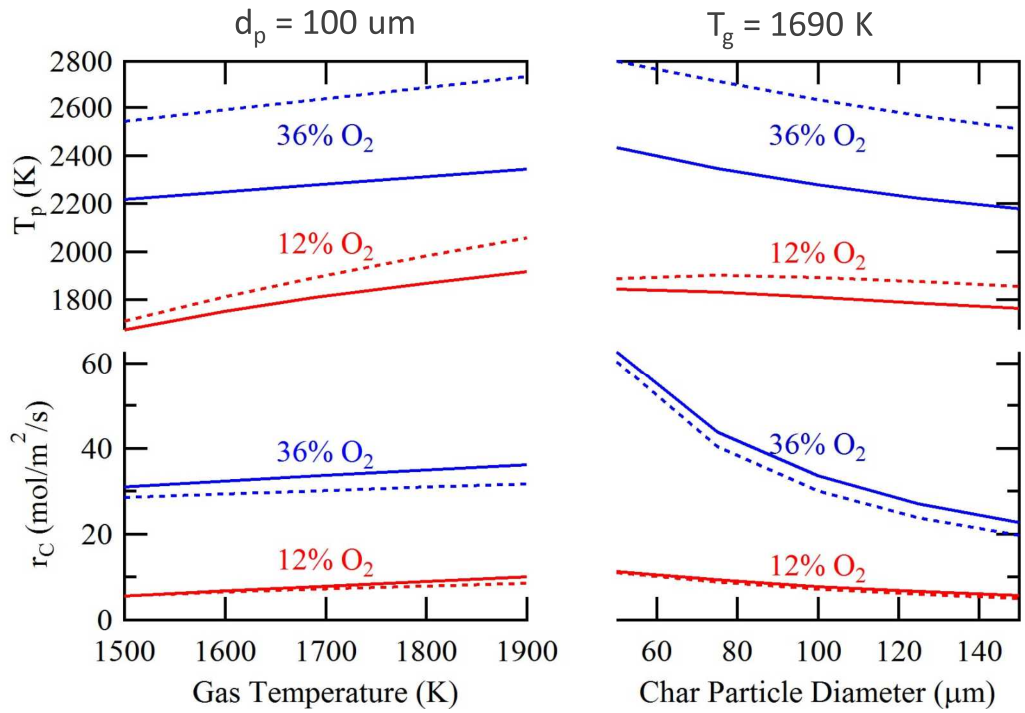
100 um, low-ash subbituminous coal char particle burning in 1690 K gas



# Effects of Char Gasification Reactions

- Endothermicity of gasification reactions substantially decrease char temperature (and even has effect for combustion in air)
- Reduction in char temperature reduces char oxidation rate
  - decrease in C *oxidation* rate is slightly *over*compensated by the added char consumption from gasification (i.e. overall char conversion rate increases)

Simulation results for reacting porous particles with detailed transport and chemistry: subbit. char particle burning in $O_2/CO_2$ mixtures (Hecht et al. CNF 2012)




dashed lines: ignoring gasification rxns

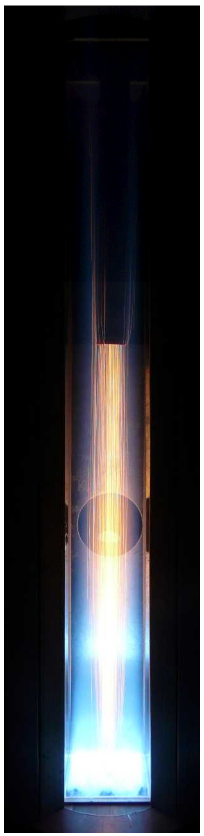
solid lines: including gasification rxns

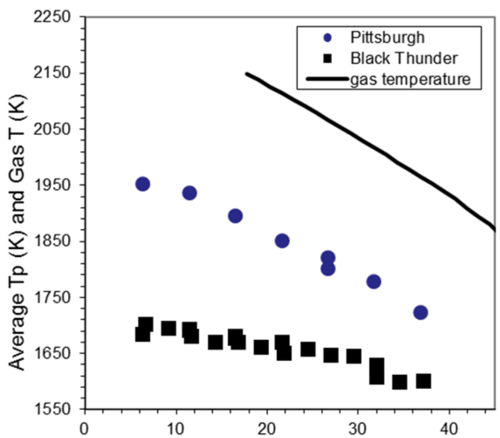
# Work in Progress

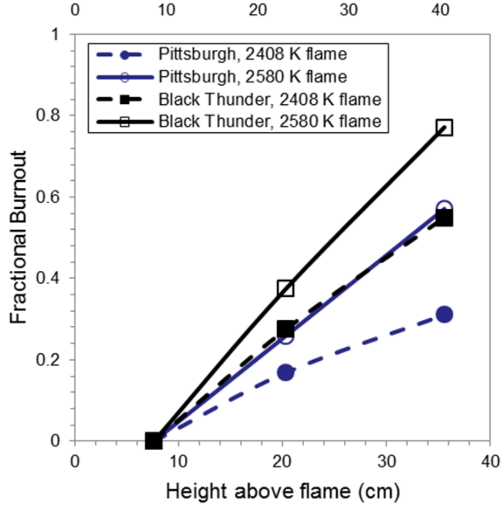
- Evaluation of effect of gas diffusivity on applicability of apparent kinetics models
- Evaluation of the high-temperature (~ 2000 K) $CO_2$ gasification rate of pc chars
- Oxyfuel char combustion kinetics at elevated pressures
  (up to 10 bar)

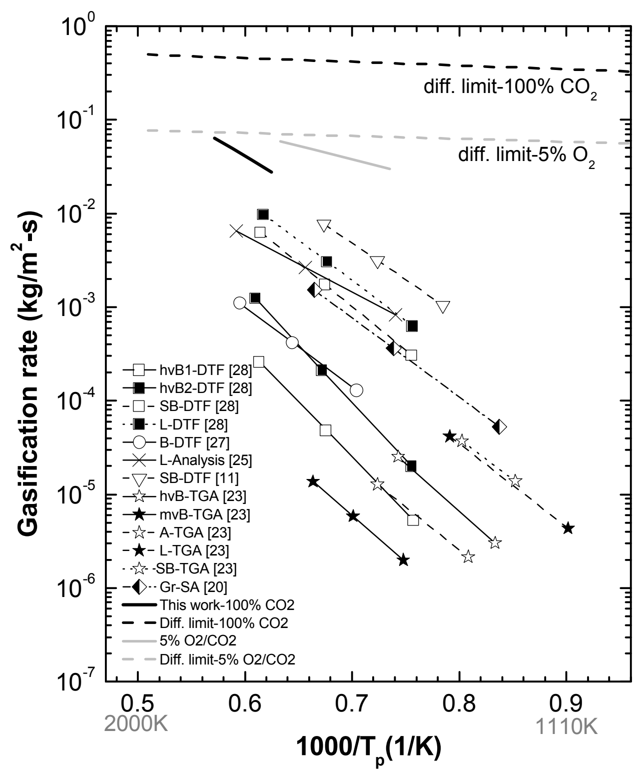
# Measurement of $CO_2$ Gasification Kinetics

- Optical particle temperature and burnout measurements used to measure pc char gasification kinetics in $CO_2$ at high temperatures characteristic of char burning in oxy-fuel environments

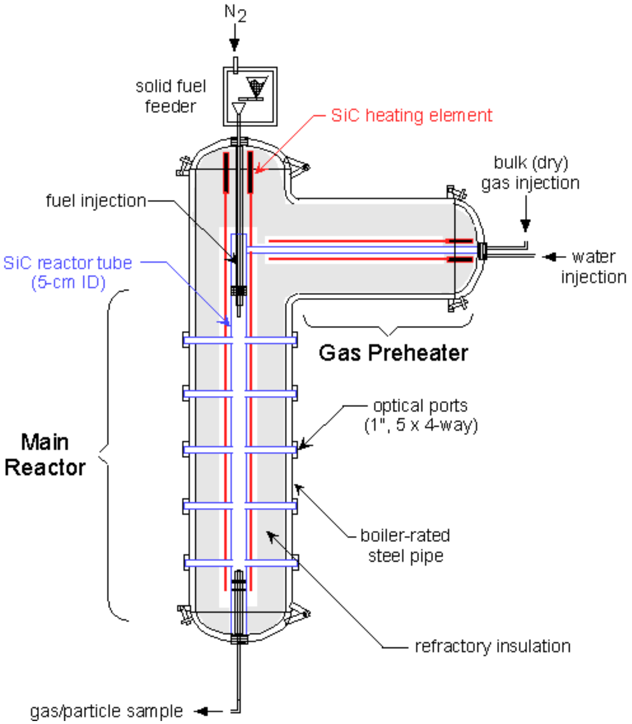




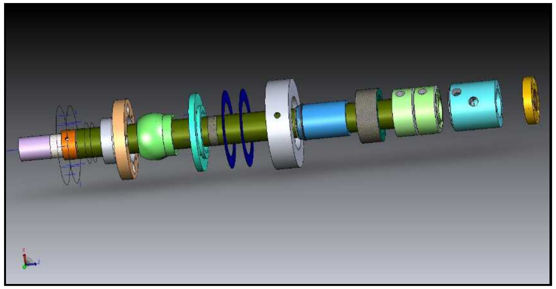



# Pressurized Combustion and Gasification Reactor




- 1–20 atm
- 300–1600 K (at pressure)
- 5 cm ID x 1.5 m long
- gasifying or oxidizing environment
- 5 point, 4-way port access
- optical sampling probe (for particle temperature)
- traversable particle and gas sampling system

Exploded diagram of water-cooled optical sampling probe



# Summary

- Oxyfuel combustion already has significant technological importance in the glass and metallurgy industries and is posed for application in the power industry, pending adoption of $CO_2$ emission regulations
- Oxyfuel combustion allows greater control of flame temperature and heat transfer
- For oxyfuel recycle applications, the first-order effect is due to higher heat capacity of $CO_2$ and $H_2O$ (relative to $N_2$)
- For oxyfuel combustion of gaseous fuels, there is a reduction in peak flame temperature and a reduction of H/O system radicals due to $H + CO_2 \rightarrow CO + OH$
- For solid fuels, the $CO_2$ and $H_2O$ gasification reactions reduce char combustion T and increase the char consumption rate

# Acknowledgments

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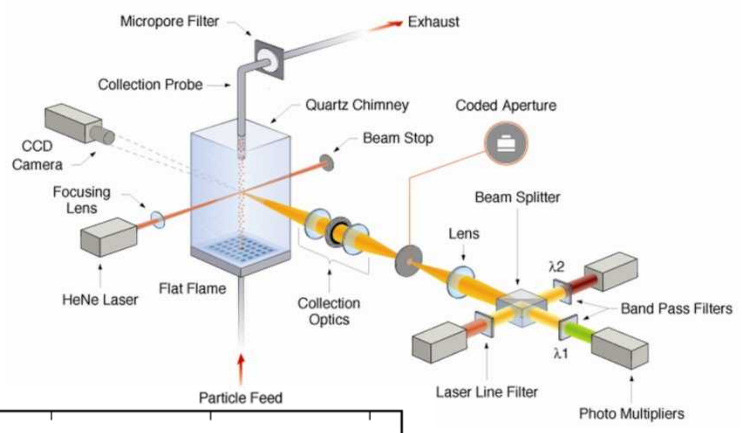
- Sangmin Lee (KIMM)
- Jeffrey Murphy (The Aerospace Corporation)
- Martin Schiemann/Victor Scherer (Ruhr-Univ. Bochum)
- Ethan Hecht (Sandia National Labs)
- Manfred Geier (Sandia National Labs)
- Timothy Williams (Sandia National Labs)

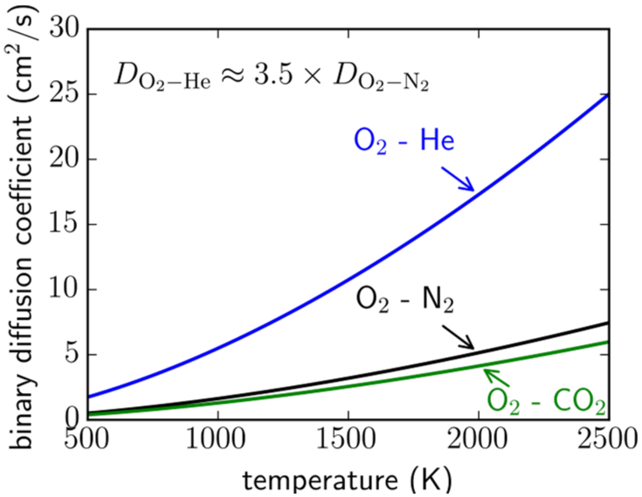
# Questions?

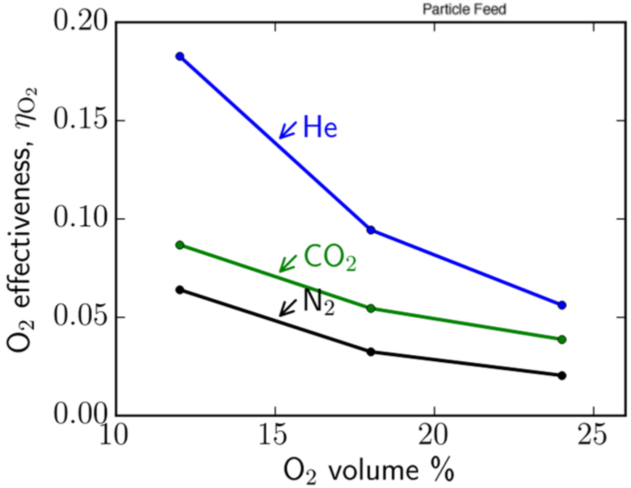
# Different diluents are used to change the reactant penetration

Approach:

- use laminar entrained flow reactor to produce same T combustion environments with $N_2$, $CO_2$, and He diluents
  - He has very high diffusivity

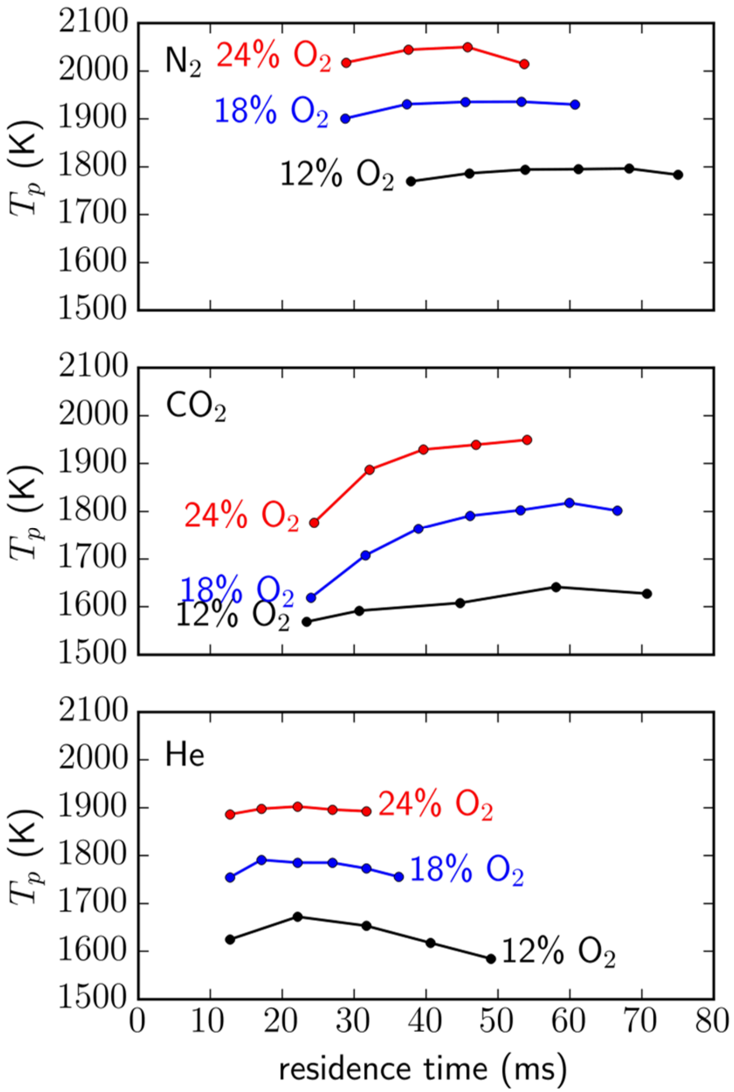



- measure 70 μm PRB subbituminous char particle combustion temperatures and burnout rates in different environments
- compare measurements against intrinsic and apparent kinetics models

# Particles ignite faster with a He diluent, but react at lower temperature than a $N_2$ diluent



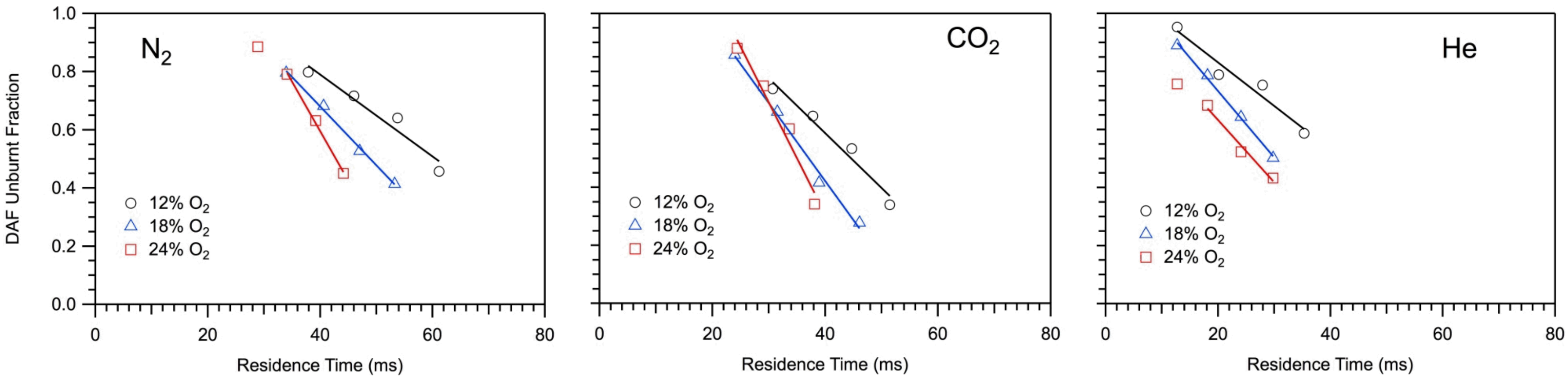

mean $T_p$ of 100 – 150 single-particle temperatures

Particles burn 100 – 150 K cooler in $CO_2$ than in $N_2$ (lower $O_2$ diffusivity and $CO_2$ gasification reaction)

Particles ignite much faster in He, but burn cooler than in $N_2$ ($\lambda_{He} \approx 5\ \lambda_{N_2}$)

# Although the temperatures are much lower, the burning rate in He is similar to $N_2$

Char Burnout Measurements:




Char mass burning rate is similar in $N_2$ and He environments, and is enhanced in $CO_2$ (gasification reaction)

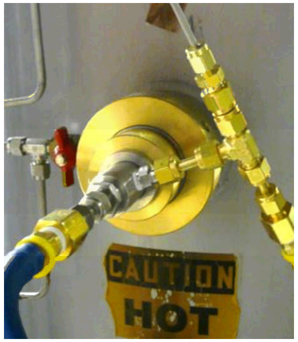
Characteristic Mass Burning Rates (1/s)

| Diluent Gas | Oxygen Concentration | | |
|---|---|---|---|
| | 12 vol-% | 18 vol-% | 24 vol-% |
| $N_2$ | 14.1 | 20.2 | 34.0 |
| $CO_2$ | 18.9 | 26.9 | 38.5 |
| He | 15.0 | 22.8 | 21.4 |

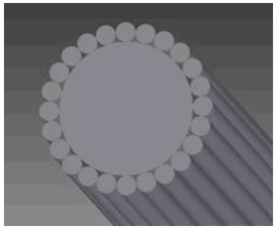
# An optical probe allows for in-situ, individual particle temperature measurements

- use calibrated fiber-optic coupled probe for in-situ particle temperature measurements
- cold target limits background radiation from hot walls

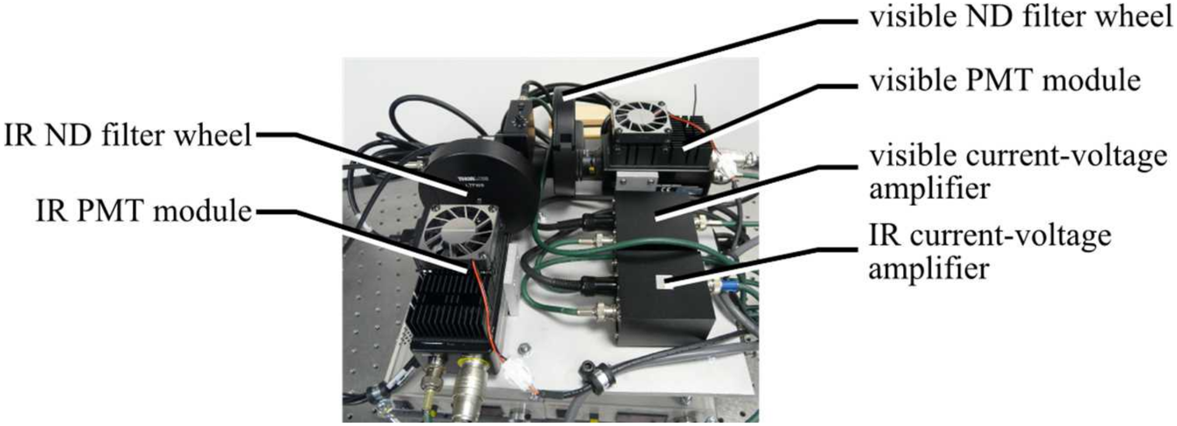
cold target probe



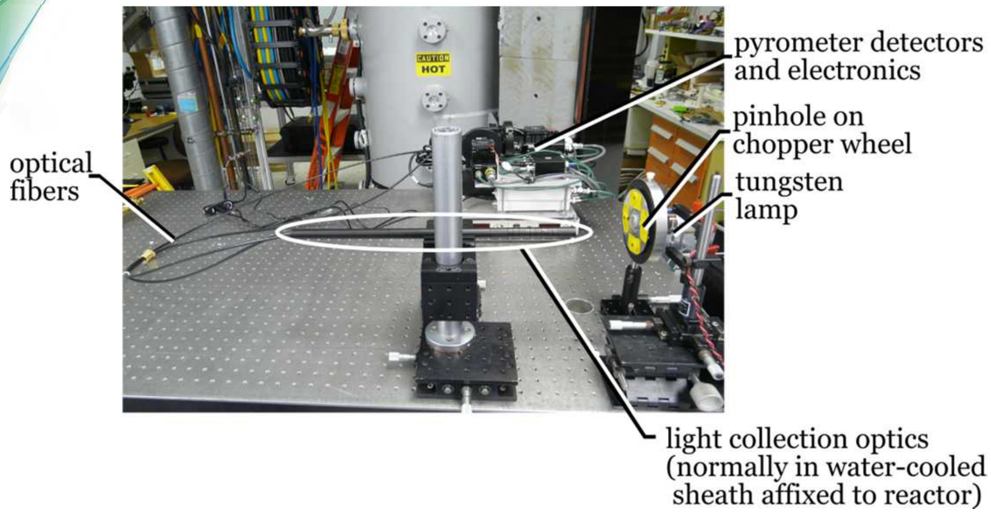

optical collection probe

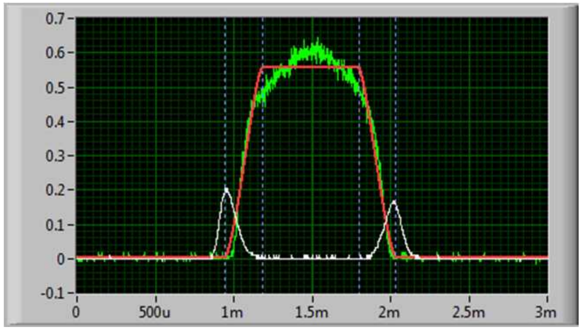


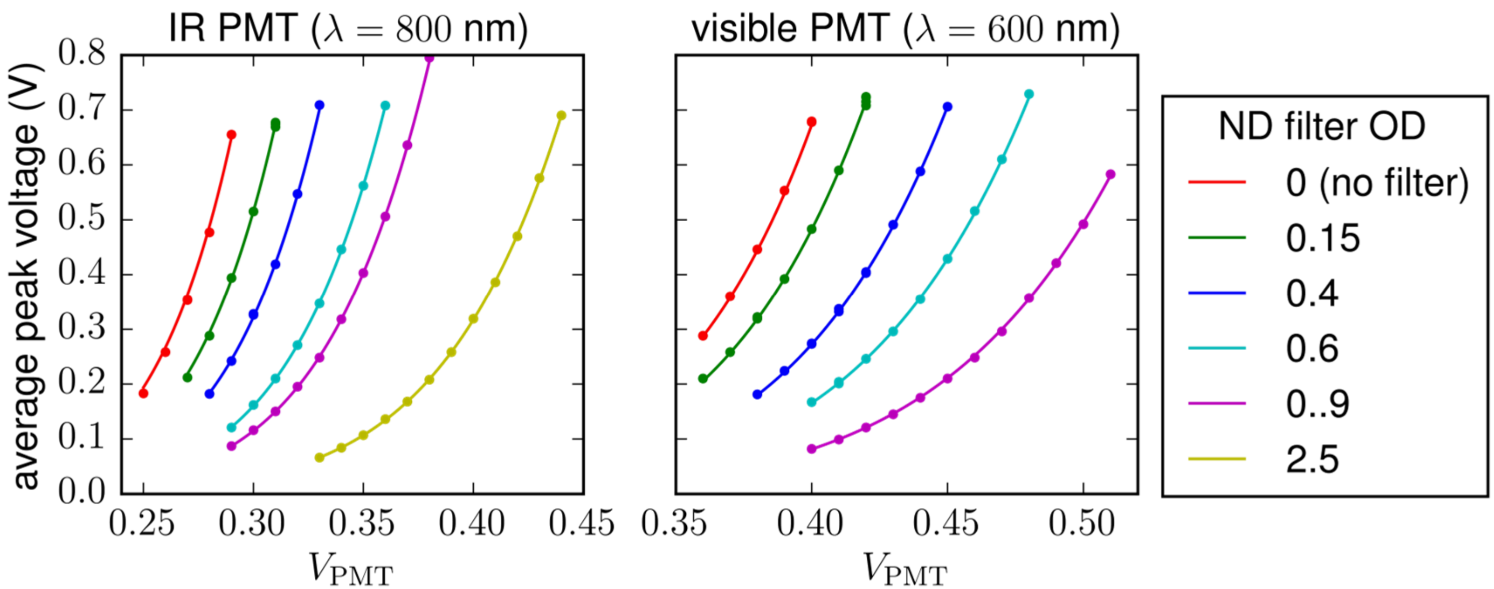
fiber bundle face



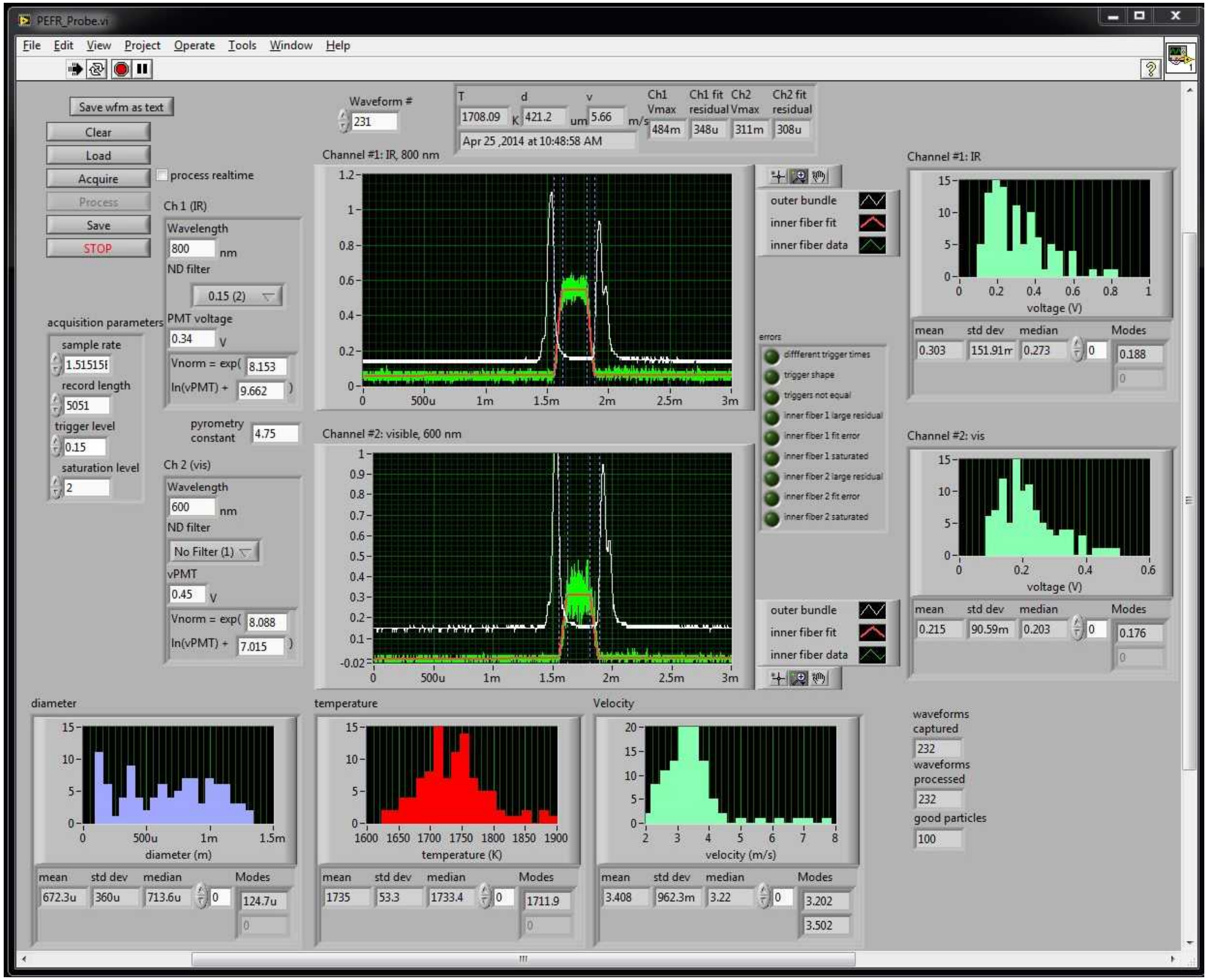
# The optics were calibrated using a tungsten lamp at nearly 3000K



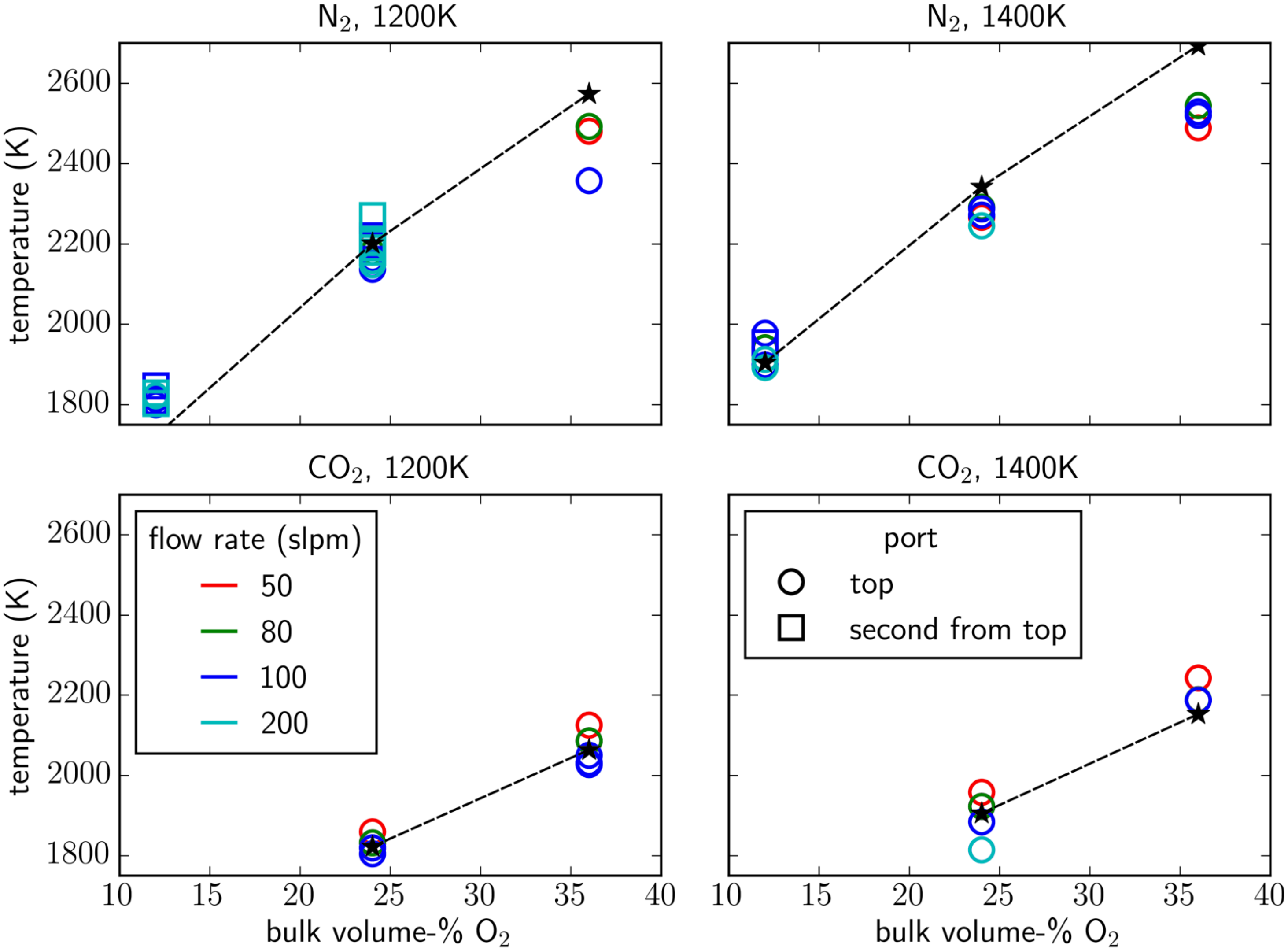



# Statistically significant data is collected to capture variability in individual particle reactivity



# Powder River Basin mean coal char reaction temperatures



# Recent Accomplishments: Oxy-fuel Combustion

- Improved semi-detailed char kinetic oxidation model developed, for the first time accurately predicting observed $O_2$ pressure dependence of key $CO/CO_2$ production ratio

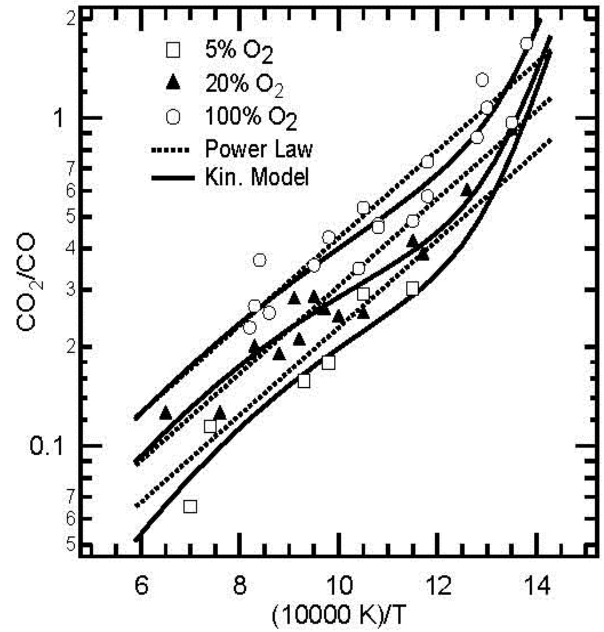
$$2C(\ )+O_2 \xrightarrow{k_1} 2C(O)$$

$$C(\ )+C_b+O_2 \xrightarrow{k_2} CO+C(O)$$

$$C_b+C(O)+O_2 \xrightarrow{k_3} CO_2+C(O)$$

$$C_b+C(O) \xrightarrow{k_5} CO+C(\ )$$

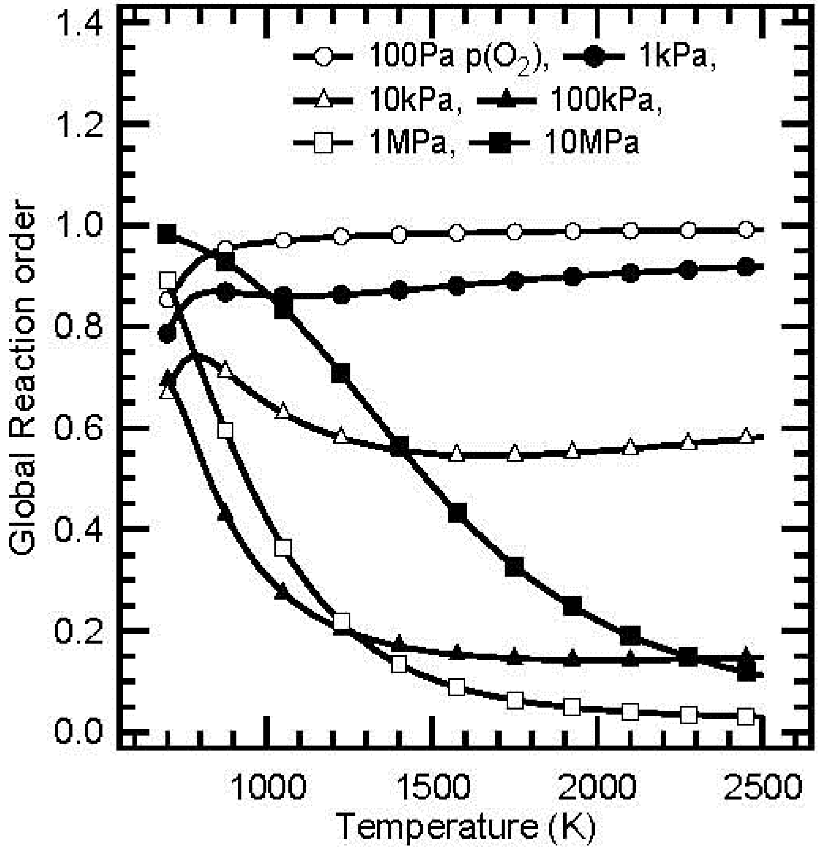
$$C_b+2C(O) \xrightarrow{k_6} CO_2+2C(\ )$$




- Enables accurate predictions of pc char burning behavior over range of T, $[O_2]$, and pressure conditions
- SKIPPY modeling validated assumptions used in analyzing experimental data (Tognotti and Sarofim)

# Oxy-Fuel Char Combustion
# – Semi-Detailed Char Combustion Mechanism

Other Predictions of New Mechanism – Reaction Order



# The Simple Math Argument for Carbon Capture

| | |
|---|---|
| 209 Gt | Est. carbon emissions to give 2 deg C global mean T rise |
| 700 Gt | Est. current recoverable fossil reserves (coal, oil, gas) |
| 4600 Gt | Est. fossil reserves + 30% of the fossil resource base |

"We have a choice – we either keep the fossil fuels in the ground or utilize CCS . . . keeping it in the ground is most unlikely"

↓

carbon capture
and sequestration

-- Filip Johnsson, Chalmers University

# Other Potentially Important Reactions during Oxyfuel Combustion

- H/O system radical recombination reactions: $CO_2$ and $H_2O$ are both very effective 3rd-bodies, e.g. in

$$O + O + M \rightarrow O_2 + M$$
$$O + H + M \rightarrow OH + M$$
$$H + H + M \rightarrow H_2 + M$$
$$H + OH + M \rightarrow H_2O + M$$
$$H + O_2 + M \rightarrow HO_2 + M$$

chaperon efficiency of $CO_2$ is **3.8 x** that of $N_2$ and efficiency of $H_2O$ is **12 x** that of $N_2$ (Li *et al.*, IJCK 2007)

- Flame modeling to-date indicates effect of $CO_2$ and $H_2O$ on radical recombination pales in comparison to $H + CO_2$ reaction

# $CO_2$ Dissociation

Some researchers attribute observed high CO concentrations in flame zone to thermal dissociation of $CO_2$

- CO is readily oxidized at high temperatures, so balance of CO and $CO_2$ is typically determined by H + $CO_2$ reaction equilibrium
- thermal dissociation is strongly temperature dependent
  - generates 1% CO (from 100% $CO_2$) at 1920 K, 2% CO at 2050 K