Coal Combustion and Gasification Science

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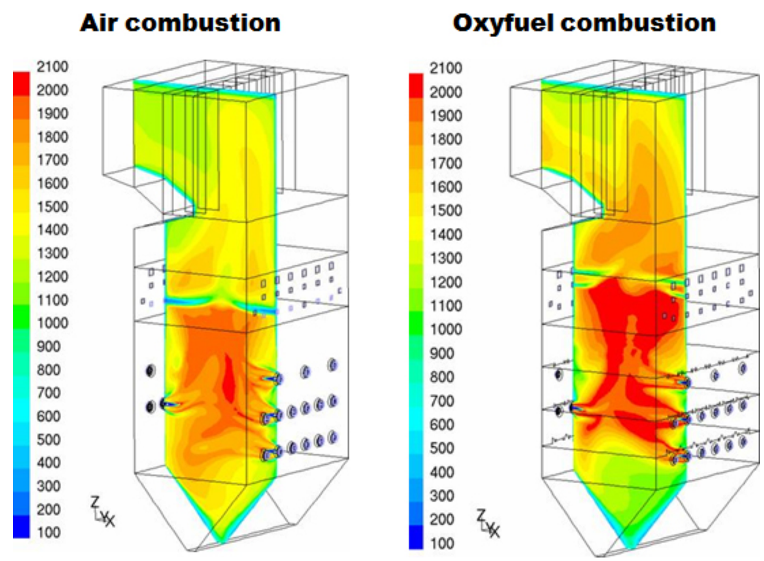
Validated CFD models can be a powerful design tool

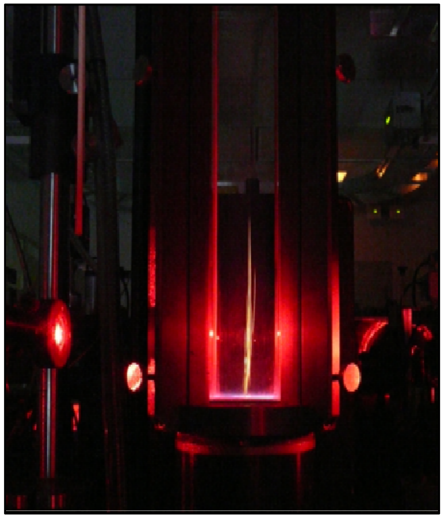
- Improvements in energy efficiency, availability, fuel flexibility, and capital effectiveness of oxy-fuel coal boilers and coal gasifiers increasingly rely on CFD modeling
- Accuracy of CFD modeling limited by
  - poor knowledge of fundamental coal conversion *rate parameters*
    - ignition delay
    - volatile loss
    - char combustion/gasification rate
  - limitations of *simplified models* used to predict coal conversion and heat-flux in CFD simulations



Simulation to determine suitability of boiler for oxyfuel combustion
www.hightechfinland.com

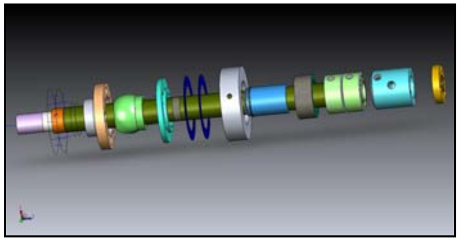
Data is collected and analyzed from unique experimental facilities

- Create relevant reaction conditions
- Perform *both* optical and sampling-based diagnostic measurements to understand fundamental physics (e.g. critical rate parameters)
- Use well-controlled particles (e.g. size, feed rate, devolatilization conditions)



1-atm entrained flow reactor

pressurized entrained flow reactor

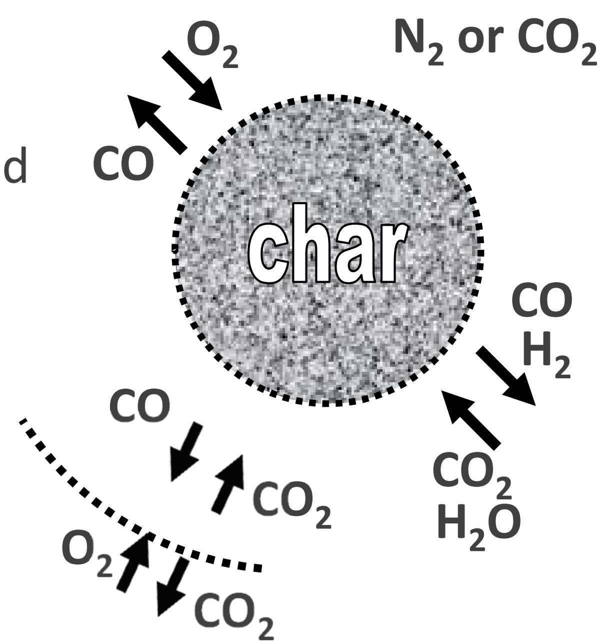


exploded diagram of optical probe

Fundamental physics are explored using a one-dimensional, continuous-film model

Use detailed reacting porous particle model to *interpret* experimental trends and *guide* the application of simplified reacting particle models

- **SKIPPY** (Surface Kinetics in Porous Particles) model, initially developed by Prof. Brian Haynes (Univ. Sydney)
- Detailed surface kinetics and gas-phase kinetics provided through calls 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

A single-film model, with reactant penetration neglects boundary layer reactions

- species conservation

$$x_{i,p} = \frac{\dot{N}''_{i,p}}{\dot{N}''_{t,p}} + \left(x_{i,\infty} - \frac{\dot{N}''_{i,p}}{\dot{N}''_{t,p}} \right) e^{-\kappa_{m,i}}$$

$$\kappa_{m,i} = \frac{r_p \dot{N}''_{t,p}}{c_t D_{i,\mathrm{eff}}}$$

- thermal energy

$$\dot{N}''_{\mathrm{C},p} h_{\mathrm{C},p} - \epsilon\sigma \left(T_p^4 - T_w^4 \right) = \sum_{i=1}^{n_{\mathrm{gas}}} \dot{N}''_i h_{i,p} + \frac{\bar{\lambda}}{r_p} \left[\frac{\kappa}{e^{\kappa} - 1} \right] (T_p - T_\infty)$$

$$\kappa = \frac{r_p}{\bar{\lambda}} \sum_{i=1}^{n_{\mathrm{gas}}} \dot{N}''_{i,p} \bar{c}_{p,i}$$

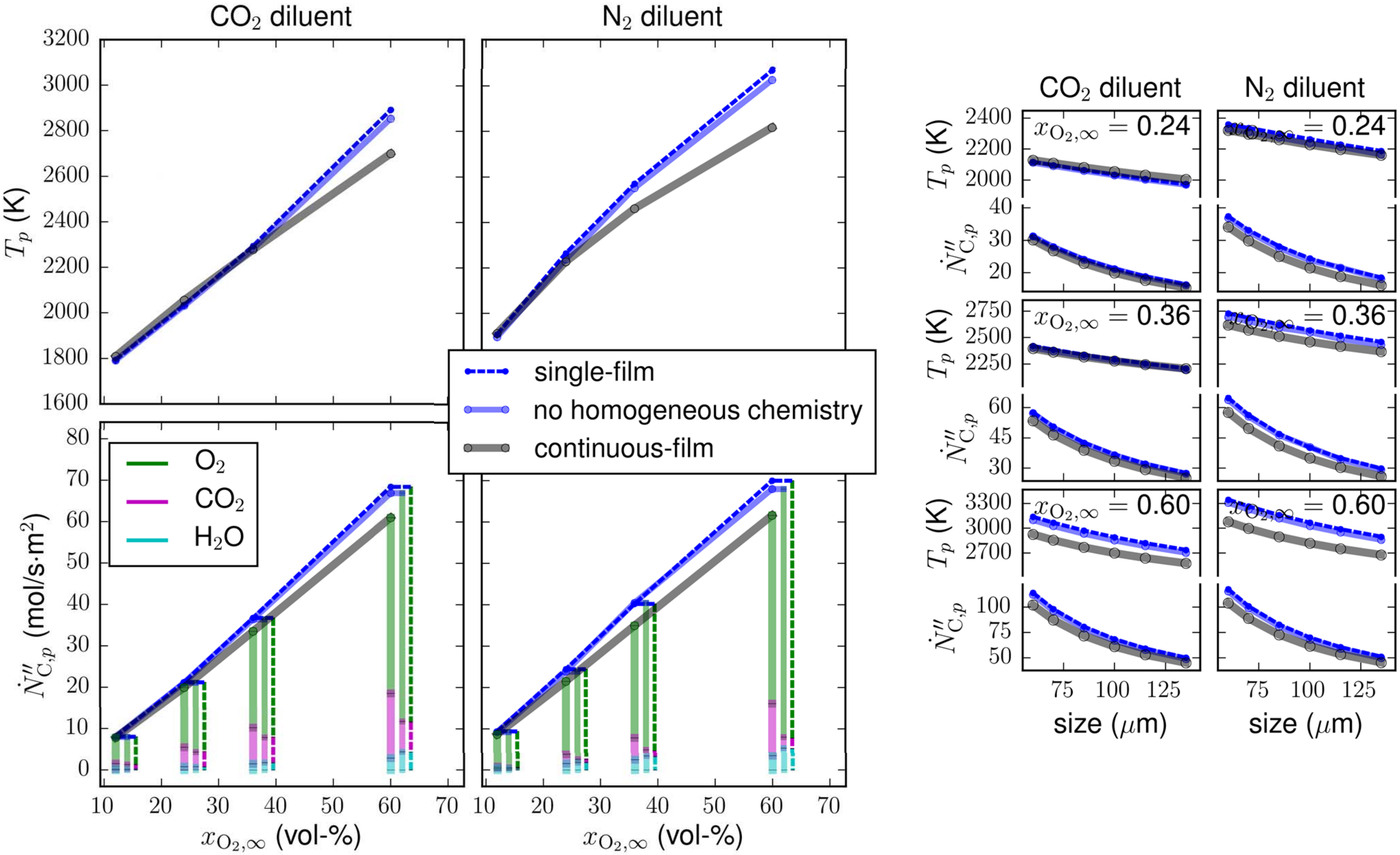
- accounts for Stefan flow

- reactant penetration (for each reactant: O_2, CO_2, H_2O)

$$\mathrm{M}_{\mathrm{T},i} = r_p \sqrt{\frac{\sigma_r k_{r,i}}{\frac{\phi}{\tau} D_{i,\mathrm{eff}}}} \qquad \eta_i = \frac{3}{\mathrm{M}_{\mathrm{T},i}} \left(\frac{1}{\tanh(\mathrm{M}_{\mathrm{T},i})} - \frac{1}{\mathrm{M}_{\mathrm{T},i}} \right)$$

$$\dot{N}''_{p,i,\mathrm{rxn}\ j} = -\eta_i k_j \left(\frac{\sigma_r r_p}{3} \right) \left(\frac{x_{i,p} P}{R T_p} \right)$$

The single-film model is sufficiently accurate as formulated, with gasification reactions



What effect does the extent of reactant penetration have on apparent kinetic rates?

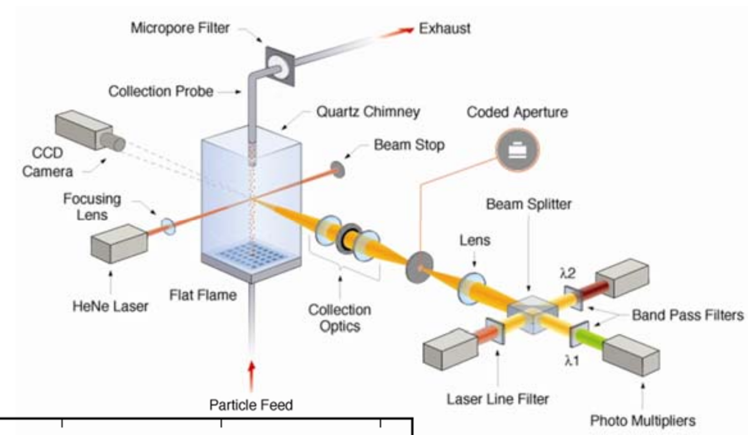
Motivation:

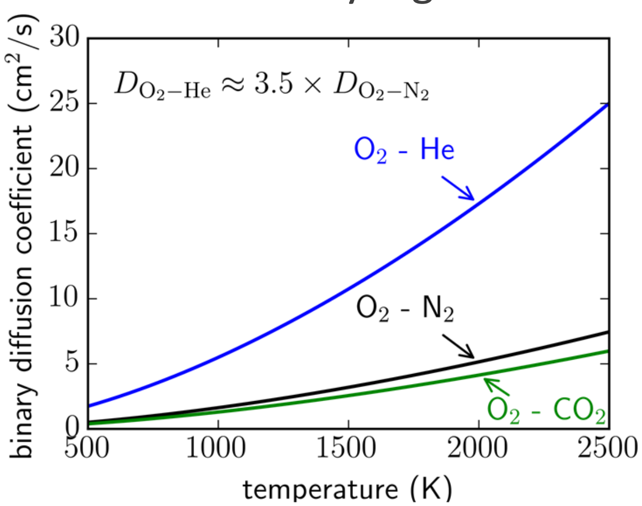
- CFD models almost always contain an apparent Arrhenius kinetics model of char combustion, neglecting the effect of different extents of reactant penetration
- during oxy-fuel combustion with FGR, char combustion occurs in a CO_2 background gas, rather than N_2
- the 20% lower diffusivity of O_2 in CO_2 has been shown to reduce apparent char burning rates, attributed to slower diffusion through the external boundary layer
- unclear how much lower gas diffusivity *through the char pores* also reduces the burning rate

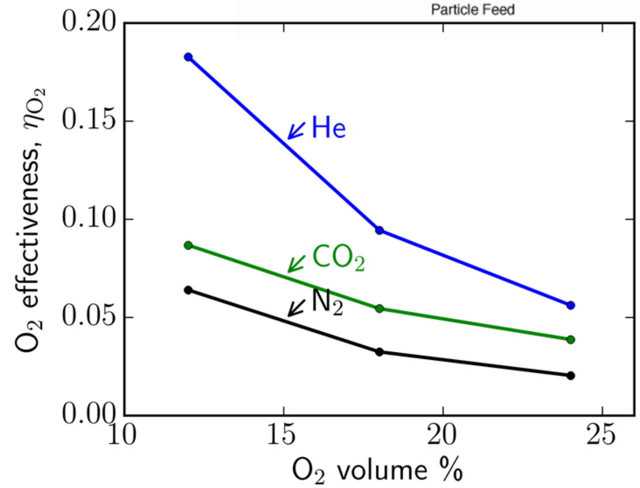
Different diluents are used to change the reactant penetration

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

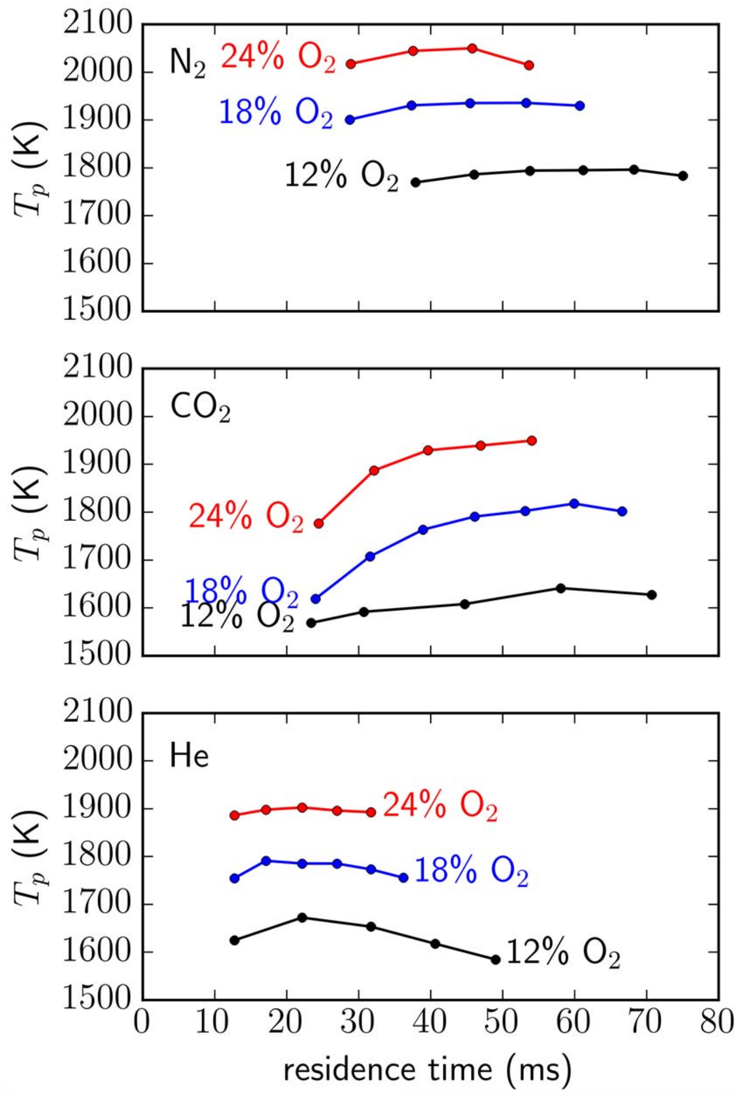






- measure 70 μm PRB subbituminous char particle combustion temperatures and burnout rates in different environments
- compare measurements against intrinsic and apparent kinetics models

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



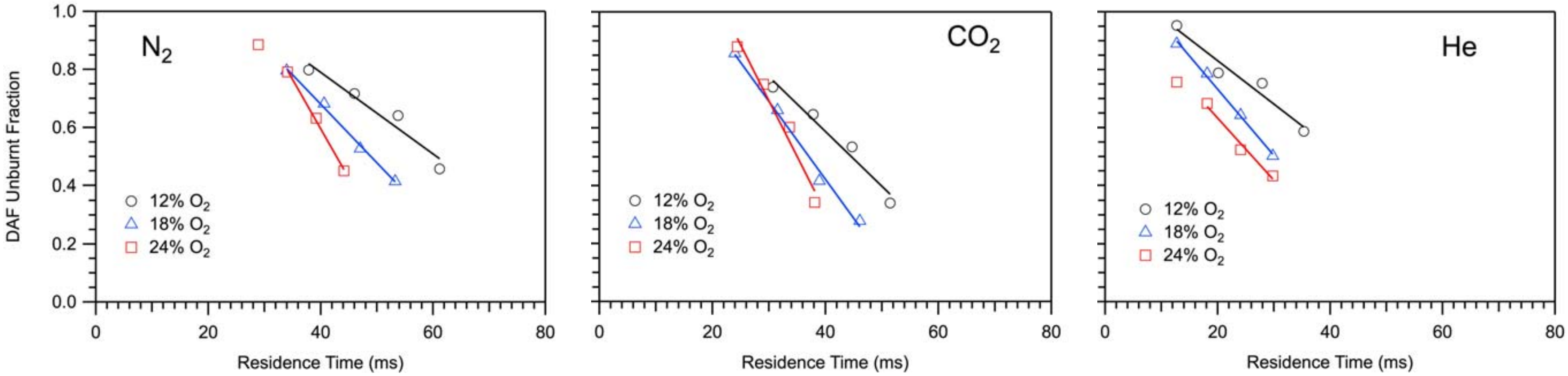
mean T_p of 100 – 150 single-particle temperatures

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

Apparent and intrinsic kinetic analyses will elucidate the effect of reactant penetration

Work in Progress:

- Apparent kinetics and intrinsic kinetics analysis will be performed in N_2 and He environments to evaluate char kinetic rates that are consistent with measured char particle temperatures
- These results will then be compared against the measured char burnout rates to evaluated suitability of the models and errors in apparent kinetic model when applied to chars burning in diluents with different diffusivity

Pressurized oxy-combustion can reduce the efficiency penalty for carbon capture

Motivation:

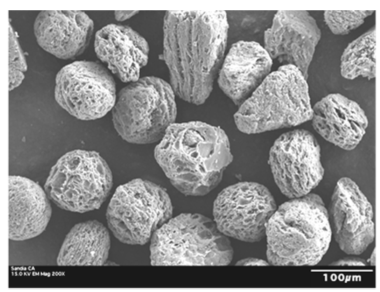
- Improved heat integration of components for pressurized oxy-combustion can improve efficiencies over atmospheric pressure oxy-combustion
- dearth of quality data and rate information at high temperatures at which this process would occur
- extrapolating rates from PTGA measurements (at 1000-1100 K) can be off significantly if activation energy is erroneous

A unique reactor is used to make kinetic measurements for pressurized oxy-combustion

Approach:

- perform experiments in the turbulent entrained flow reactor – low particle loading, isothermal conditions
- separate char formation step from char combustion/gasification, to clearly quantify rates – i.e. pre-form chars
- perform optical measurements of char particle temperatures, as well as extractive measurements of carbon conversion, to quantify rates

Pressurized entrained flow reactor

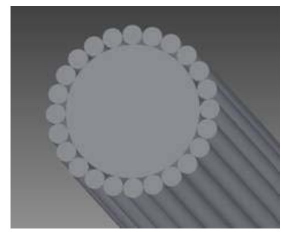


SEM of generated coal char

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

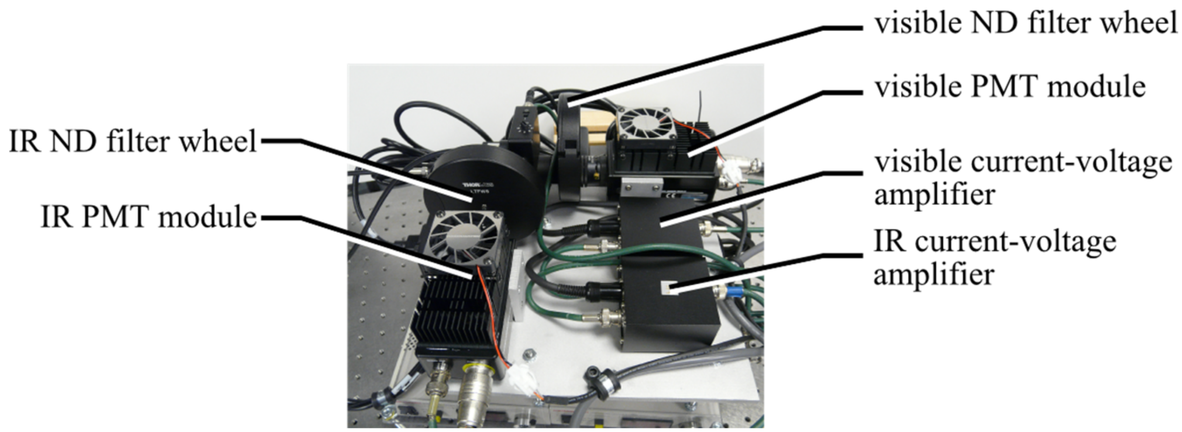
- use calibrated fiber-optic coupled probe for in-situ particle temperature measurements
- cold target limits background radiation from hot walls

cold target probe

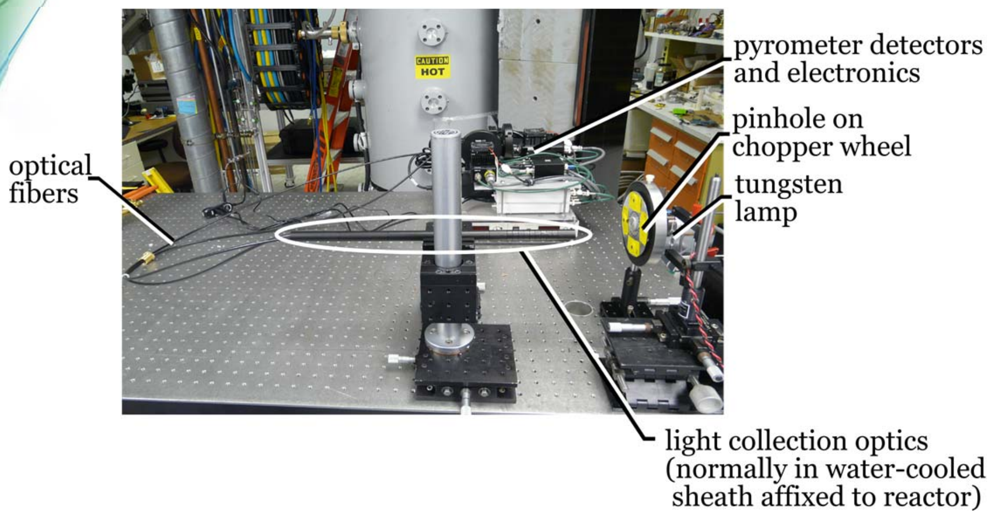


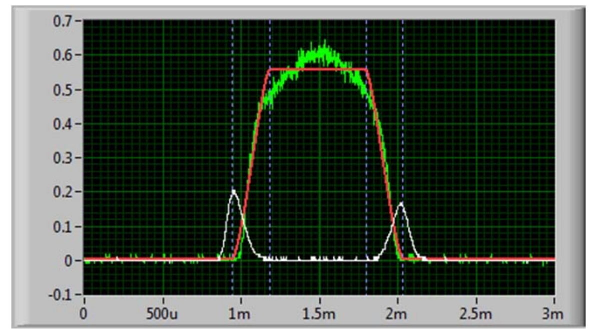
fiber bundle face

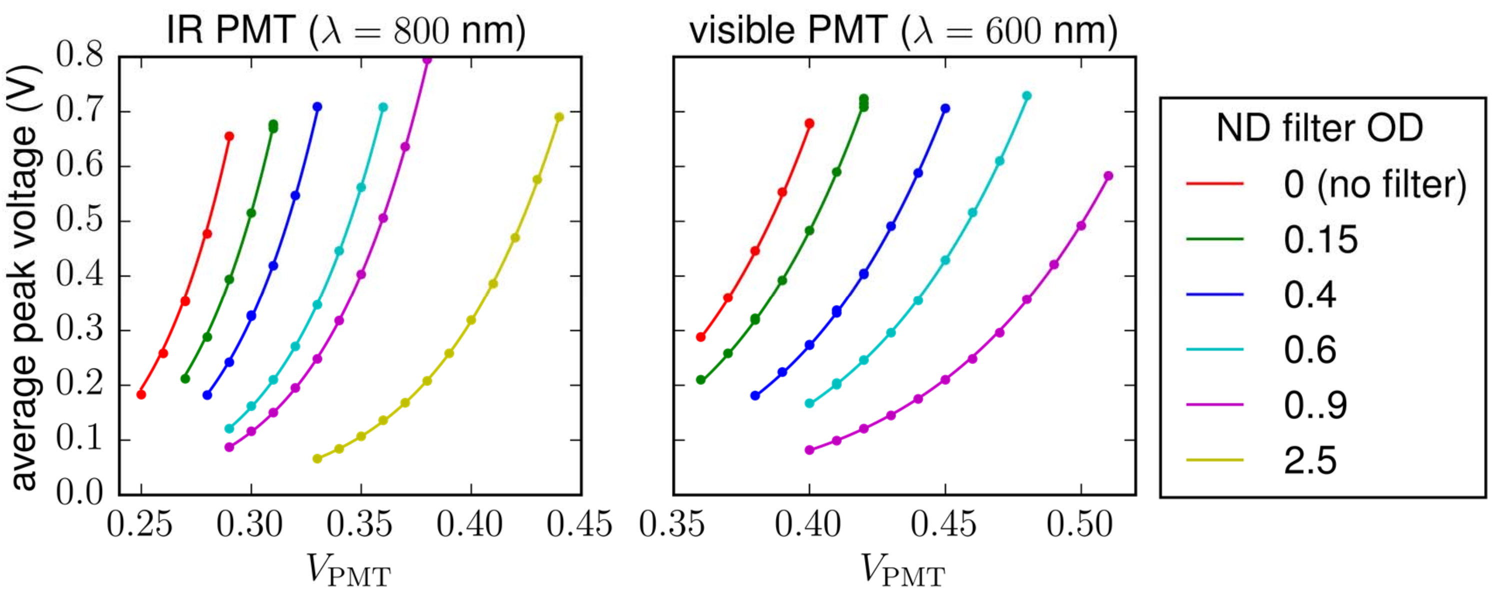
optical collection probe



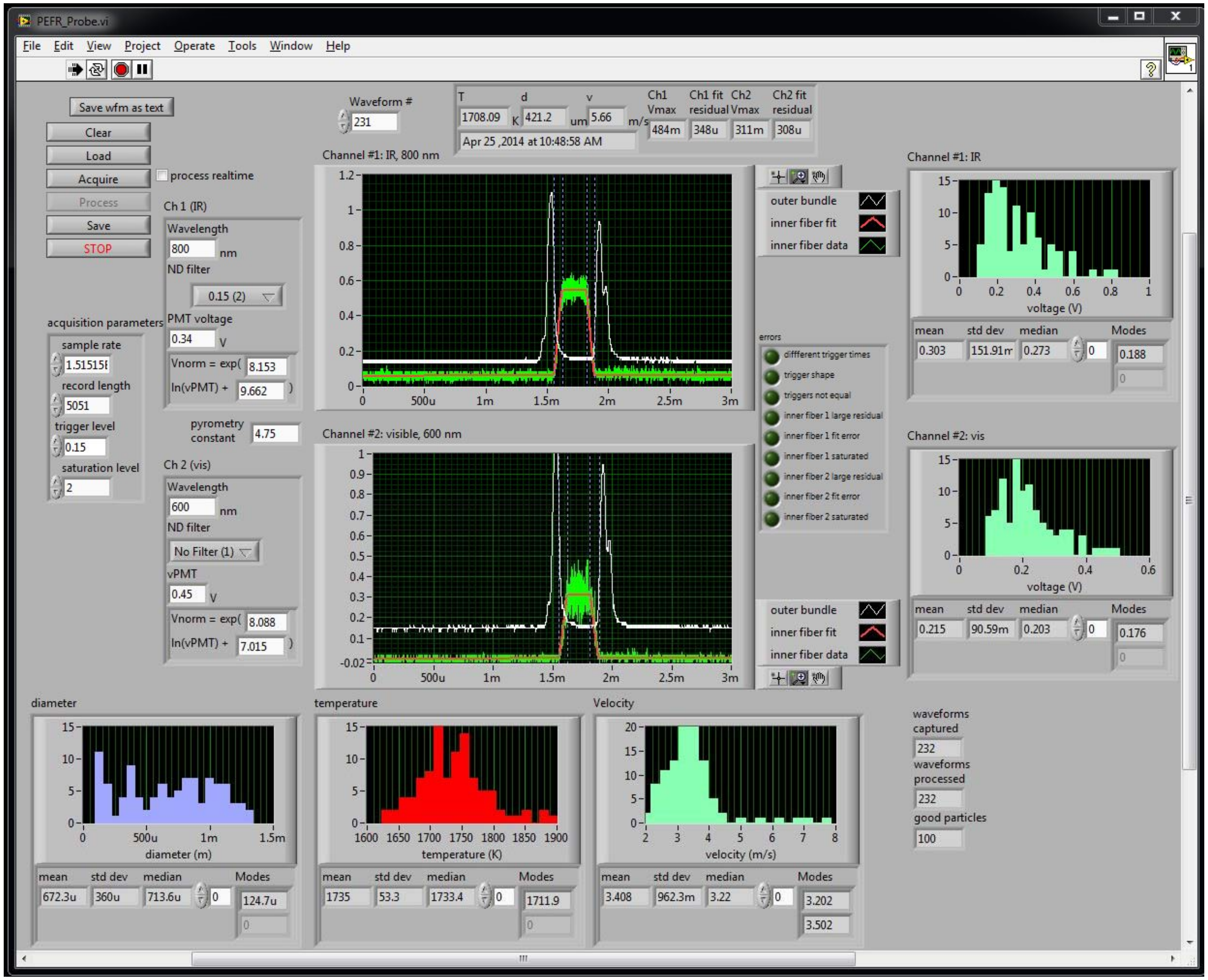
The optics were calibrated using a tungsten lamp at nearly 3000K



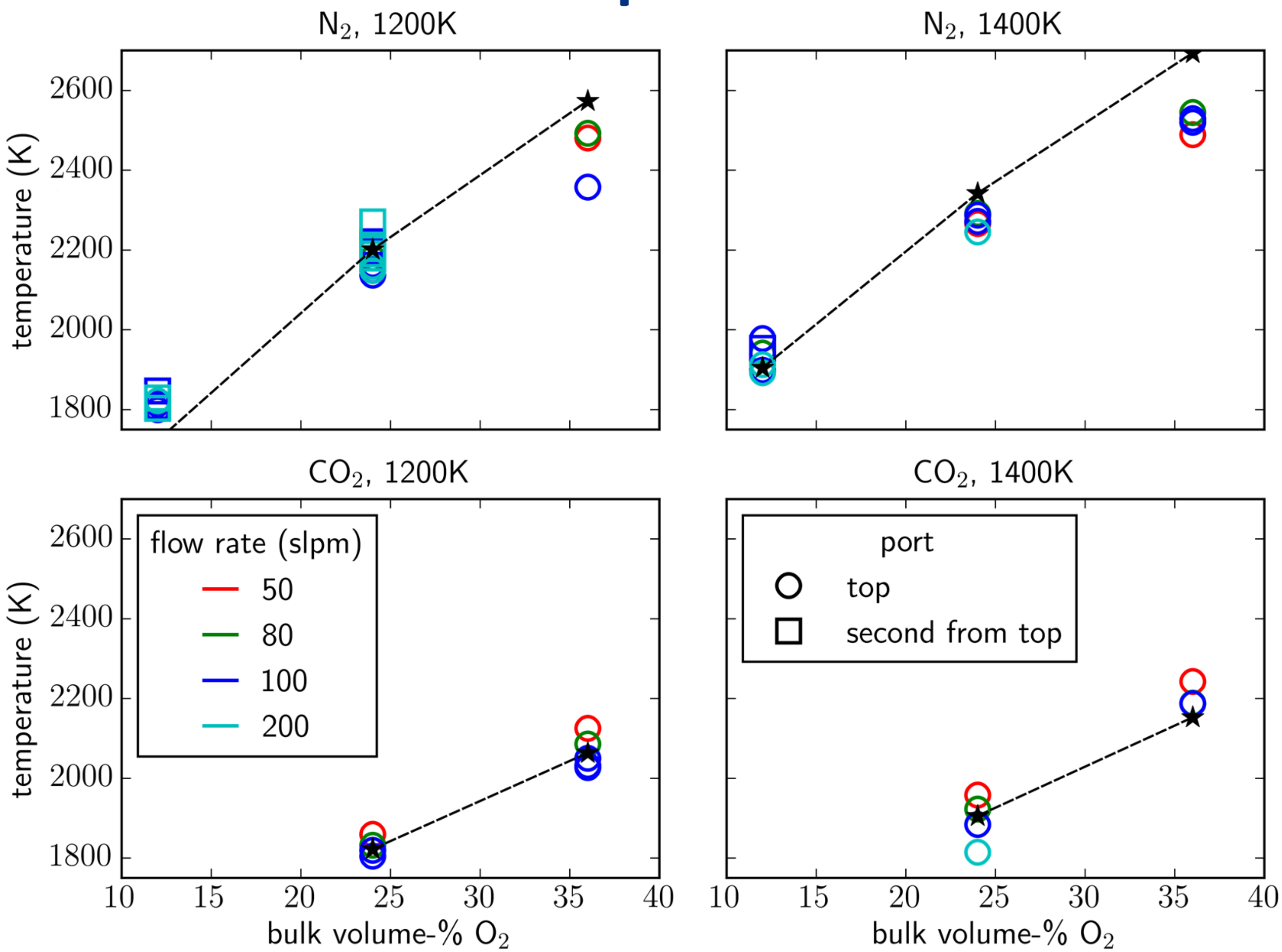




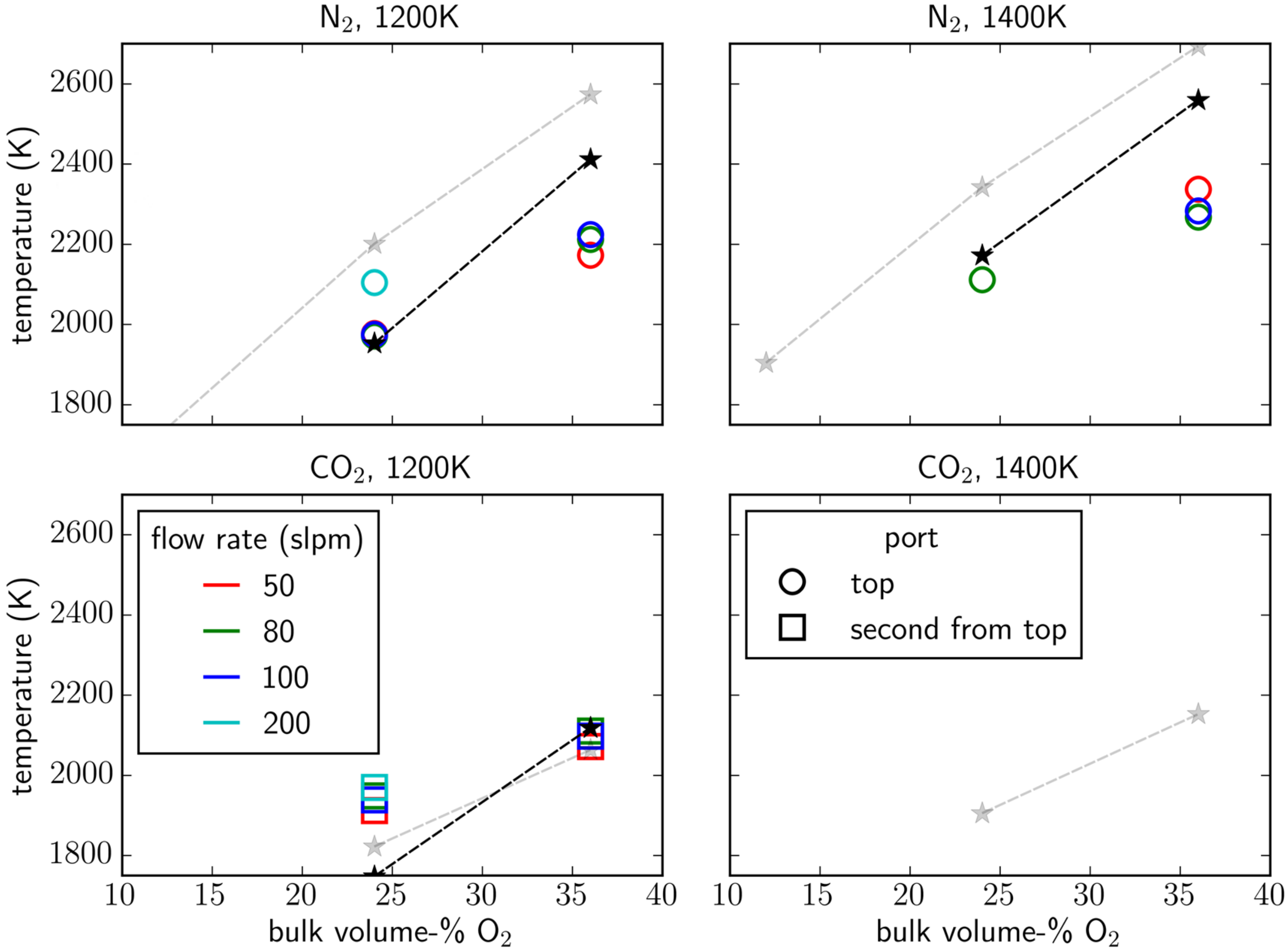
Statistically significant data is collected to capture variability in individual particle reactivity



Powder River Basin mean coal char reaction temperatures

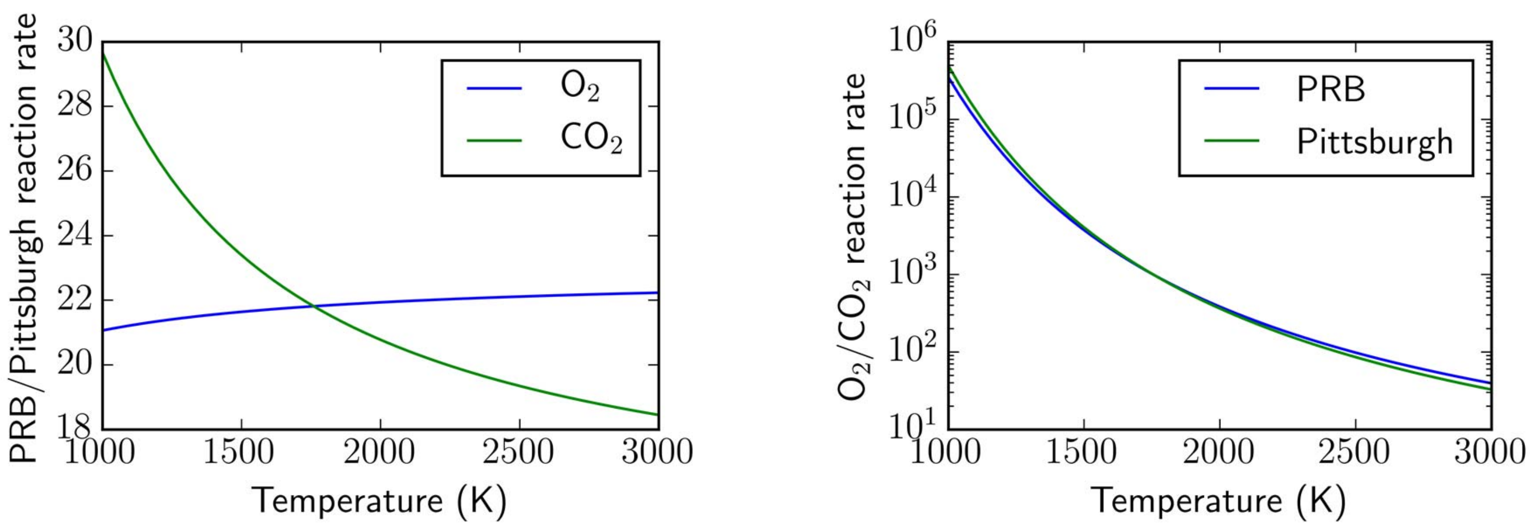


Pittsburgh seam mean coal char reaction temperatures



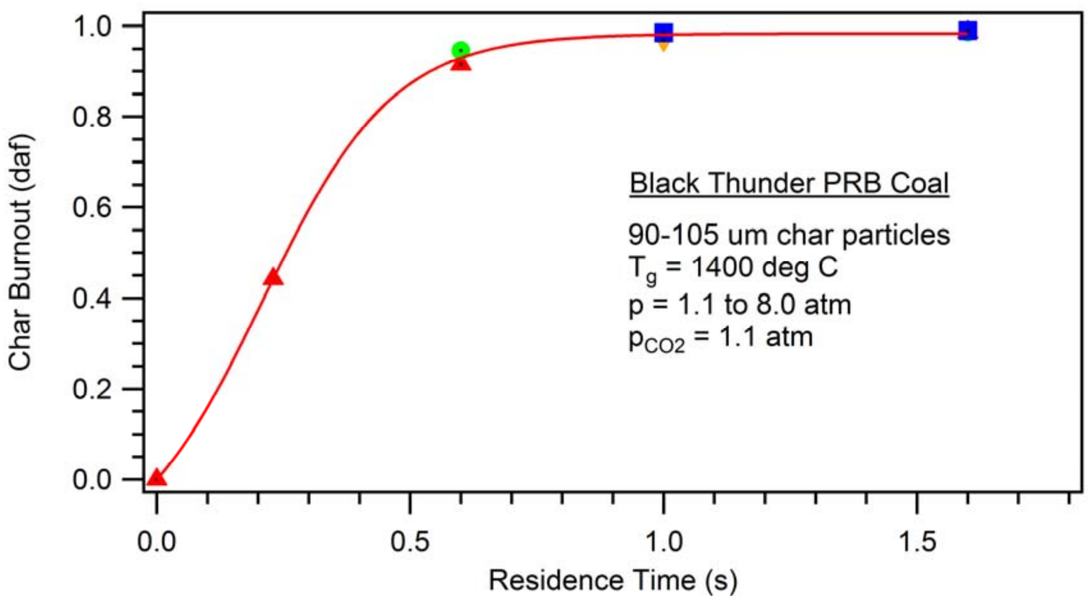
The sub-bituminous coal char is more reactive to O_2 and CO_2

Coal char	A_{O_2} (km/s)	E_{O_2} (kJ/mol)	A_{CO_2} (km/s)	E_{CO_2} (kJ/mol)
PRB	322	151	769	264
Pittsburgh	14	150	53	270



Gasification measurements in pure CO_2 can confirm oxy-combustion measured rates

- performed char gasification experiments with various CO_2 concentrations at 1400 ° C and pressures up to 8 atm (improved heating and thermal management will allow experiments up to 20 atm)



- performed char gasification experiments in atmospheric pressure, high-T (2200 K) CO_2
- New diagnostic (Rayleigh scattering) being implemented to measure gas temperatures

Summary of Recent Progress

- Char combustion temperature higher with N_2 diluent than with CO_2 or He
- Char conversion rate with N_2 diluent similar to He diluent, but increases with CO_2 diluent
- Single-film model has been applied to extract intrinsic kinetics for oxidation and CO_2 gasification for two coal chars
  - Optical pyrometry probe used to make *in-situ* temperature measurements
  - Reaction rate of PRB coal char is 20-30 times higher than Pittsburgh
  - Gasification reactions affect burning rate at high temperature (oxygen-enhanced combustion)
- CO_2 gasification kinetics of pc char has been quantified from 1 – 8 atm

Continuing and Future Work

- Rayleigh-based gas temperature measurements in atmospheric pressure reactor
  - gas temperature profile in 2200 K CO_2 environments – to complete quantification of char gasification kinetics at 1 atm in 100% CO_2
- Fit apparent and intrinsic kinetic models to N_2, He, CO_2 diluent data
  - evaluate the effect of reactant penetration
- Additional char gasification kinetic measurements in high-pressure entrained flow reactor, utilizing optical pyrometry probe
  - redesign extraction probe
  - steam gasification
  - inhibition reactions (CO, H_2)
- Oxy-fuel char combustion kinetics at elevated pressure
  - conversion measurements on collected chars
  - other rank coal chars
  - wider range of conditions
  - compare gasification rates to those in pure gasification (CO_2, H_2O) environments
- Incorporation of kinetic model and measured kinetic rates into carbonaceous chemistry for computational modeling (C3M) code

Acknowledgments

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- Funding provided through FE Crosscutting Research Program

Recent Publications

Refereed journal articles

- Y. Niu, C.R. Shaddix, "A sophisticated model to predict ash inhibition during combustion of pulverized char particles," *Proceedings of the Combustion Institute* 35 (2015) 561-569.
- M. Schiemann, M. Geier, C.R. Shaddix, N. Vorobiev, V. Scherer, "Determination of char combustion kinetics parameters: Comparison of point detector and imaging-based particle-sizing pyrometry," *Review of Scientific Instruments* 85 (2015) 075114.
- D. Kim, S. Choi, M. Geier, C.R. Shaddix, "Effect of CO_2 gasification reaction on char particle combustion in oxy-fuel conditions," *Fuel* 120 (2014) 130-140.
- C.R. Shaddix, F. Holzleithner, M. Geier, B.S. Haynes, "Numerical assessment of Tognotti determination of CO_2/CO production ratio during char oxidation," *Combustion and Flame* 160 (2013) 1827-1834.
- E.S. Hecht, C.R. Shaddix, J.S. Lighty, "Analysis of the errors associated with typical pulverized coal char combustion modeling assumptions for oxy-fuel combustion," *Combustion and Flame* 160 (2013) 1499-1509.
- M. Geier, C.R. Shaddix, F. Holzleithner, "A mechanistic char oxidation model consistent with observed CO_2/CO production ratios," *Proceedings of the Combustion Institute* 34 (2013) 2411-2418.
- E.S. Hecht, C.R. Shaddix, M. Geier, A. Molina, B.S. Haynes, "Effect of CO_2 and steam gasification reactions on the oxy-combustion of pulverized coal char," *Combustion and Flame* 159 (2012) 3437-3447.
- C.R. Shaddix, "Coal combustion, gasification, and beyond: Developing new technologies for a changing world," invited article, *Combustion and Flame* 159 (2012) 3003-3006.
- M. Geier, C.R. Shaddix, K.A. Davis, H.-S. Shim, "On the use of single-film models to describe the oxy-fuel combustion of pulverized coal char," *Applied Energy* 93 (2012) 675-679.