COMBUSTION RESEARCH FACILITY

Coal Combustion and Gasification Science

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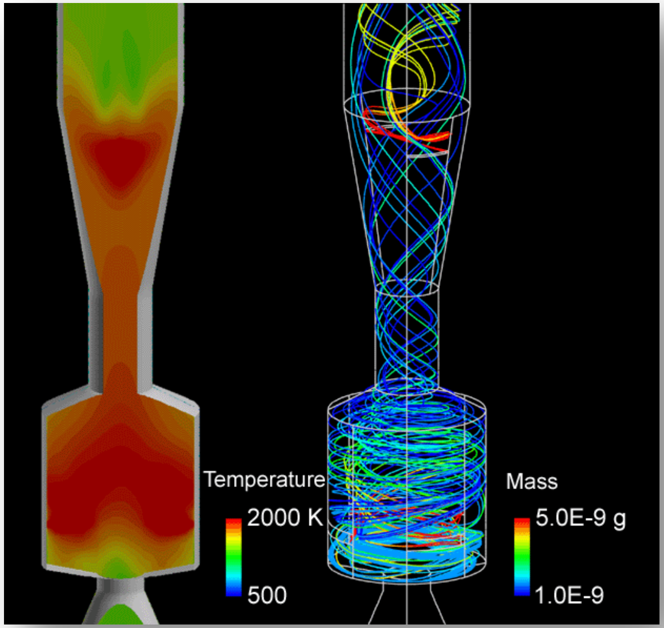
Outline

- Motivation
- Research Approach
- Recent Research Results
  - Model Evaluation for Oxy-Fuel Combustion
    - CO_2/CO production ratio
    - Single-film vs. double-film models
    - Apparent kinetics and gas diffusivity
    - Ash inhibition
  - Pressurized Gasification Kinetics
- Future Plans
- Summary

Motivation

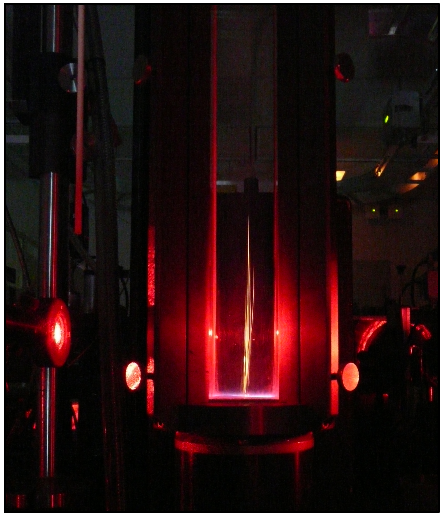
- Improvements in energy efficiency, availability, fuel flexibility, and capital effectiveness of oxy-fuel coal boilers and coal gasifiers increasingly rely on CFD modeling
- Accuracy of CFD modeling limited by
  - poor knowledge of fundamental coal conversion *rate parameters*
    - ignition delay
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



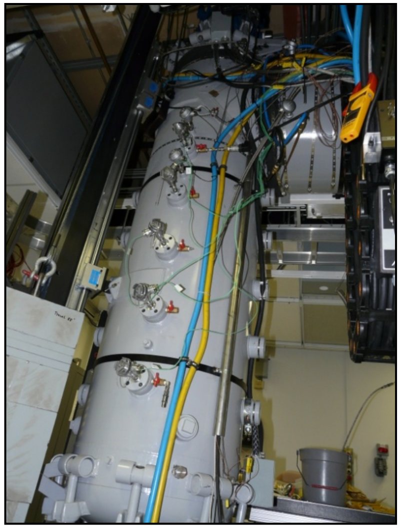
Simulation of 2-stage coal gasifier

Our Research Approach – Experimental

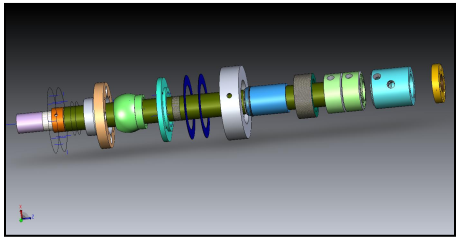
- Utilize unique experimental facilities that recreate relevant reaction conditions, while allowing for optical measurements
- Perform both optical and sampling-based diagnostic measurements to collect data on critical rate parameters
- Use well-controlled particle sizes and particle feed rates



1-atm entrained flow reactor



pressurized entrained flow reactor



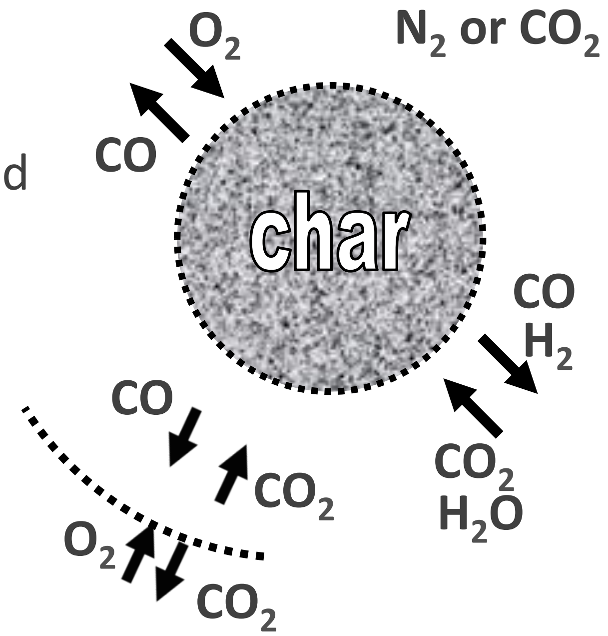
exploded diagram of optical probe

Our Research Approach – Modeling

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 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



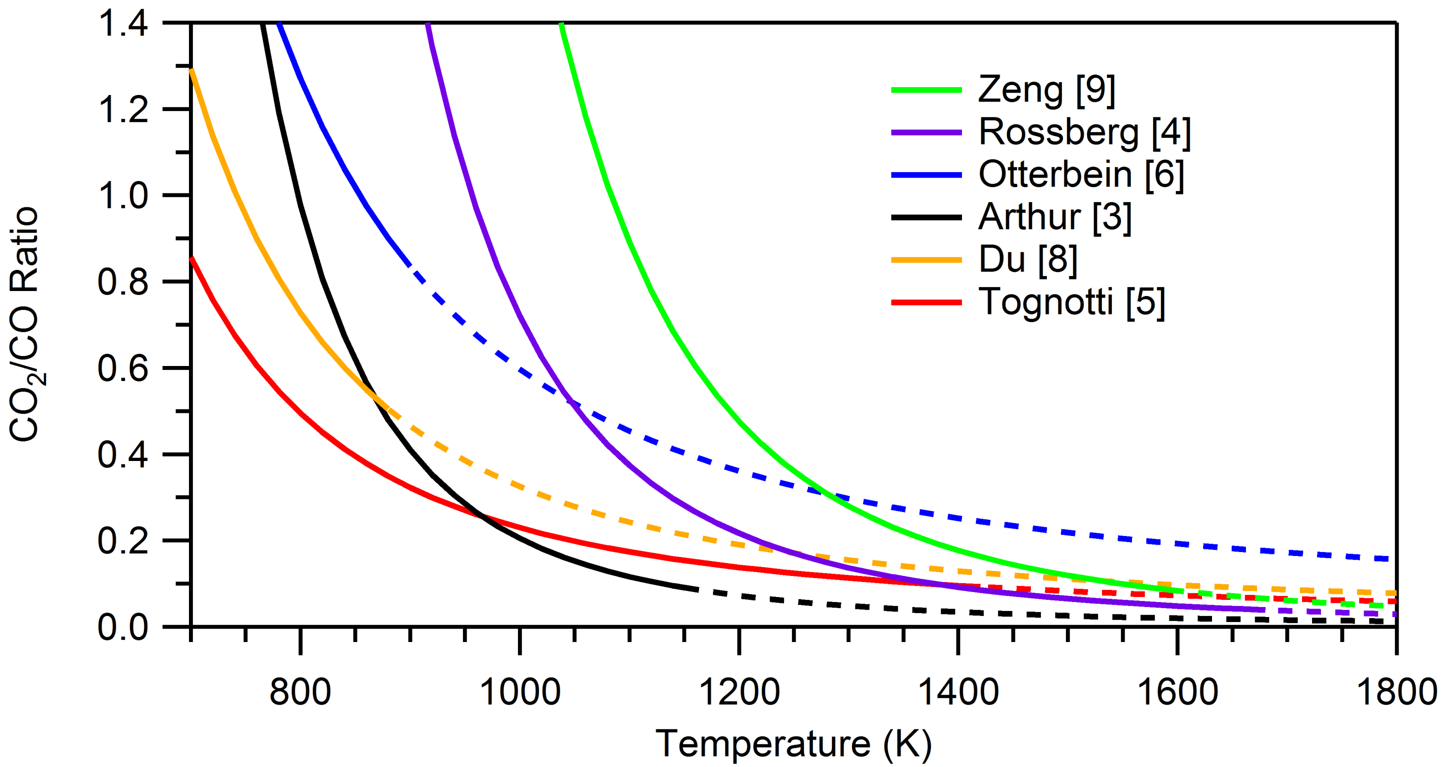
Recent Results – CO_2/CO Production Ratio

Motivation:

- reaction of O_2 with C produces mostly CO_2 at low temperatures and CO at high temperatures
  - Important effect on char combustion rates due to difference in heat release (394 kJ/mol-C_s vs 110 kJ/mol-C_s) and difference in O_2 consumption

Recent Results – CO_2/CO Production Ratio

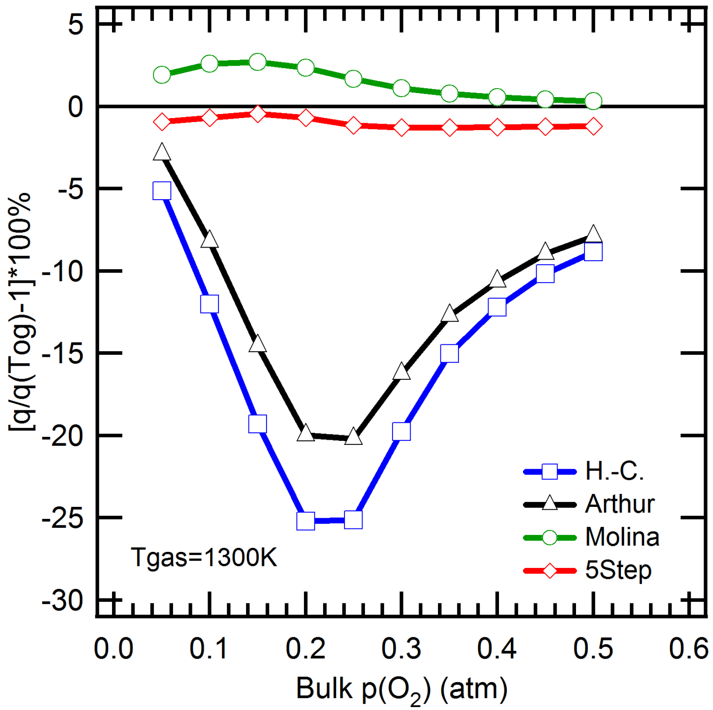
Published studies of CO_2/CO production ratio



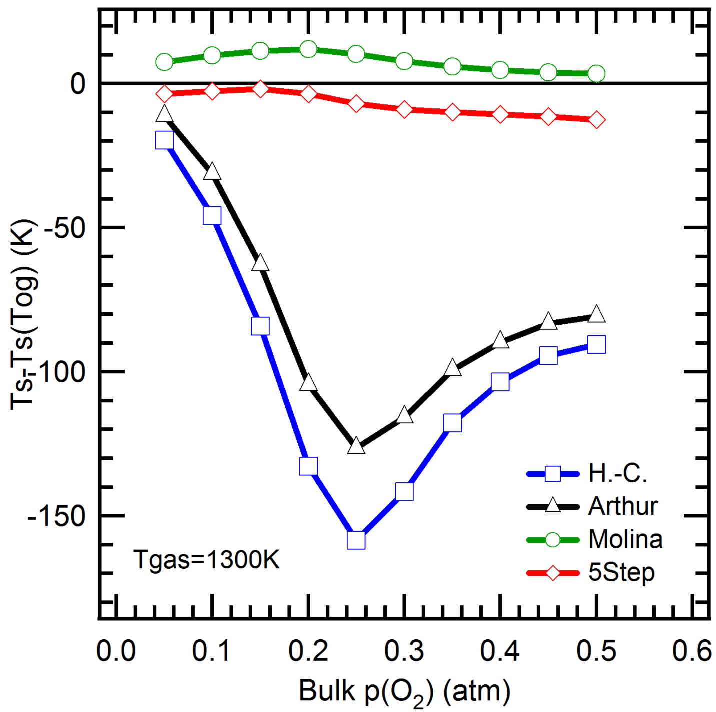
Recent Results – CO_2/CO Production Ratio

Assessment of importance of assumed CO_2/CO production ratio

Error in burning rate predictions*



Error in char particle T predictions*



* relative to Tognotti correlation

-- calculations based on measured kinetics for 50 um subbituminous (N. Antelope) char particles

Recent Results – CO_2/CO Production Ratio

Motivation (cont'd):

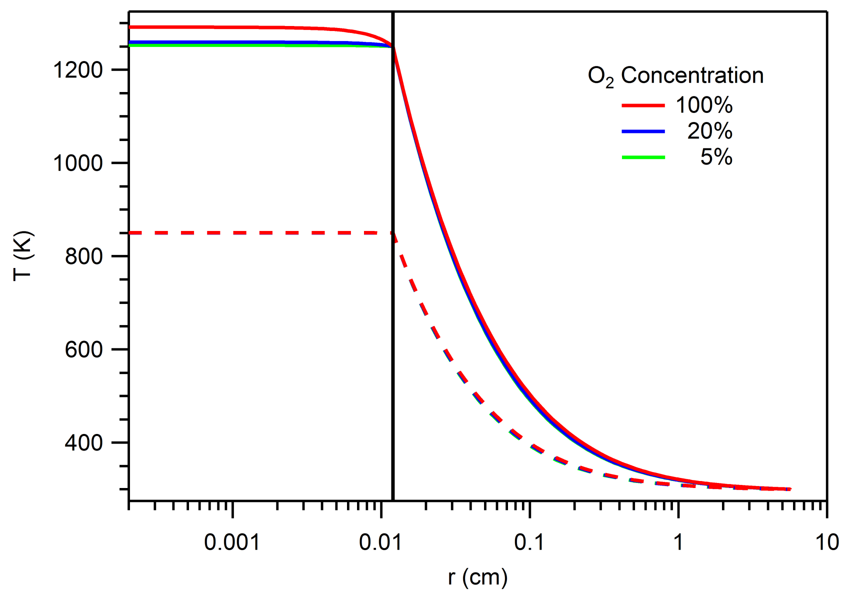
- most commonly employed relationships in CFD are Arrhenius expressions from Arthur (with E_a = -52 kJ/mol) and Tognotti et al. (E_a = -26 kJ/mol + weak power law dependence on surface O_2)
  - dependence on O_2 is expected

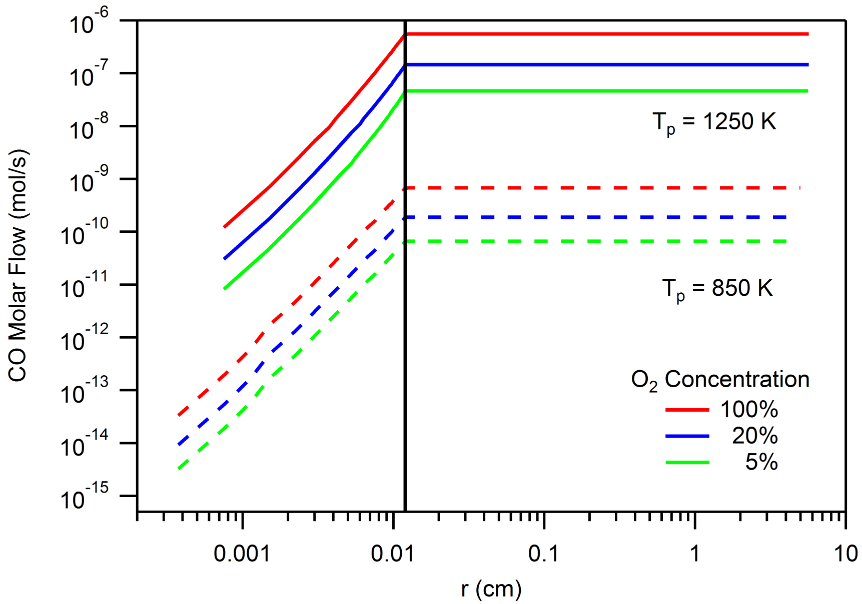
$$C_b + C(O) + O_2 \xrightarrow{k_3} CO_2 + C(O)$$ *O_2-assisted desorption*

- Tognotti levitated individual spherocarb particles (≈ 200 μm diameter) at room temperature, heated them with a laser, measured particle T with pyrometry, mass loss by virtue of balance voltage, and CO_2/CO ratio in combustion products
- Tognotti assumed Zone I combustion conditions (uniform particle T, no CO conversion in particle or in boundary layer, negligible O_2 gradient)

Recent Results – CO_2/CO Production Ratio

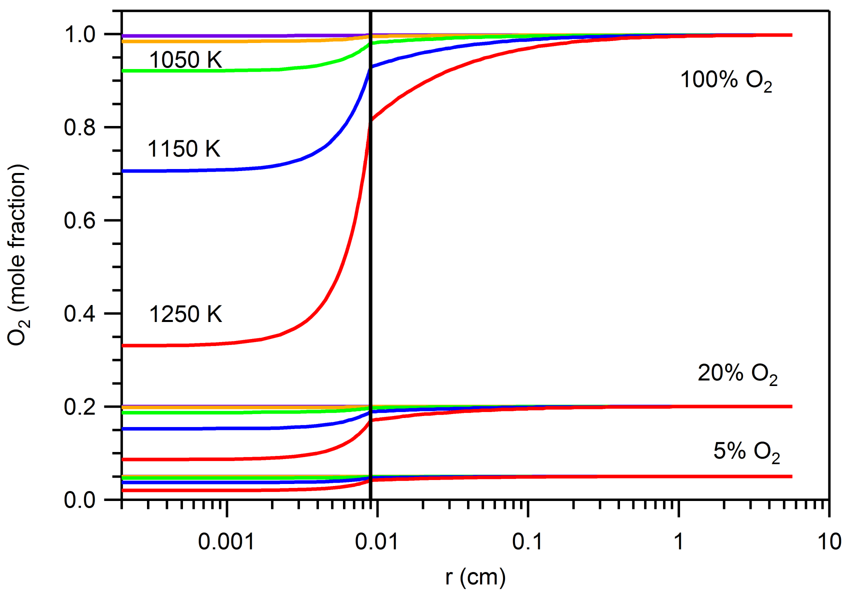
- Approach: use SKIPPY to assess Tognotti experiments
- Results:
  - Particle temperature is uniform (for experiments up to 1250 K)
  - Negligible CO consumption in the boundary layer (for T ≤ 1250 K) nor within the particle

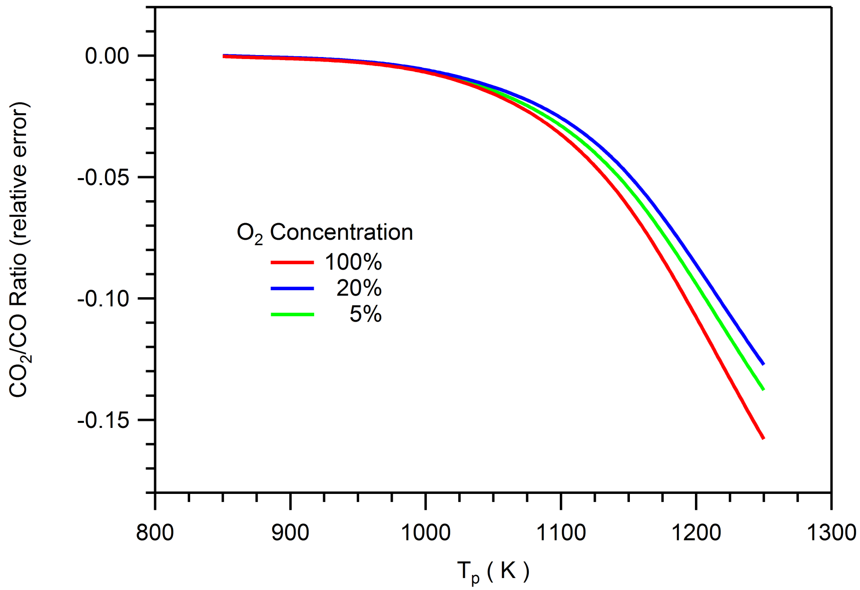




Recent Results – CO_2/CO Production Ratio

- Results (cont'd):
  - Diffusional resistance becomes significant for T > 1050 K
  - Because of weak sensitivity of CO_2/CO production ratio to [O_2], Zone I interpretation of Tognotti measurements is valid to 1150 K



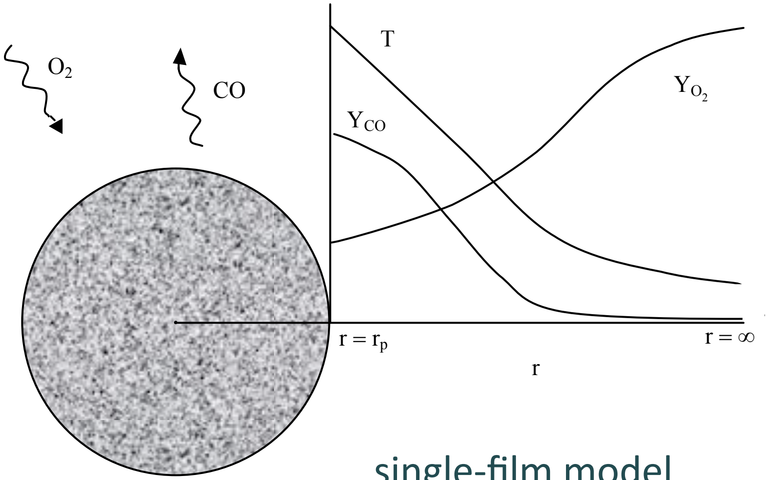


Results support use of Tognotti expression: $CO_2/CO = 0.02\,p_{O_{2,s}}^{0.21}\exp\left(3070/T_p\right)$

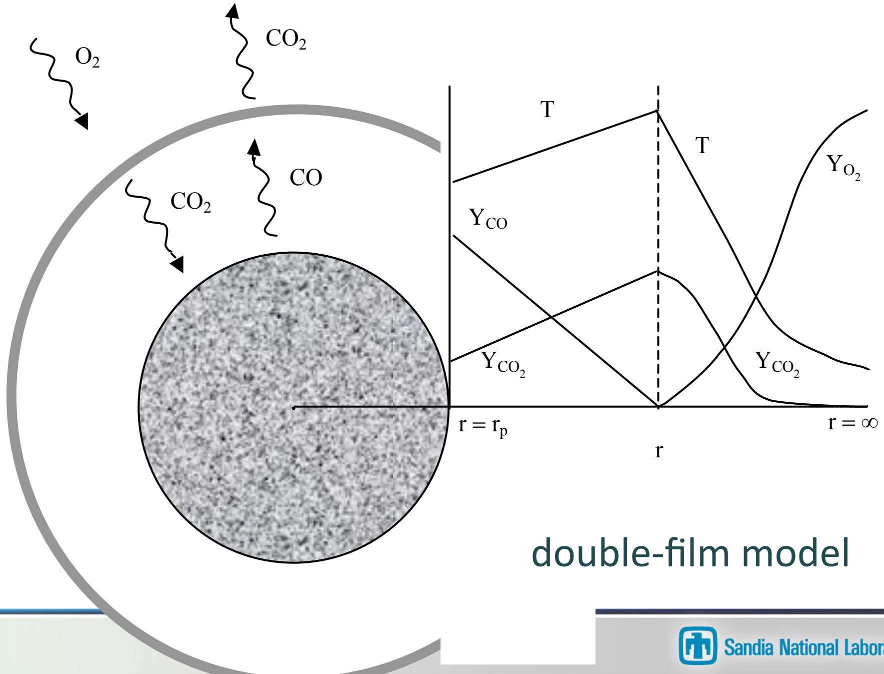
Recent Results – Single-Film and Double-Film Models

Motivation:

- most CFD modelers use so-called 'single-film' apparent kinetics model of char combustion, whereas others use 'double-film' model
  - both neglect effect of different extents of reactant penetration
  - single-film model neglects CO conversion in particle boundary layer
  - double-film model assumes all of the CO emitted from the particle is consumed at a flamefront in the boundary layer



single-film model



double-film model

Recent Results – Single-Film and Double-Film Models

Motivation (cont'd):

- our previous results demonstrate that CO is partially converted in the boundary layer (continuous film) for high particle/gas temperatures, e.g. during oxygen-enriched combustion
- our previous results demonstrate char gasification reactions with CO_2 and steam are important and lead to partial reactant penetration during oxy-fuel combustion
- unclear which of the two models is most accurate under oxy-fuel combustion conditions

Recent Results – Single-Film and Double-Film Models

Approaction:

- Use SKIPPY to assess predictions of single-film and double-film models
  - employ combination of oxidation and gasification reactions
  - analyze range of particle sizes burning in both N_2 and CO_2 diluent environments with 14 vol-% H_2O and 12 – 60 vol-% O_2
  - use particle reactivity corresponding to a PRB subbituminous coal char

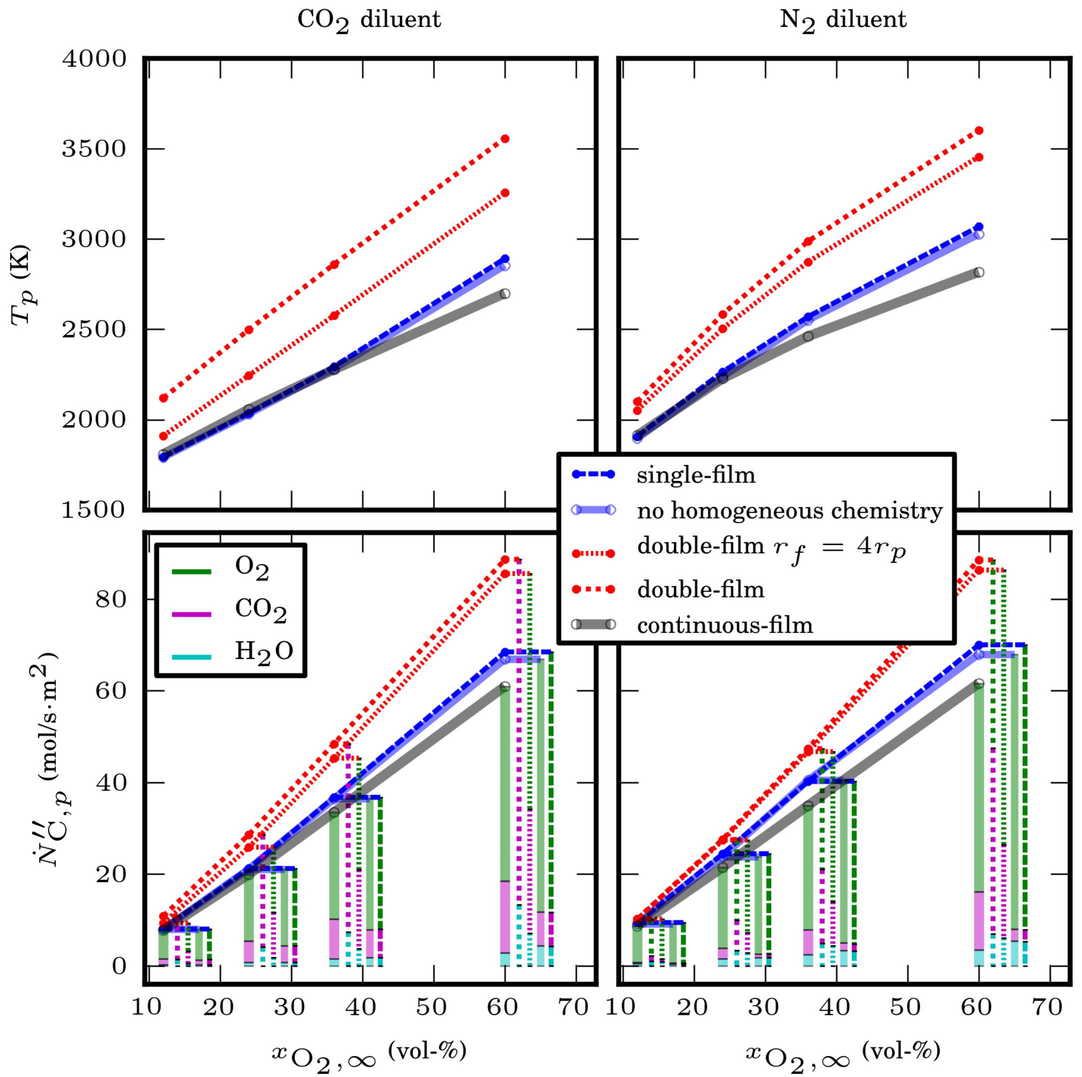
Recent Results – Single-Film and Double-Film Models

Results:

- Over evaluated range of d_p (60 – 135 μm), single-film model is always superior to double-film model, no matter where the flame sheet is assumed to occur in the boundary layer
  - heat release from CO flame in double-film model always leads to overpredicted T_p and carbon burning rate
- CO_2 and steam gasification reactions must be included to give accurate prediction of T_p and, to a lesser extent, carbon burning rate (in agreement with our previous analyses)
- Stefan flow must be included to give accurate predictions for high reaction rate conditions (e.g. oxygen-enriched char combustion)

Recent Results – Single-Film and Double-Film Models

Results:



Recent Results – Single-Film and Double-Film Models

Conclusions:

- Use of the single-film model appears to be generally warranted
- For broad applicability in oxy-fuel combustion environments, gasification reactions and Stefan flow should be included

Recent Results – Apparent Kinetics and Gas Diffusivity

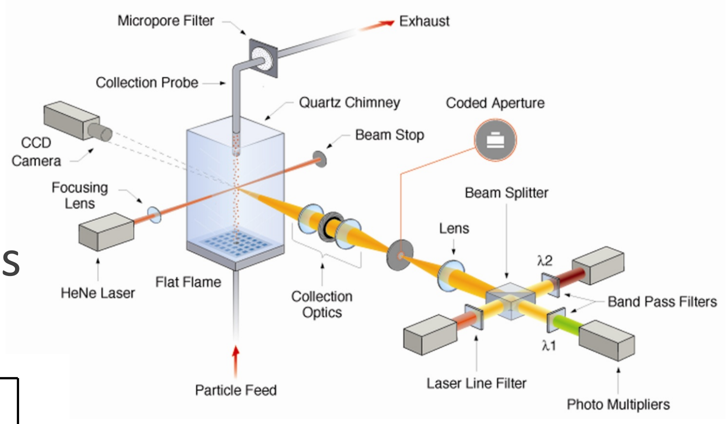
Motivation:

- CFD modelers almost always use apparent Arrhenius kinetics model of char combustion, neglecting 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

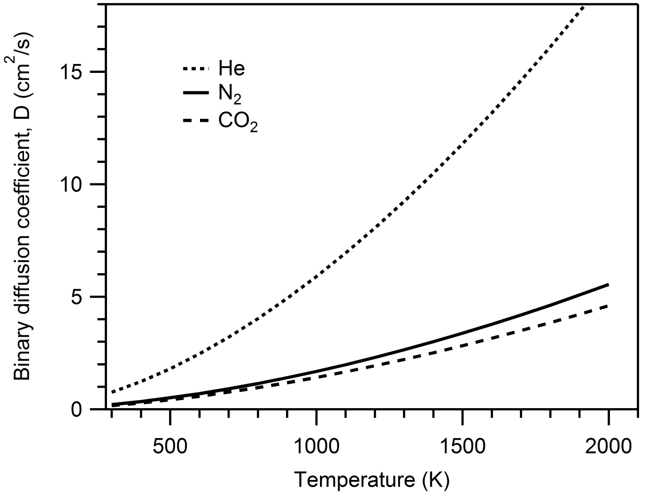
Recent Results – Apparent Kinetics and Gas Diffusivity

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



Diffusivity of O_2 in Diluent Gases



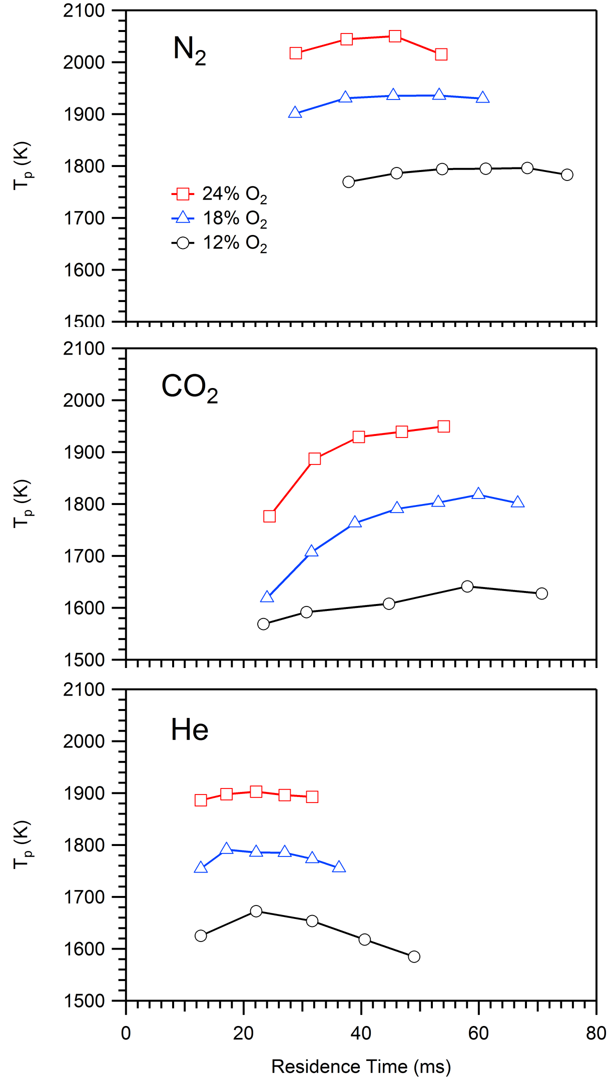
$D_{O_2\text{-}He} \approx 3.5\ D_{O_2\text{-}N_2}$

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

Recent Results – Apparent Kinetics and Gas Diffusivity

Results:

mean T_p of 100 – 150 single-particle data points



Particles burn 100 – 150 K cooler in CO_2 than in N_2 (as seen previously)

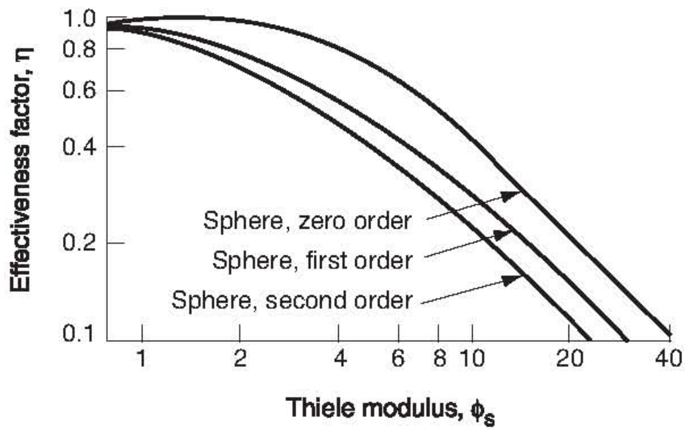
Particles ignite much faster in He, but burn cooler (relative to N_2)

$\lambda_{O_2\text{-}He} \approx 5\ \lambda_{O_2\text{-}N_2}$

Recent Results – Apparent Kinetics and Gas Diffusivity

Results:

- preliminary application of apparent kinetics model to the data suggests > 2X greater reactivity in He
- from catalyst theory, greatest variation in effectiveness factor (extent of char particle participating in reaction) with thiele modulus is for high modulus, with a slope of $\eta \sim 1/\phi_n$, so maximum difference in apparent rate one would expect for He vs. N_2 would be a factor of 1.9 (= sqrt(3.5))



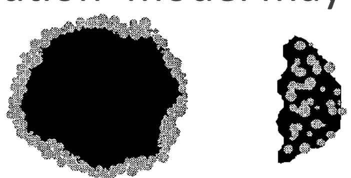
- extension to CO_2 vs N_2 suggests maximum apparent kinetics rate decrease of 11%, for same actual intrinsic kinetic rate

Recent Results – Ash Inhibition of Char Combustion

Motivation:

- final burnout of char always occurs with carbon embedded in ash
- in some parts of the world (e.g. India and Brazil), coals with high ash content are increasingly being mined and used
- ash inhibition of pulverized coal combustion has always been modeled (when it has been modeled) as an ash film effect, despite little evidence that ash films are commonly formed
- our previous experimental measurements have suggested mineral components exposed at pore surface can diffuse back into char matrix (Lunden et al., PCI 27:1695-1702, 1998)
  - suggests 'ash dilution' model may be appropriate

ash film?



(a) (b)

or ash dilution?

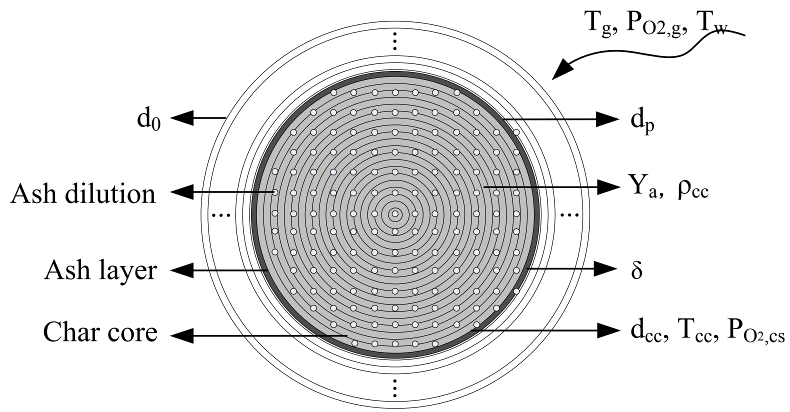
- we previously showed that ash dilution will result in low apparent reaction order (Murphy and Shaddix, CNF 157:535-539, 2010)

Recent Results – Ash Inhibition of Char Combustion

Approach:

- develop robust transient, intrinsic kinetics model of ash inhibition that can treat ash film effect as well as ash dilution, and which can assign a user-specified fraction of liberated ash to either effect
- compare model predictions against experimental measurements of char combustion temperatures and C burnout over range of O_2 concentrations (all previous ash film models only compared against burnout data, and for small variation in O_2)

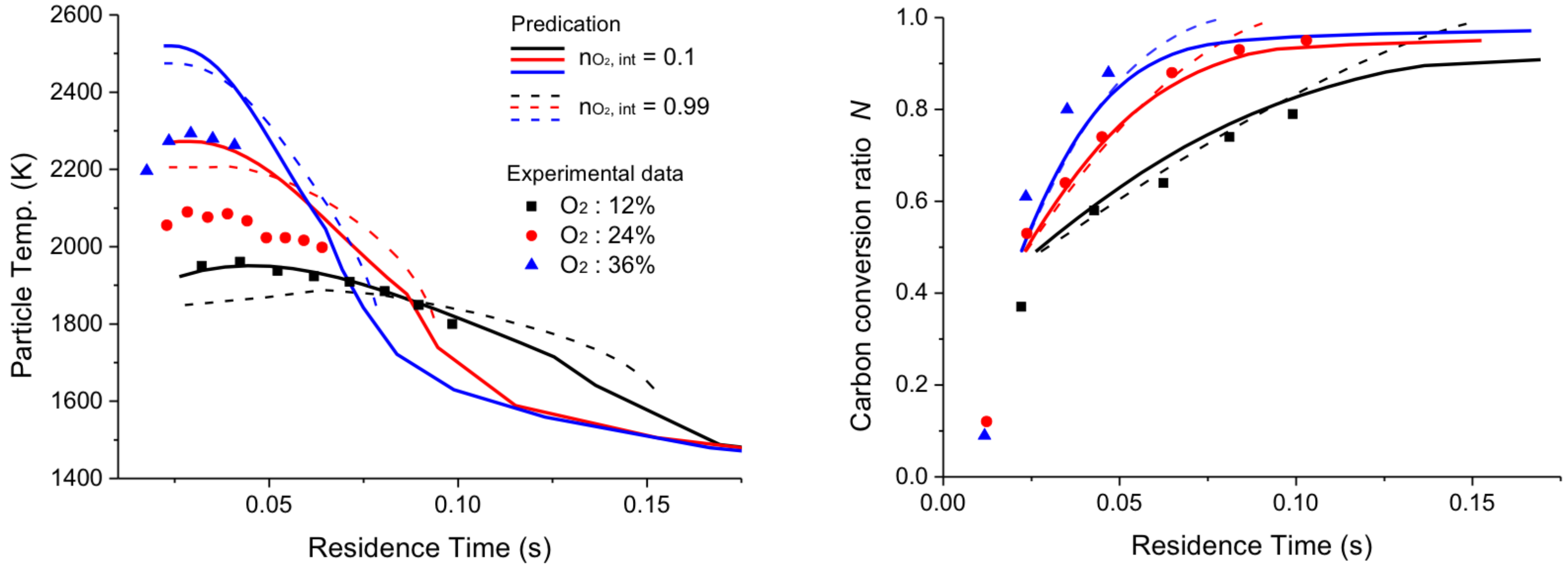
schematic of ash inhibition model



presence of ash reduces internal diffusivity and available surface area, as well as external diffusion to the char particle

Recent Results – Ash Inhibition of Char Combustion

Results (modeling char oxidation only):



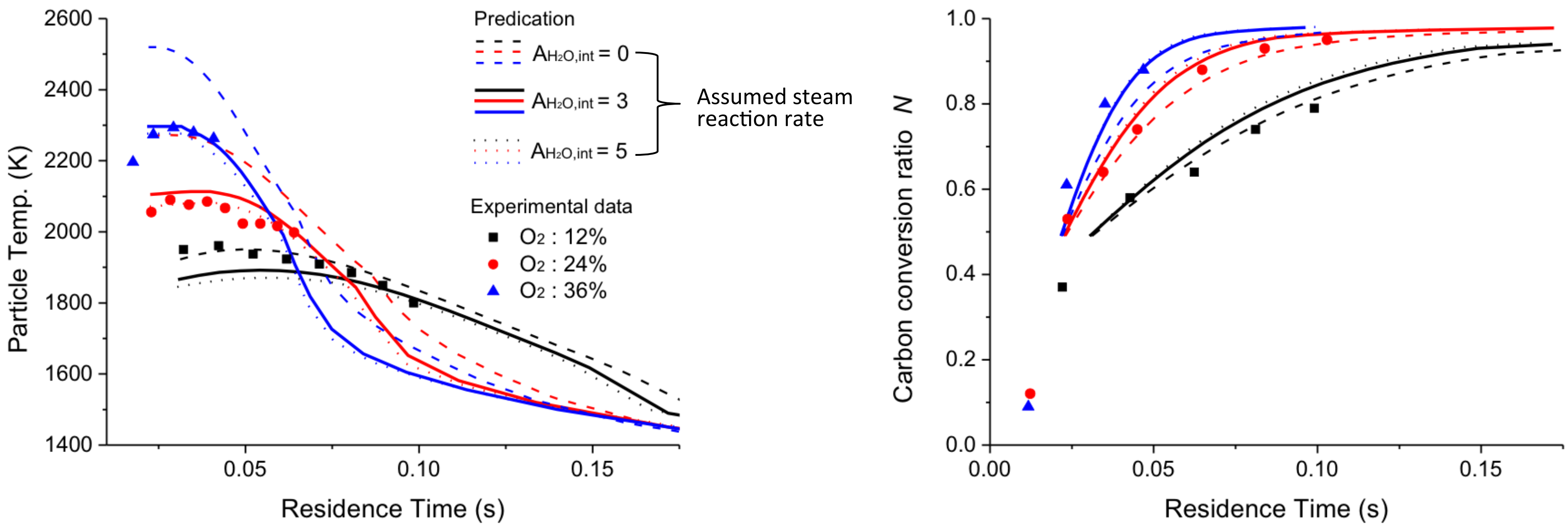
– predicted char combustion temperatures increase too rapidly as p_{O2} increases

– assumed intrinsic reaction order has minor influence on trends

– burnout predictions are quite accurate

Recent Results – Ash Inhibition of Char Combustion

Results (modeling char oxidation + steam gasification):

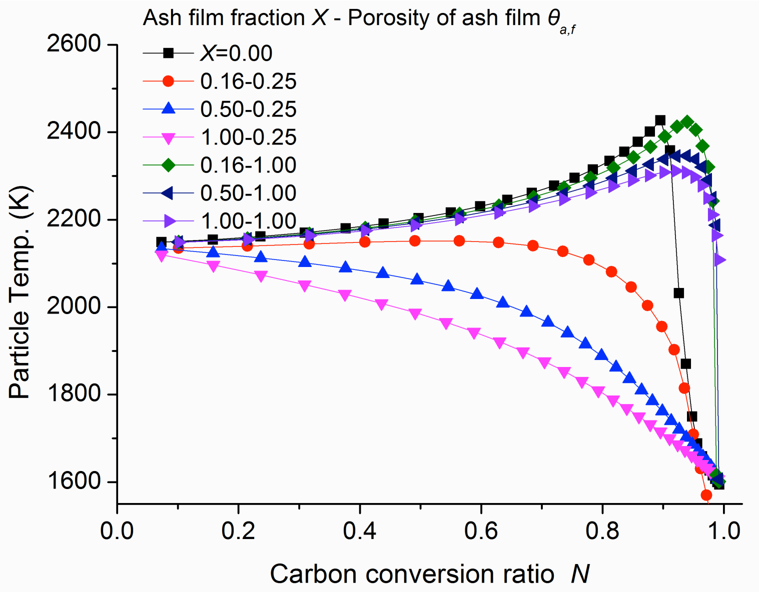


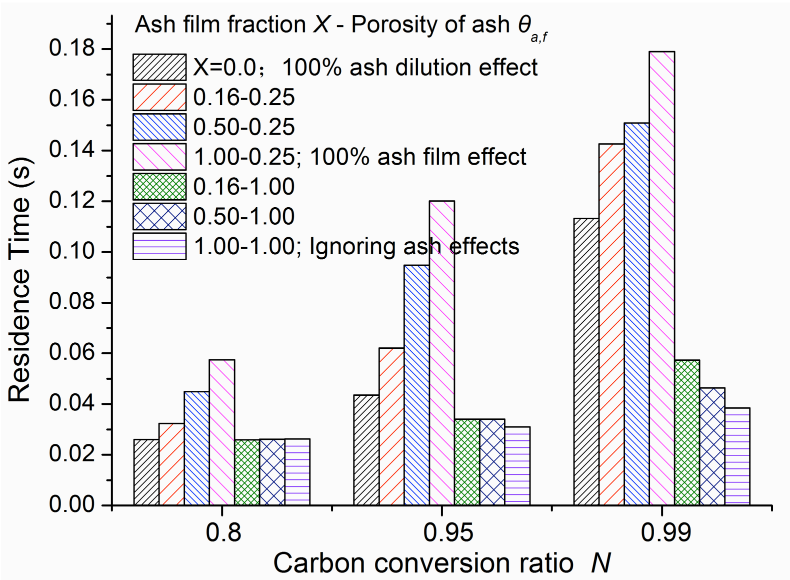
– inclusion of steam gasification reaction improves predicted char combustion temperatures (consistent with our previous findings for oxy-fuel combustion)

– burnout predictions are still accurate – inclusion of gasification rate slightly increases burnout

Recent Results – Ash Inhibition of Char Combustion

Results (ash film vs. ash dilution effects):





- ash film cools particle throughout char conversion, resulting in slower burnout
- ash dilution effect is primarily manifested at large extents of burnout
- char kinetic reactor data are *inconsistent* with model results assuming dominant fraction of liberated ash contributes to external ash film

Recent Results – Pressurized Gasification Kinetics

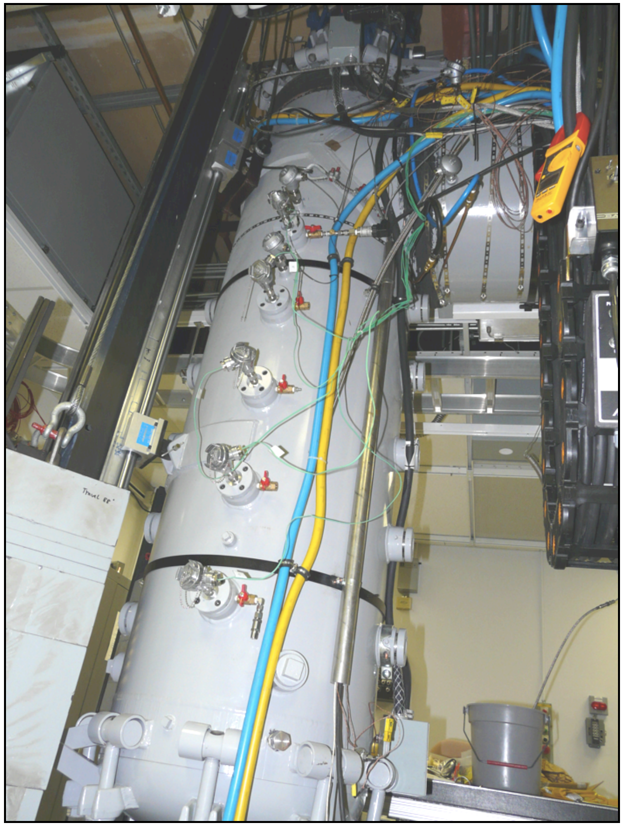
Motivation:

- carbon conversion is inherently a limiting factor in gasifier design and operation – is closely linked to minimum operating T of gasifier and to refractory wear
- dearth of quality data and rate information at high temperatures at which gasifiers operate
- high activation energy of char gasification means extrapolating rates from TGA measurements (at 1000-1100 K) gives erroneous results
- gasification kinetics are complicated at pressure, because of action of reverse reactions involving gasification products (CO and H_2)

Recent Results – Pressurized Gasification Kinetics

Approach:

- perform experiments in specially designed, turbulent entrained flow reactor – low particle loading, isothermal conditions
- separate char formation step from char 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
- build-up kinetic knowledge sequentially: measure char gasification in CO_2 only, and in H_2O only, then in mixtures of CO_2 and H_2O, then add in H_2 and CO

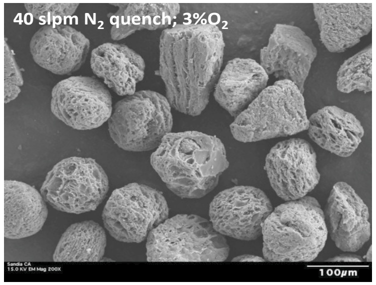


Pressurized entrained flow reactor

Recent Results – Pressurized Gasification Kinetics

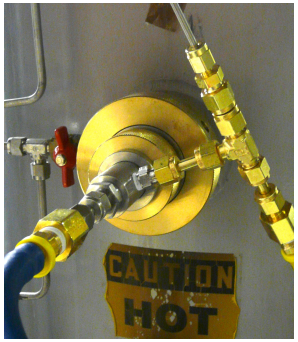
Results:

- developed procedure for generating high heating rate char particles – 1200 °C, 250 ms
- designed, fabricated, and calibrated fiber-optic probe for in situ particle T measurements

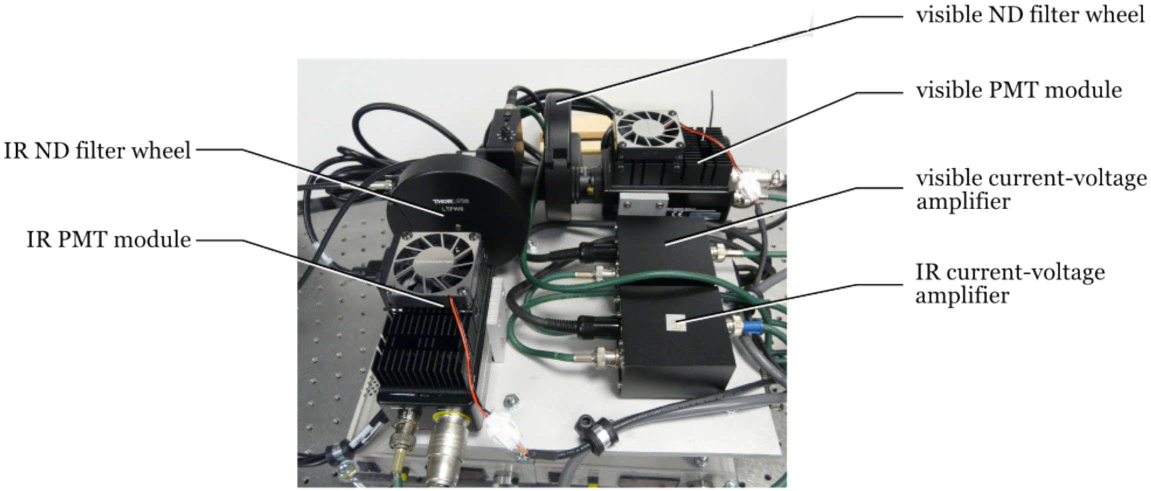


SEM of generated coal char

cold target probe



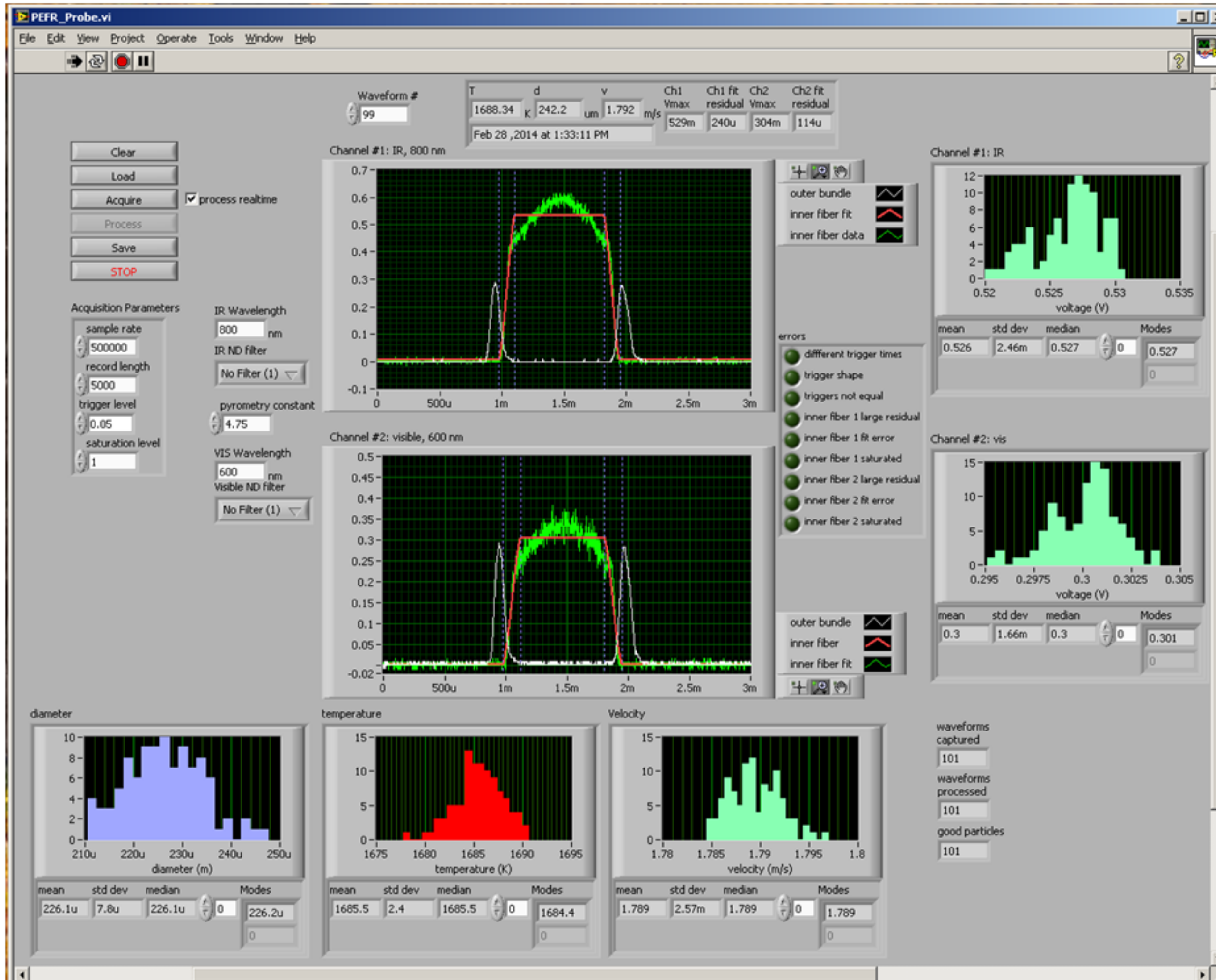
optical collection probe



Recent Results – Pressurized Gasification Kinetics

Results:

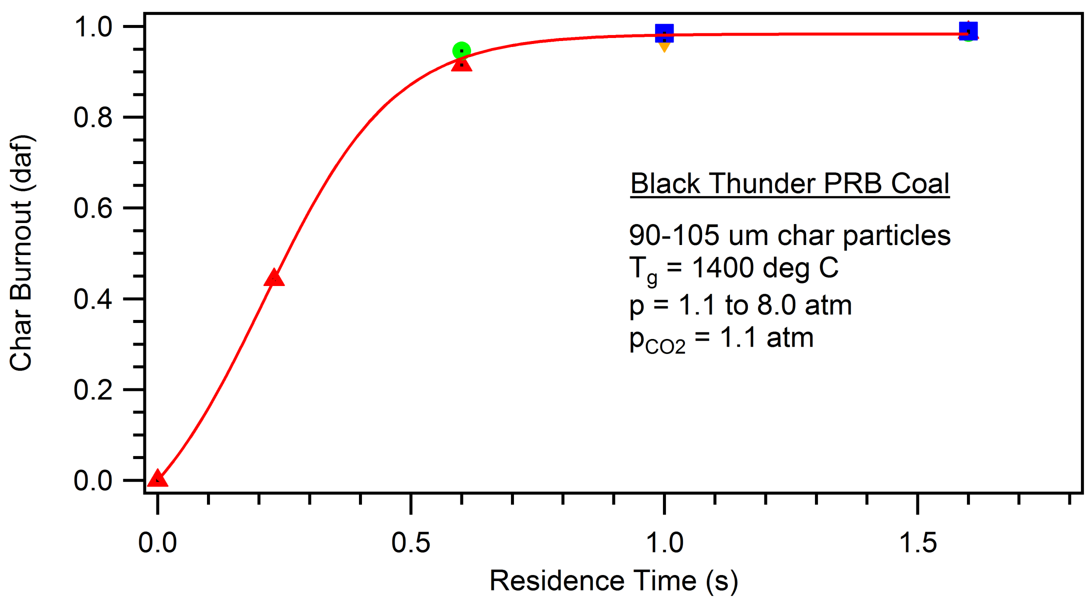
Labview display of optical probe calibration data



Recent Results – Pressurized Gasification Kinetics

Results:

- 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)



Measured char burnout for partial pressure of CO_2 of 1.1 atm, over total pressure range of 1 – 8 atm

Continuing and Future Work

- Measurement of gas temperature profile in 2200 K CO_2 environments – to complete quantification of char gasification kinetics at 1 atm
- Complete analysis of apparent and intrinsic kinetics in 'He study'
- Additional char gasification kinetic measurements in high-p entrained flow reactor, utilizing new optical pyrometry probe
- Oxy-fuel char combustion kinetics at elevated p

Summary of Recent Progress

- Tognotti expression for CO_2/CO production at char surface has been numerically justified, based on Tognotti data (for $T < 1150$ K)
- The single-film char combustion model, when accounting for Stefan flow and combined oxidation/gasification kinetics, has been shown to give reasonably accurate predictions for a wide range of oxy-fuel combustion environments
- Lower diffusivity of O_2 in CO_2 has been shown to result in lower apparent kinetic rates (by up to 11%)
- Ash inhibition of char burnout has been shown to *not* be accurately modeled as due to ash film formation, but to a mix of ash film and ash dilution effects
- A new optical probe has been developed for application to pressurized gasification and oxy-fuel combustion environments
- CO_2 gasification kinetics of pc char has been quantified from 1 – 8 atm

Acknowledgments

- Research collaborators Manfred Geier (postdoc), Cristina Gonzalo-Tirado (visitor), Yanqing Niu (visitor), and Brian Haynes
- Funding provided through FE Crosscutting Research Program

Recent Publications

Refereed journal articles

- 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," submitted to *Review of Scientific Instruments*.
- Y. Niu, C.R. Shaddix, "A sophisticated model to predict ash inhibition during combustion of pulverized char particles," accepted for publication in *Proceedings of the Combustion Institute*.
- 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.