Coal Combustion and Gasification Science

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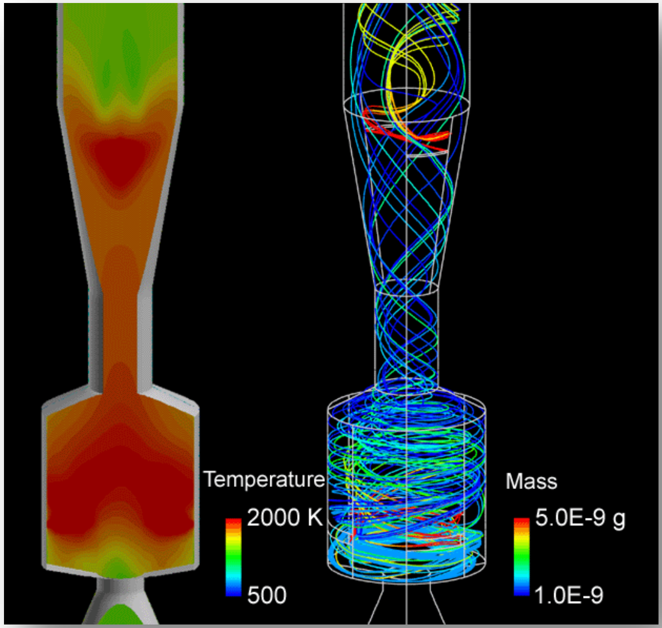
DOE FE Cross-Cutting Research Program Review
Morgantown, WV USA
March 12-14, 2012

Outline

- Motivations
- Oxy-Fuel Combustion
  - Ignition delay
  - Char combustion
    - Measurements
    - SKIPPY simulations
    - Semi-detailed mechanism
    - Extended single-film model
- Gasification Kinetics
  - 1 atm
  - p > 1 atm
- Summary

Motivations

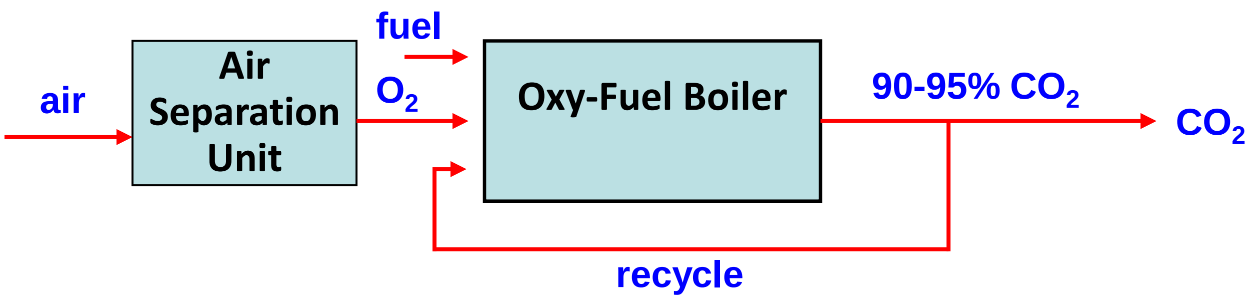
- Improvements in energy efficiency, availability, fuel flexibility, and capital effectiveness of modern coal boilers and gasifiers increasingly rely on CFD modeling
- Accuracy of CFD modeling limited by lack of knowledge of fundamental coal conversion rate parameters
  - Ignition delay
  - Volatile loss
  - Char combustion/gasification rate
- Oxy-fuel combustion and gasification of coal are two of the most promising techniques to cost-effectively capture CO_2 while continuing to utilize coal



CRIEPI model of 2-stage coal gasifier

Oxy-Fuel Combustion

- One of the more promising options for carbon capture when using coal for power production:



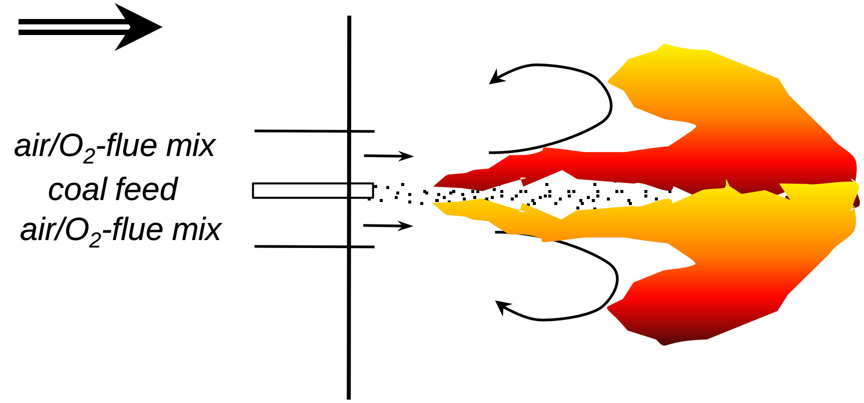
- can be retrofitted to existing boilers
- modest modification of existing technology
- concurrent emissions reductions

- Elimination of N_2 diluent and its partial replacement with recycled CO_2 results in:
  - lower gas velocity
  - more concentrated product gases in the boiler
  - significant differences in gas transport properties
  - radiantly active gas medium (IR abs. and emission)

Schwarze Pumpe pilot plant

Oxy-Fuel Combustion Ignition Delay – Background

- For overall $[O_2] < 30\%$, observations of poor flame stability during oxy-fuel combustion with flue gas recycle. Unclear if cause is
  - chemical/physical influence of CO_2
  - influence of lower jet velocities
  - lower overall flame temperature

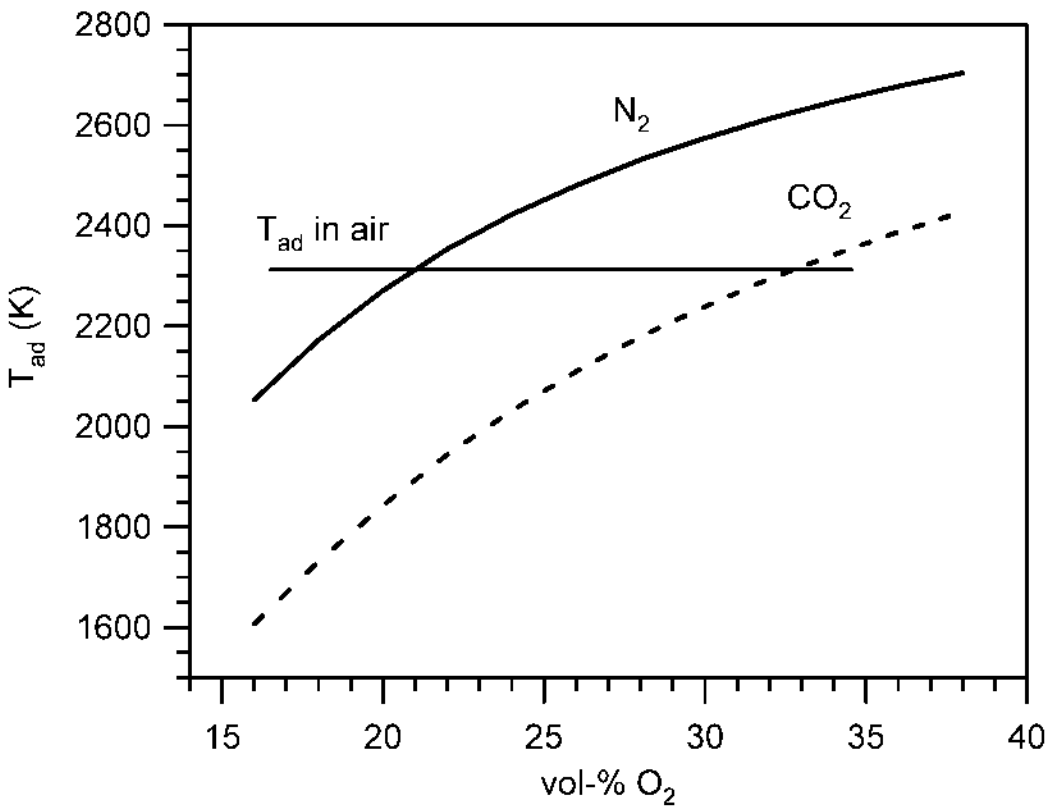


Ignition of coal stream in burner

- Literature review shows only one laminar flow study of dense coal stream ignition (Annamalai, 1990)
  - 9 vol-% O2
  - 53-75 μm Pee Wee coal
  - apparent ignition from camera image

Oxy-Fuel Combustion Ignition Delay – Background

Computed Adiabatic Flame Temperature of Coal Volatiles (Xu and Tomita, 1987)



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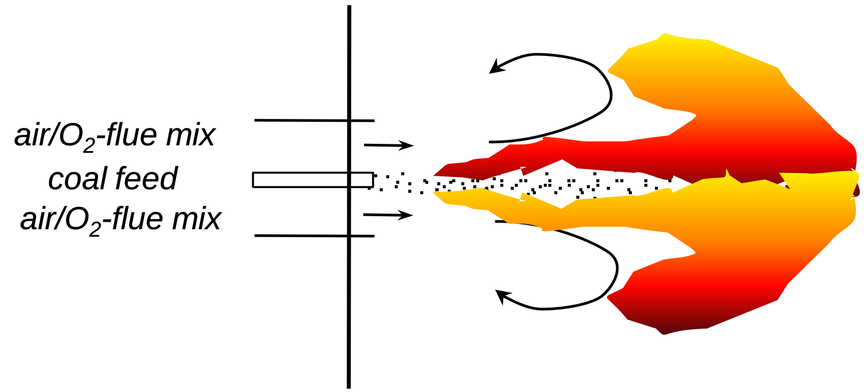
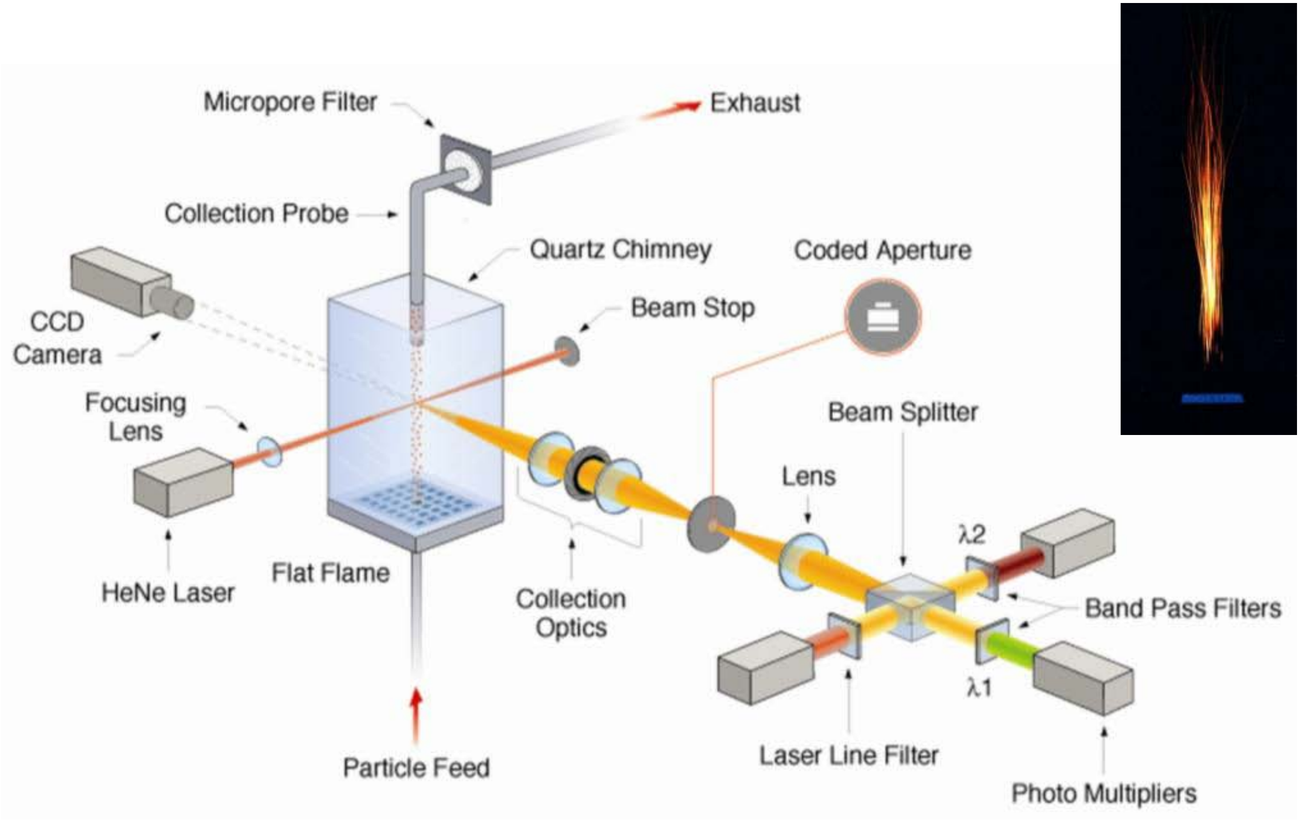


Ignition of coal stream in burner

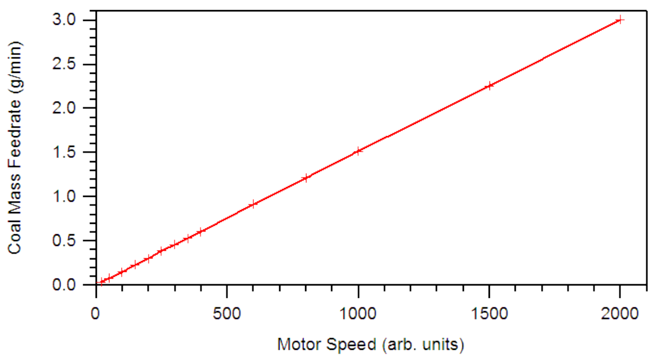
Oxy-Fuel Combustion Ignition Delay – Experimental Approach



- 5 cm X 5 cm x-section
- 1 atm
- furnace flow from compact, diffusion-flamelet burner
- coal particles introduced along centerline
- quartz chimney
- CCD for imaging of furnace central plane
- 431 nm bandpass filter to accentuate CH* detection

Oxy-Fuel Combustion Ignition Delay – Coal Feeder

- Accurate, steady coal feed is requisite for quantifying ignition delay as function of coal feed density
  - Custom coal feeder developed from design originated by Sarofim at MIT
  - feed rate determined by rate of displacement of coal-containing test tube
  - similar feeders in use at Univ. of Utah and U.S. EPA
  - coal entrained by 0.033 slpm feed gas (diluent)

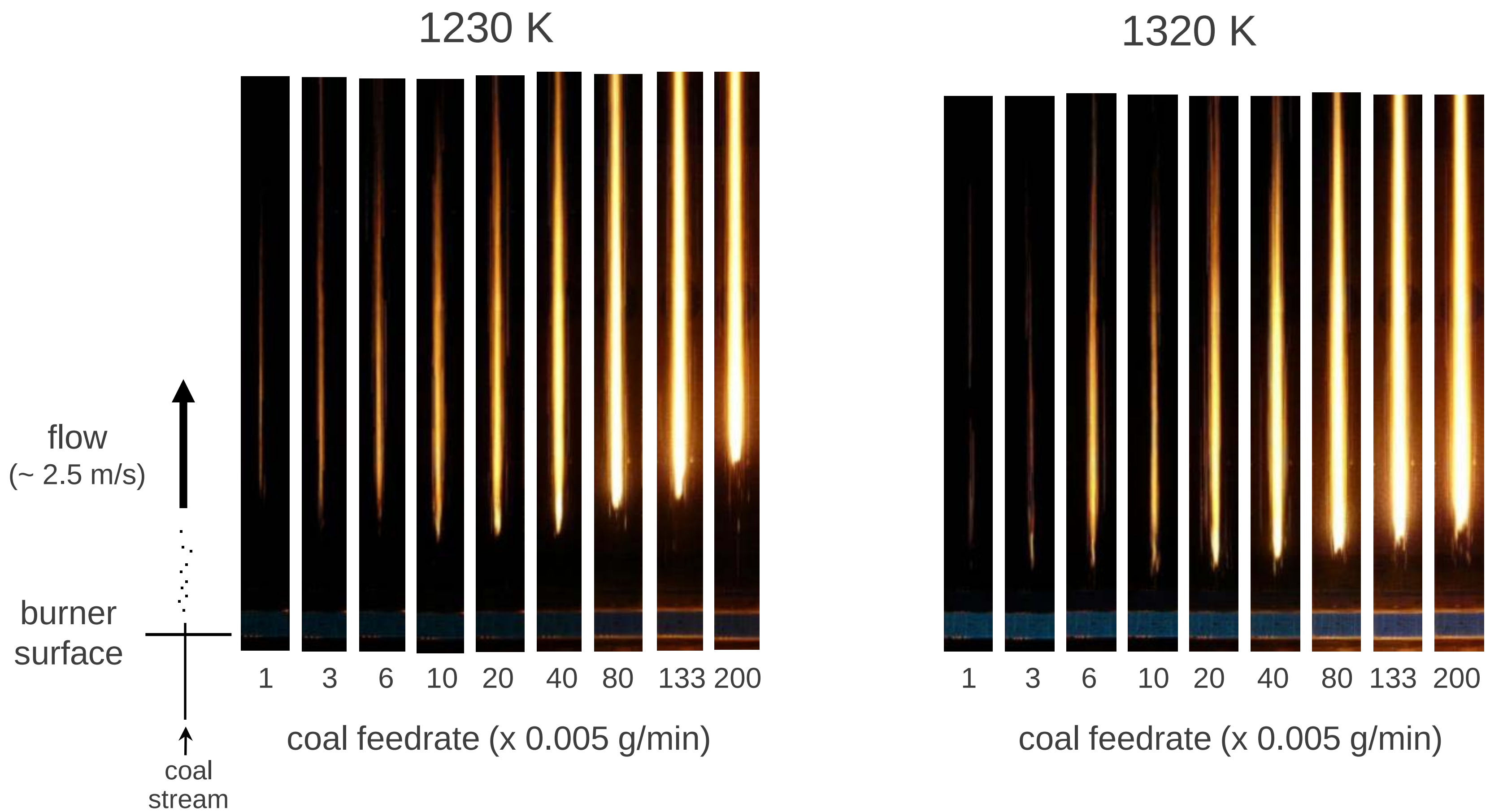


Coal feed calibration plot

Photograph of pulverized coal feeder

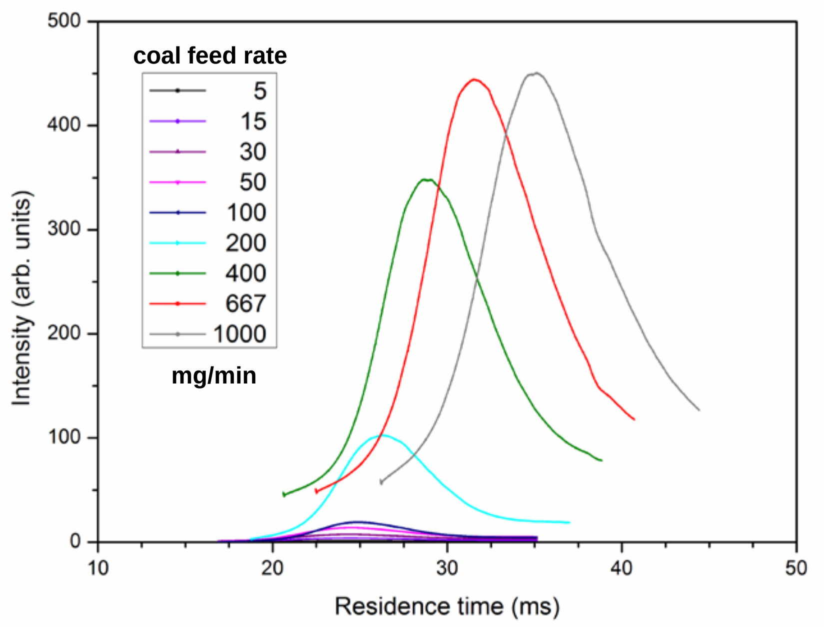
Oxy-Fuel Combustion Ignition Delay – Photographs

Black Thunder coal, 12 vol-% O_2 in N_2 bulk gas

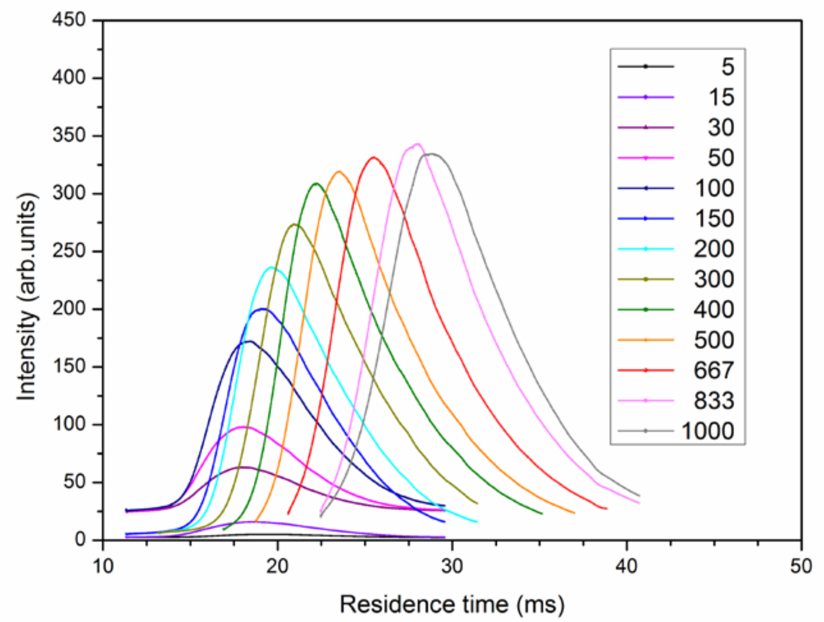


Oxy-Fuel Combustion Ignition Delay – Processed CCD Images

Shenmu coal, 20% O_2 in CO_2, 1280 K

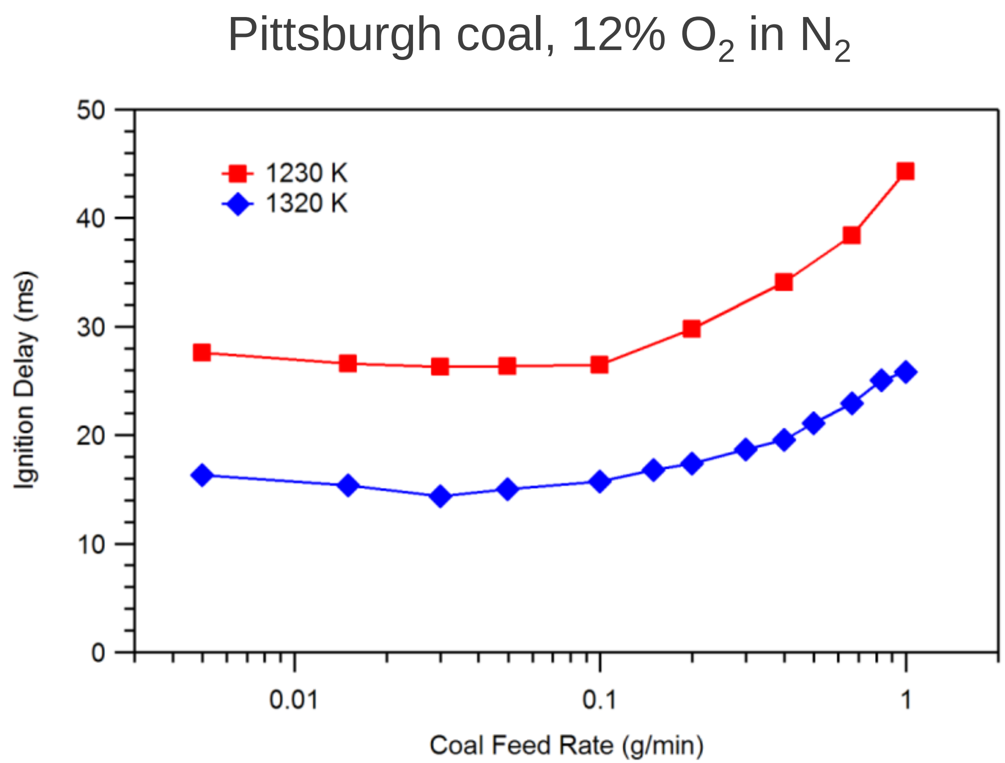


Pittsburgh coal, 12% O_2 in N_2, 1320 K



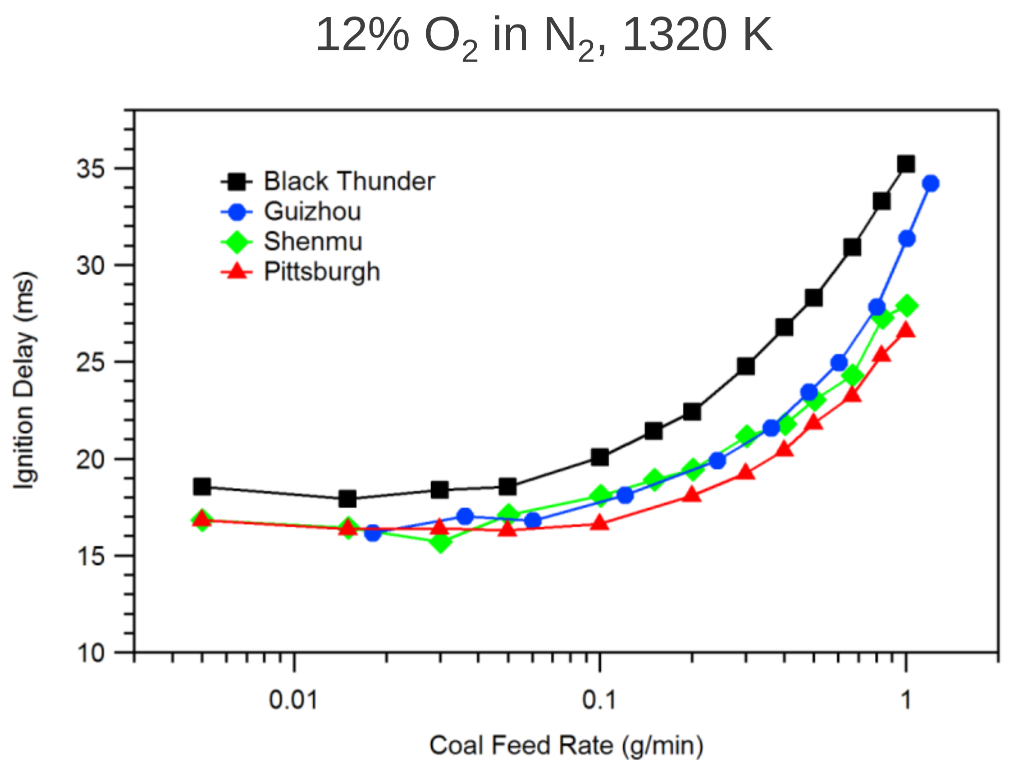
- ignition criteria: location where binned signal = ½ of max signal
- max upslope criteria gives same trends, slightly lower values

Oxy-Fuel Combustion Ignition Delay – Influence of Feed Rate and Temperature



- at intermediate T, ignition delay highly sensitive to T
- minimum ignition delay occurs for feed rate of 0.05 – 0.10 g/min (for Annamalai, min. occurred at 3 – 6 g/min)

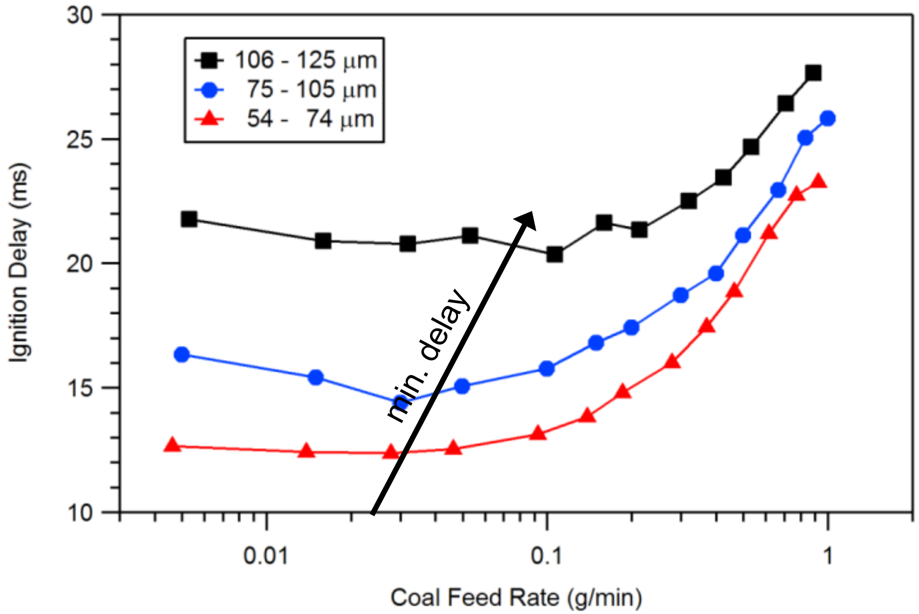
Oxy-Fuel Combustion Ignition Delay – Influence of Coal Type

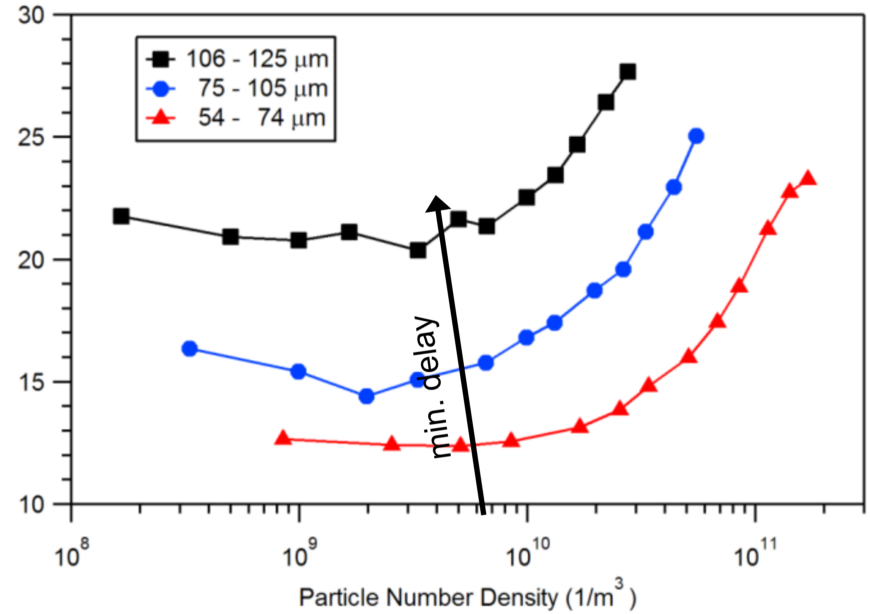


- 3 high-volatile bituminous coals show nearly identical ignition delay, except at high particle loadings
- apparent ignition delay of subbituminous coal is slightly longer

Oxy-Fuel Combustion Ignition Delay – Influence of Particle Size

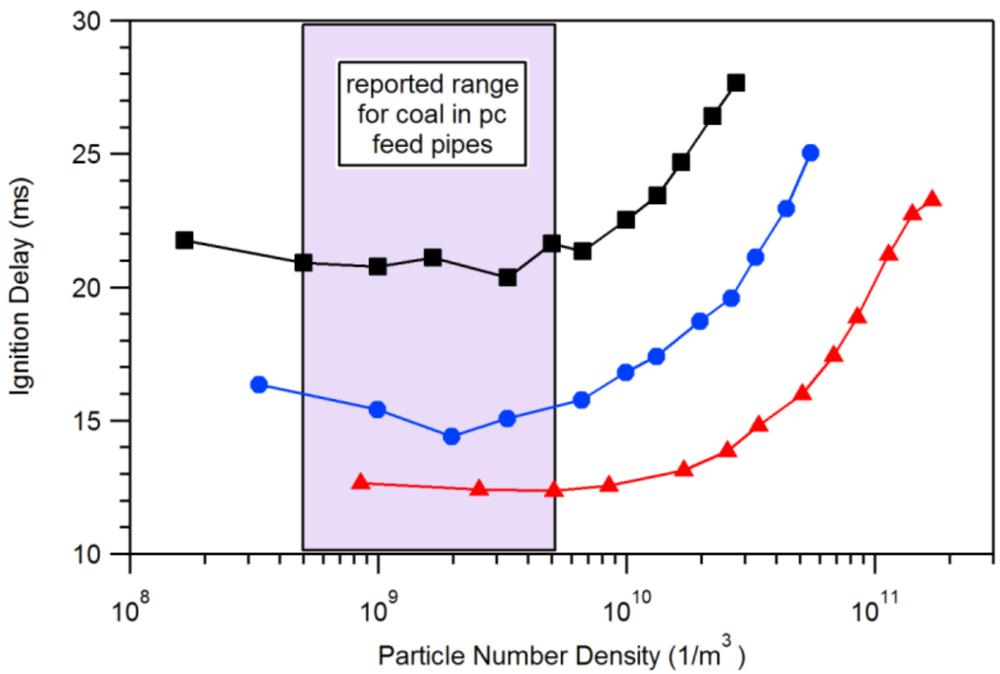
Pittsburgh coal, 12% O_2 in N_2, 1320 K



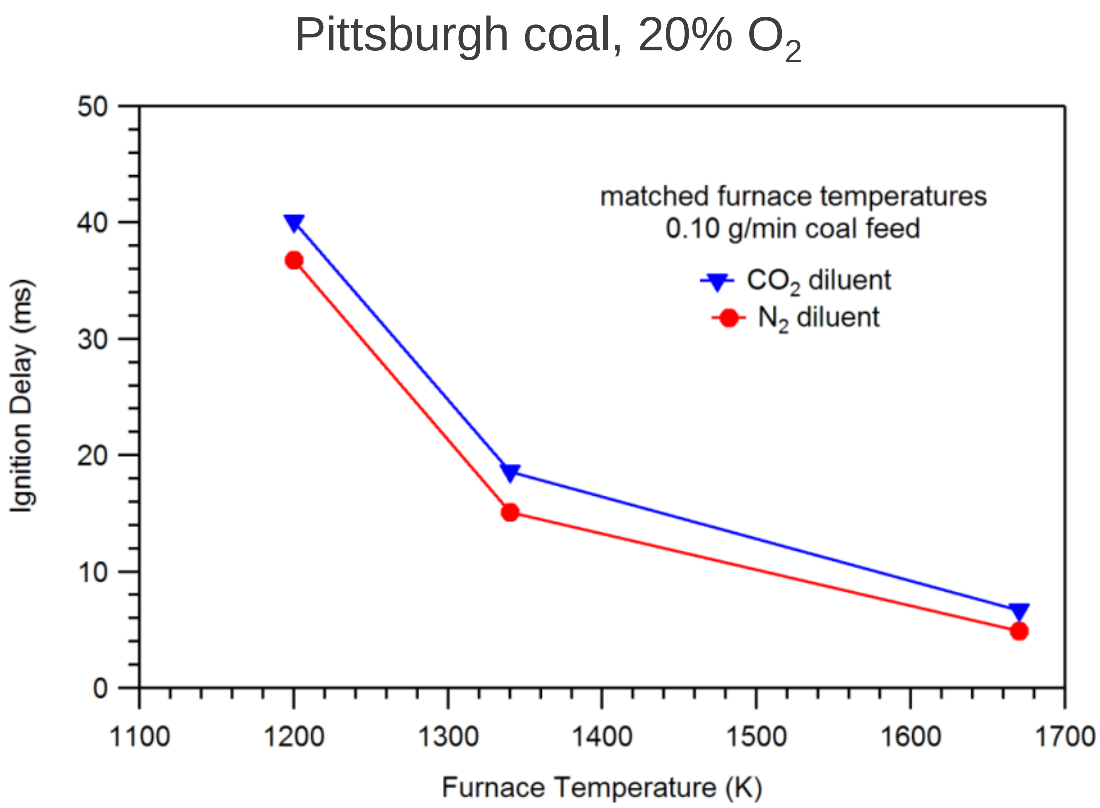


- ignition delay is a strong function of particle size
- minimum ignition delay correlates better with particle number density than particle mass feed rate
- Annamalai found similar number density for min. ignition delay (4×10^9)

Oxy-Fuel Combustion Ignition Delay – Industrial Relevance of Particle Number Densities



Oxy-Fuel Combustion Ignition Delay – Influence of CO_2



- presence of CO_2 adds small ignition delay relative to N_2 environments

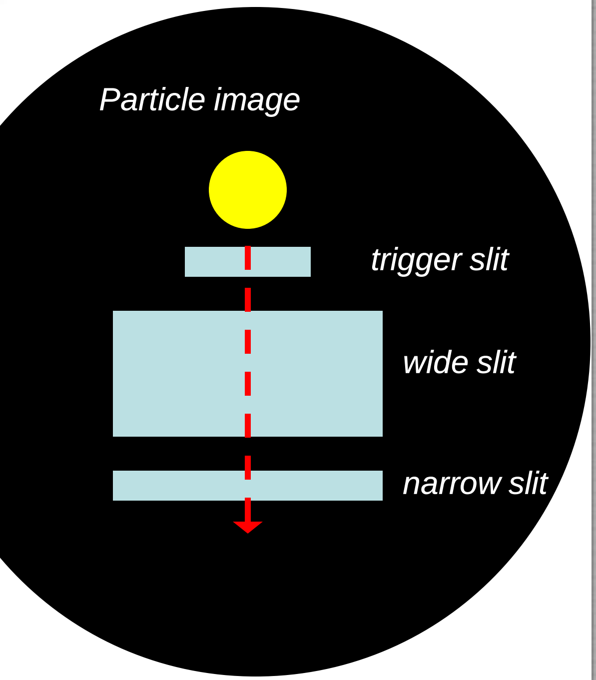
Oxy-Fuel Char Combustion – Background

- Elevated O_2, CO_2, and H_2O concentrations in oxy-fuel combustion can alter char combustion rates and particle temperatures (furnace heat transfer)
  - Higher O_2 concentration increases char combustion rate and temperature (enhancing CO conversion in boundary layer)
  - CO_2 reduces O_2 diffusivity (by 20%), reducing char burning rate
  - High C_v of CO_2 (1.7x C_v of N_2) can affect heat transfer through boundary layer
  - CO_2 and H_2O can react endothermically with char (gasification), reducing char combustion temperature
- Focus of our work has been on understanding and quantifying these effects and incorporating this knowledge into computationally efficient submodels for CFD

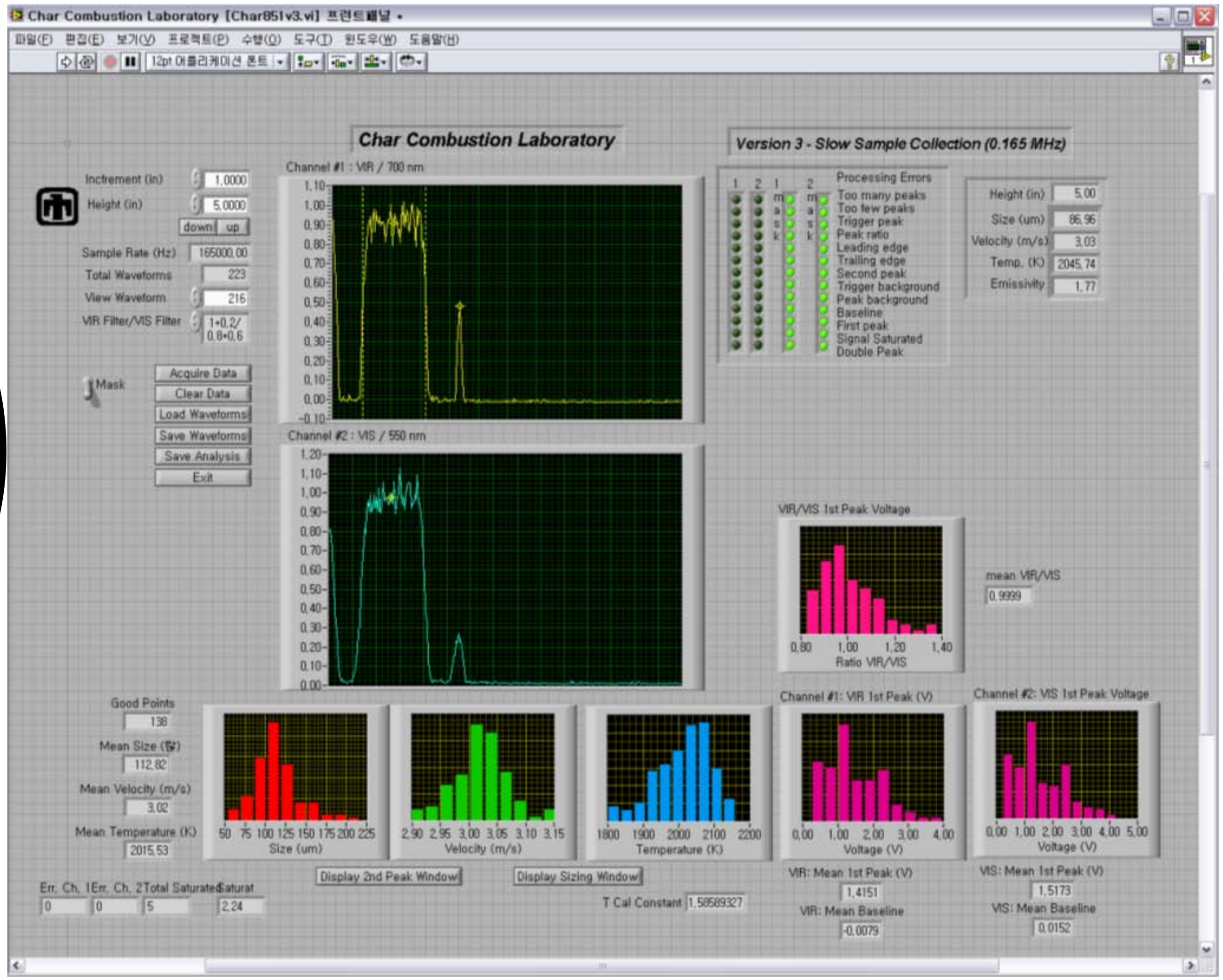
Oxy-Fuel Char Combustion
– Effects of Reaction Enthalpies

Reaction			ΔH_{rxn} (kJ/mole-C_s)
2C(s) + O_2	→	2CO	-110.5
C(s) + O_2	→	CO_2	-393.5
C(s) + CO_2	→	2CO	172.5
C(s) + H_2O	→	CO + H_2	131.3

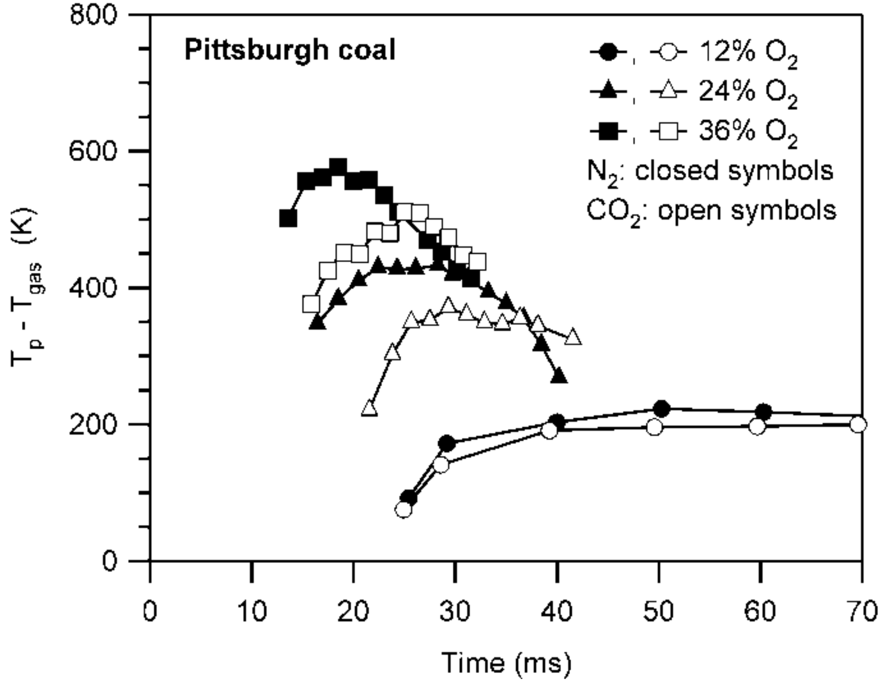
Oxy-Fuel Char Combustion
– Key Diagnostic: Particle-Sizing Pyrometry

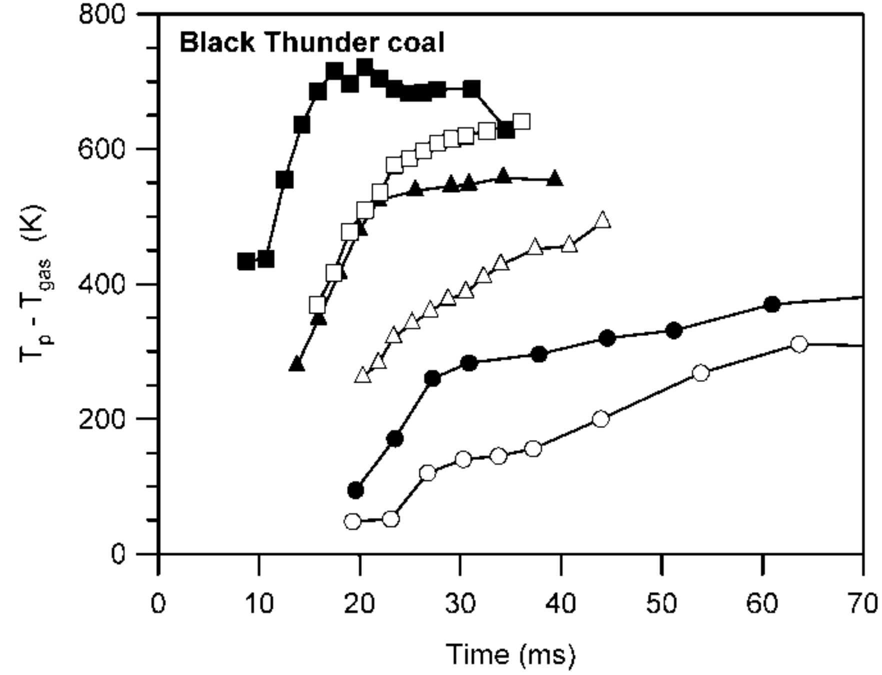


schematic of coded aperture



Oxy-Fuel Char Combustion
– Measured Char Particle Combustion Temp



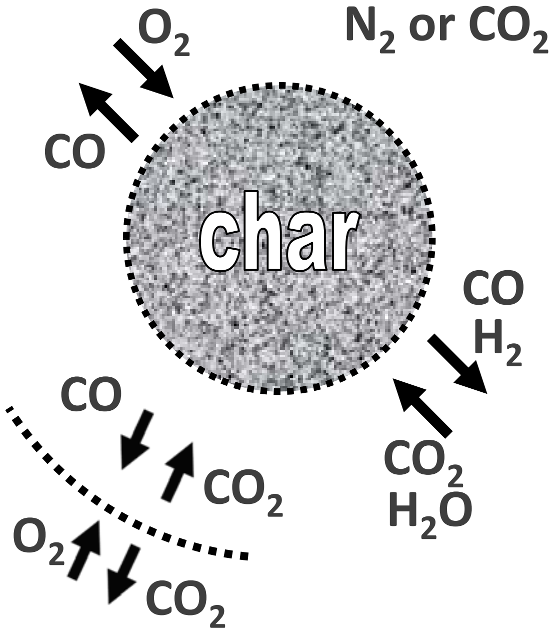


Oxy-Fuel Char Combustion – Detailed Particle Modeling

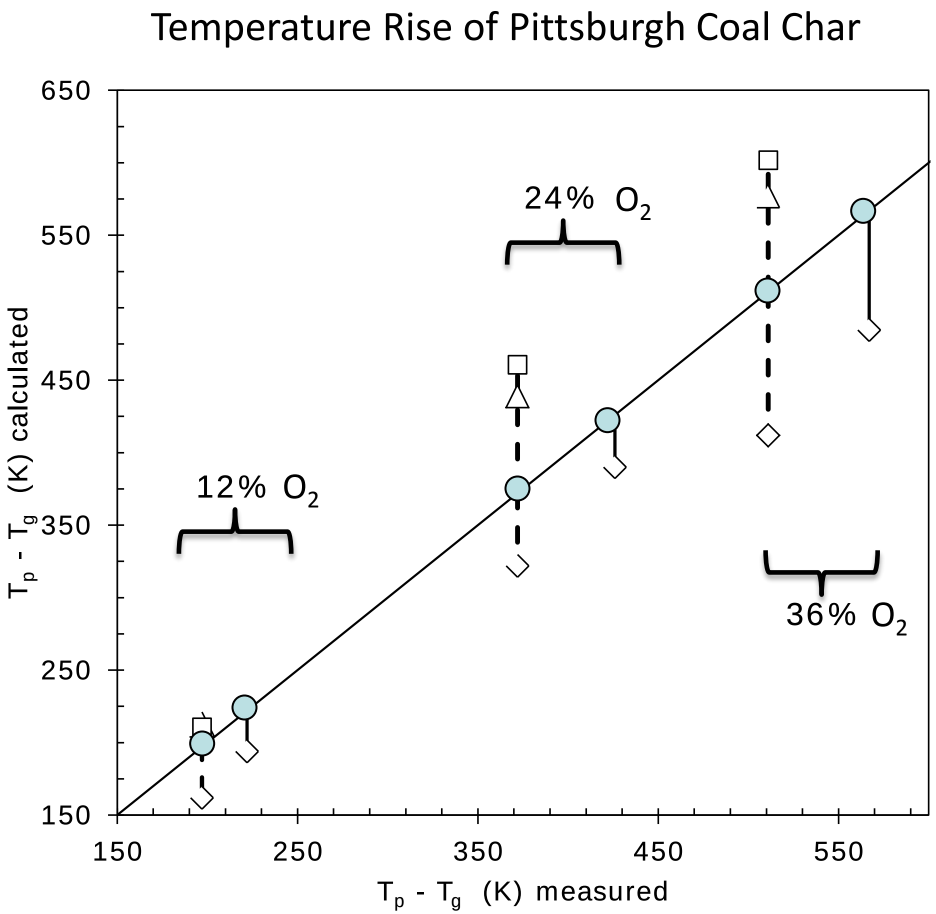
SKIPPY (Surface Kinetics in Porous Particles)

- 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
- Useful tool in evaluation relative effects of kinetic mechanism or rate parameters

Reaction	*A* (g/cm² 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



Oxy-Fuel Char Combustion – SKIPPY Evaluation of Physical/Transport Effects of CO_2

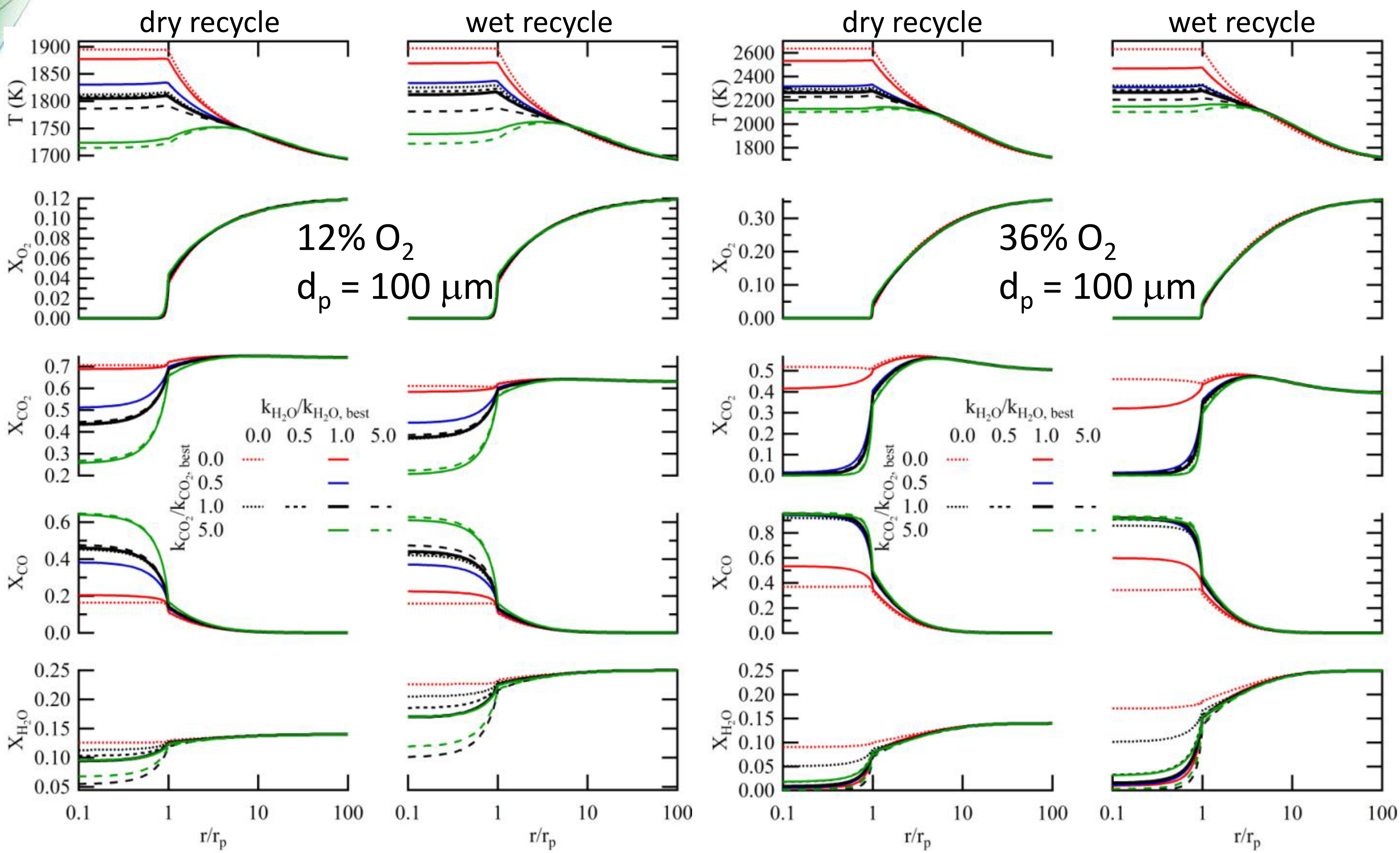


△: CO_2 diffusivity set equal to N_2

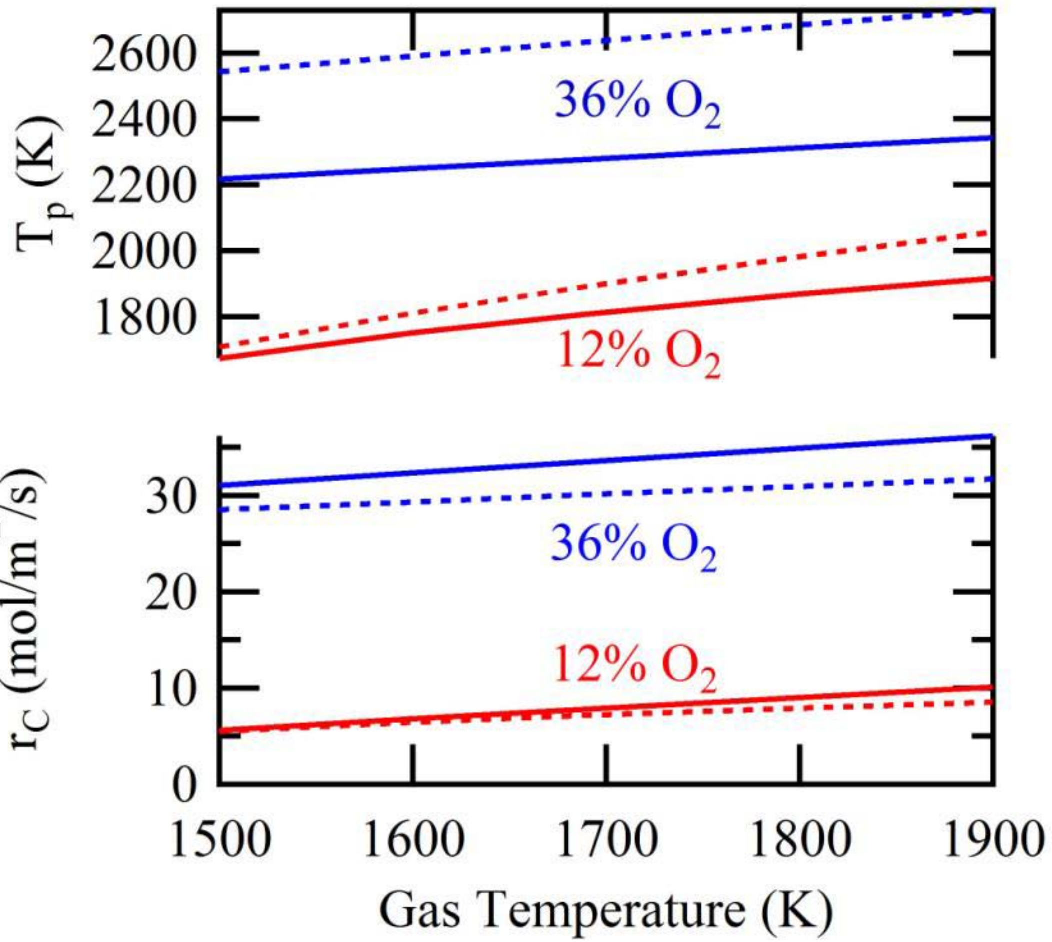
□: CO_2 C_v set equal to N_2

◇: Boundary Layer chemistry turned off

Oxy-Fuel Char Combustion
– Effect of Gasification Reactions



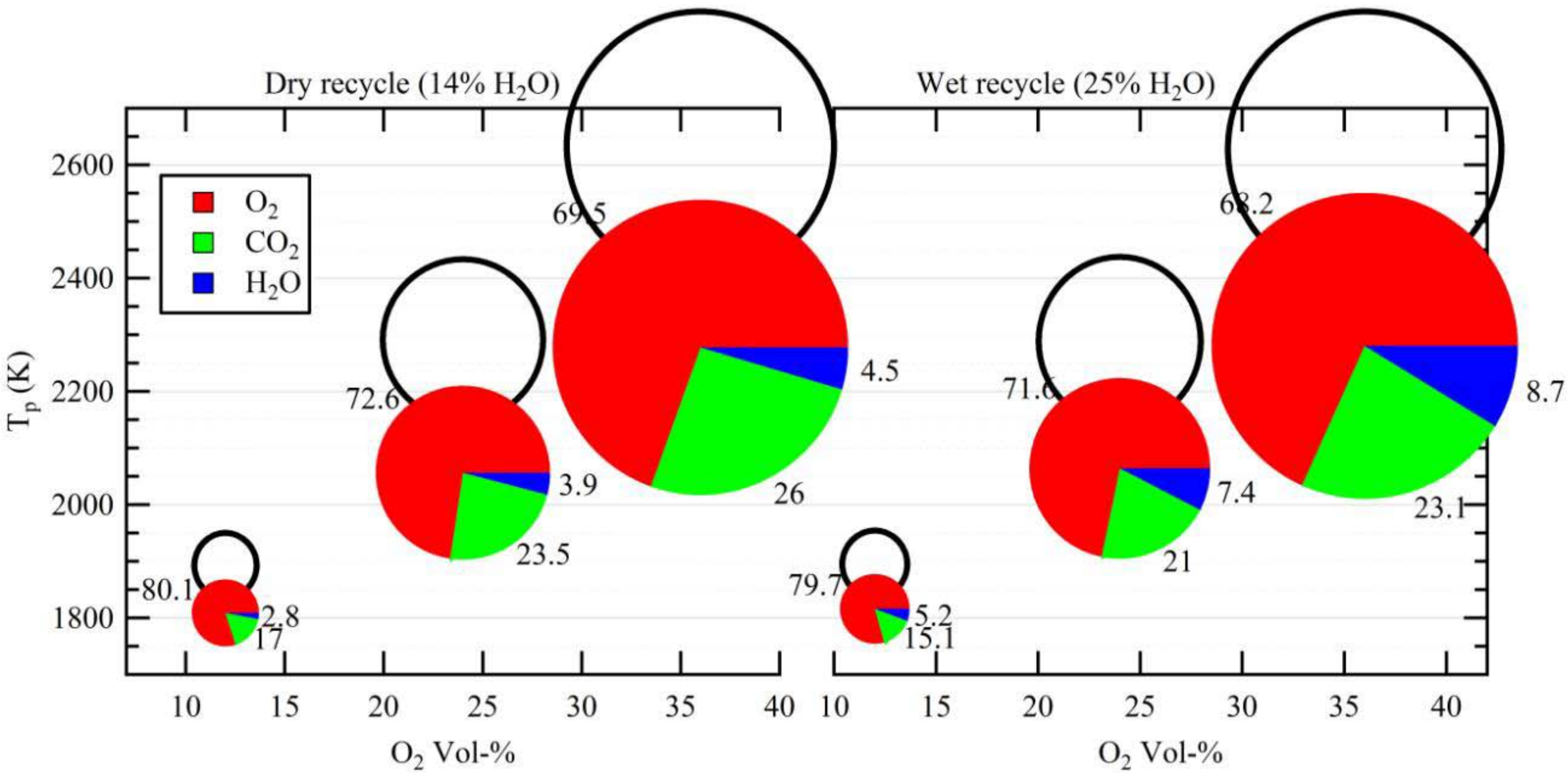
Oxy-Fuel Combustion Char Combustion Kinetics – Effect of Gasification Reactions on T_p and Char Conversion



Dashed lines: no gasification rxns

Solid lines: with gasification rxns

Oxy-Fuel Combustion Char Combustion Kinetics – Effect of Gasification Reactions on T_p and Char Conversion



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

- Several semi-detailed char oxidation mechanisms suggested in literature (from 3 to 20 reaction steps)
- None of existing mechanisms predicts O_2-dependence of CO_2/CO production ratio measured by Tognotti et al. (1990) and others

$$CO_2/CO = 0.02\, p_{O_{2,s}}^{0.21} \exp\left(3070/T_p\right)$$

- We employed SKIPPY to verify key assumptions used in analyzing Tognotti dataset
- Then, we employed best-justified reaction steps and showed that 5 steps were required to capture basic elements of char combustion and observed T- and O_2-dependence of CO_2/CO production ratio

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

Proposed Mechanism

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

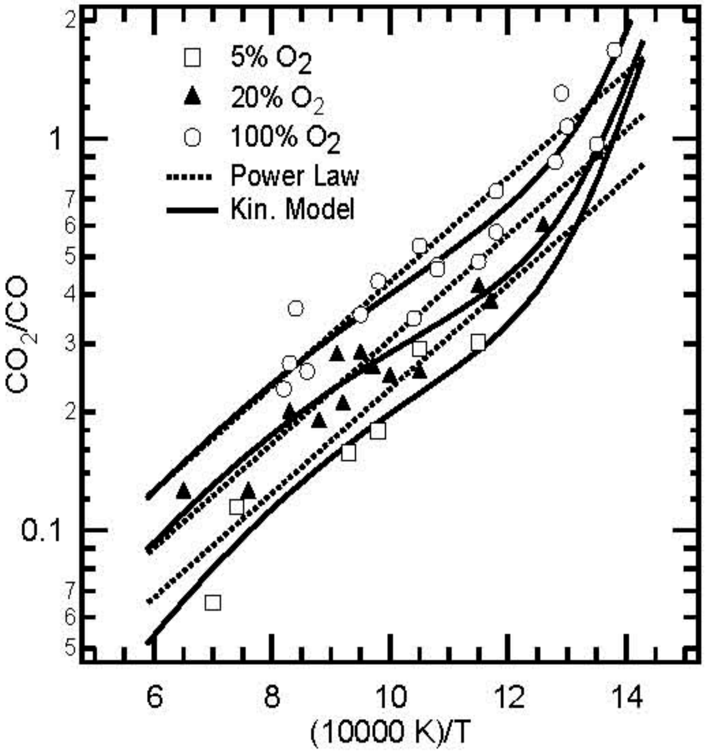
$$C(\ )+C_b+O_2 \xrightarrow{k_2} CO+C(O)$$

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

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

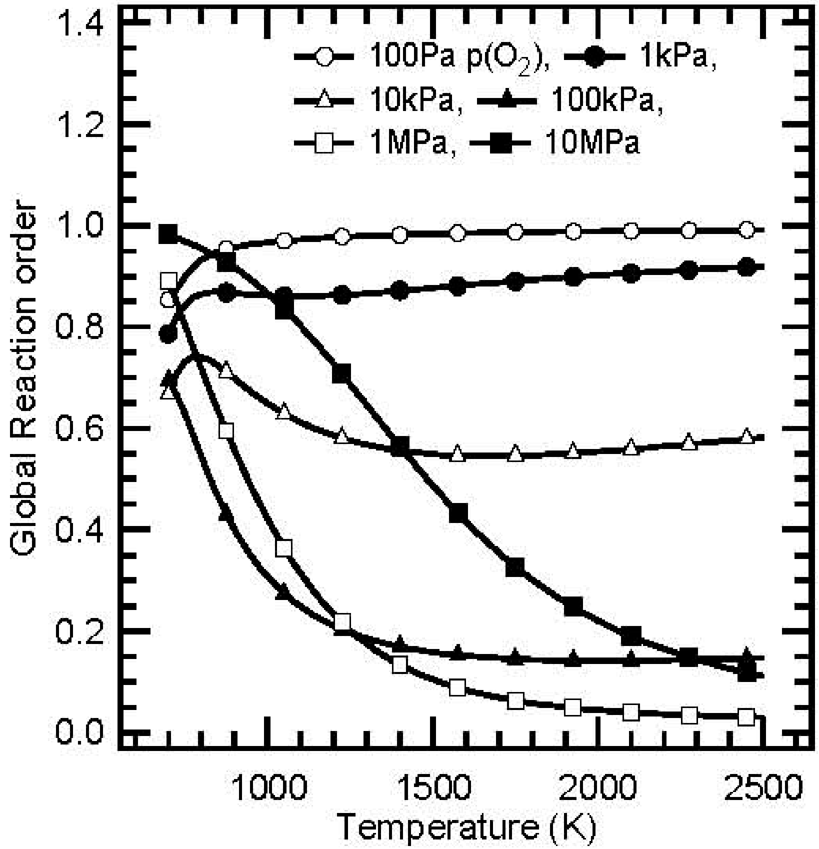
$$C_b+2C(O) \xrightarrow{k_6} CO_2+2C(\ )$$

Mechanism Performance



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

Other Predictions of New Mechanism – Reaction Order



Oxy-Fuel Char Combustion
– Motivation for Extended Single-Film Model

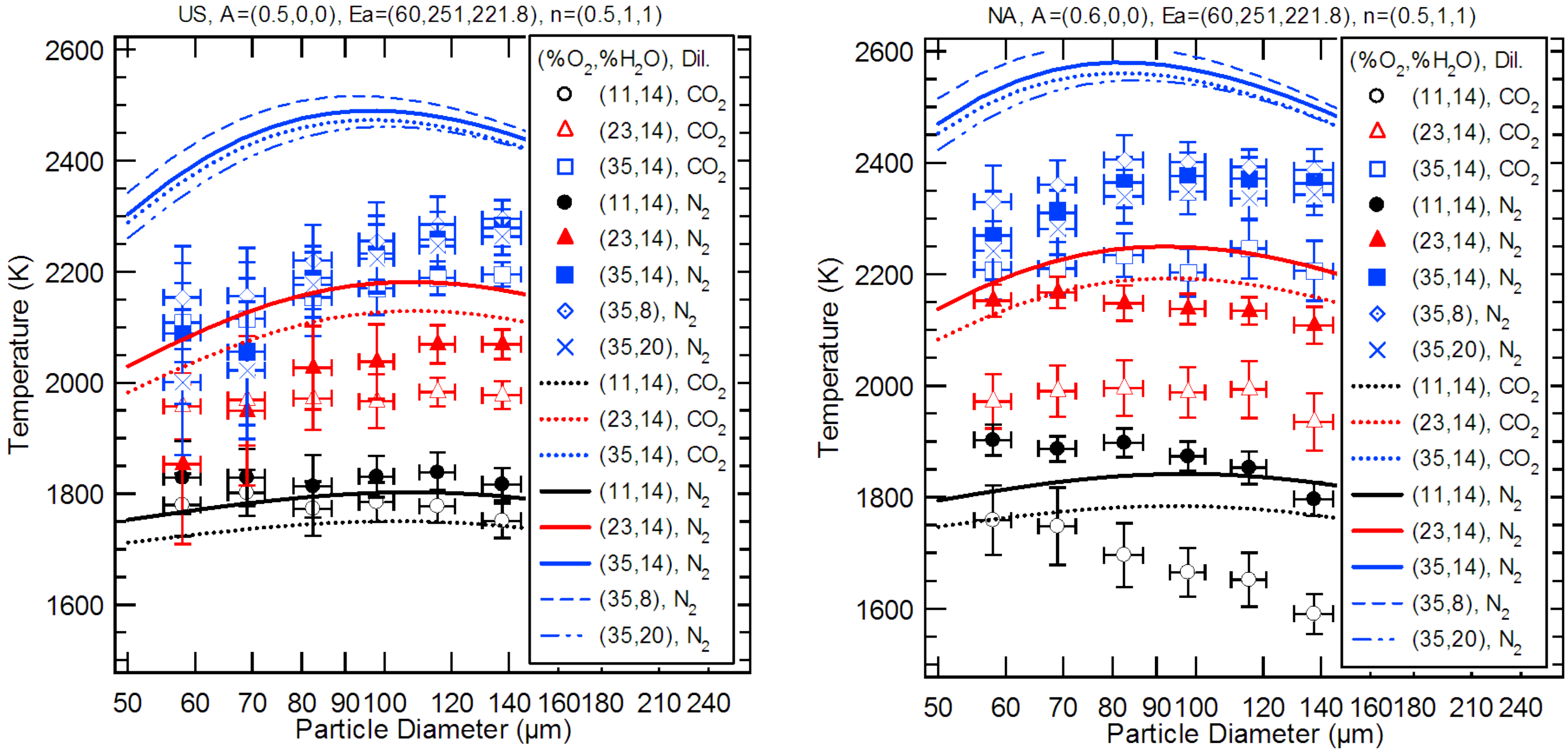
- Practical CFD codes for modeling coal combustion in full-scale boilers/gasifiers cannot calculate boundary layer chemistry – must use single-film models
- Our comparison of modeling and experiments shows traditional combustion kinetic models must incorporate gasification reactions to treat oxy-fuel combustion
- Properly tuned kinetic mechanism might correct for neglect of boundary layer chemistry

Oxy-Fuel Char Combustion – Extended Single-Film Model

Predictions of Best-Fit Oxidation-only Model

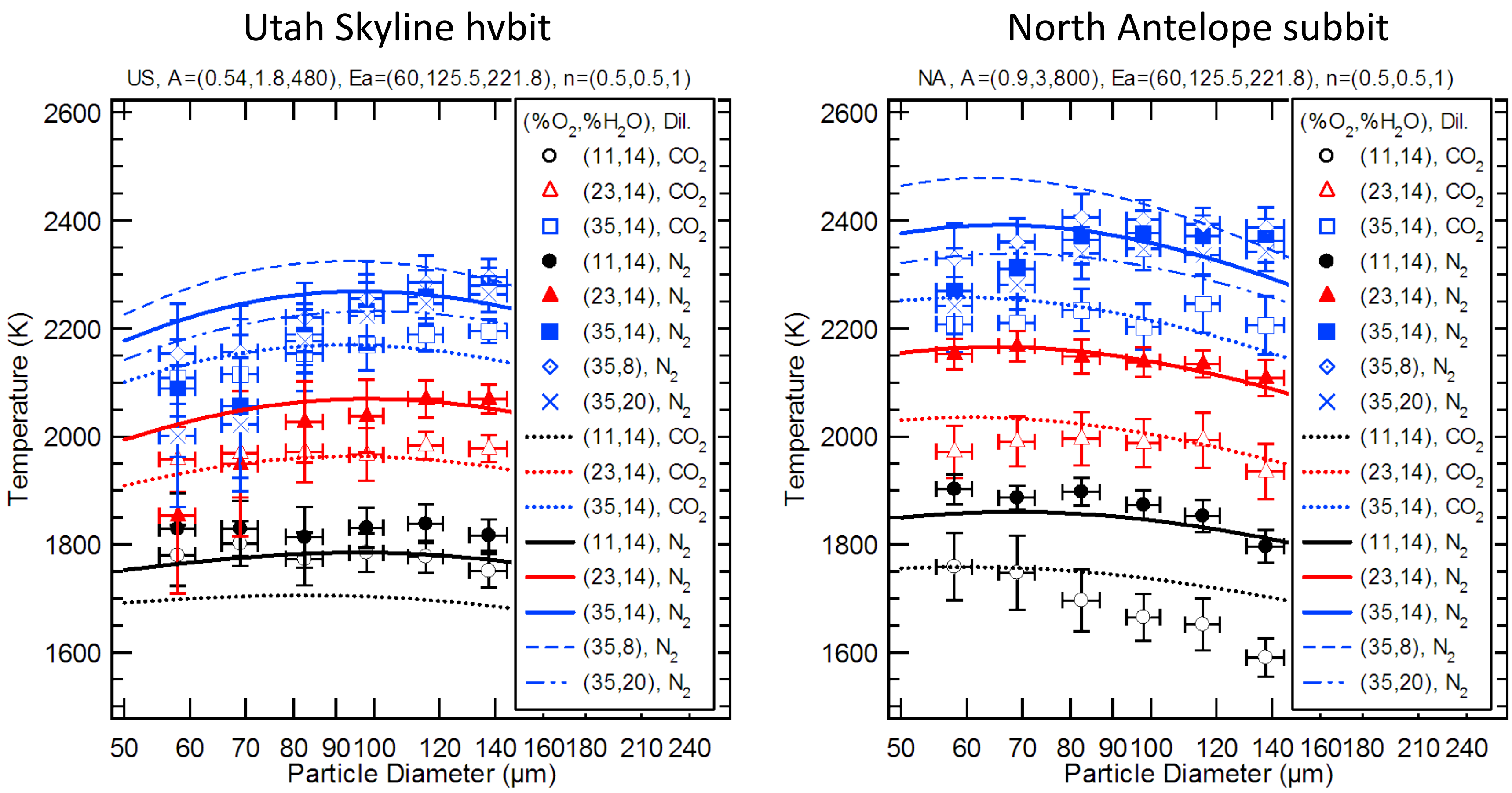
Utah Skyline hvbit

North Antelope subbit



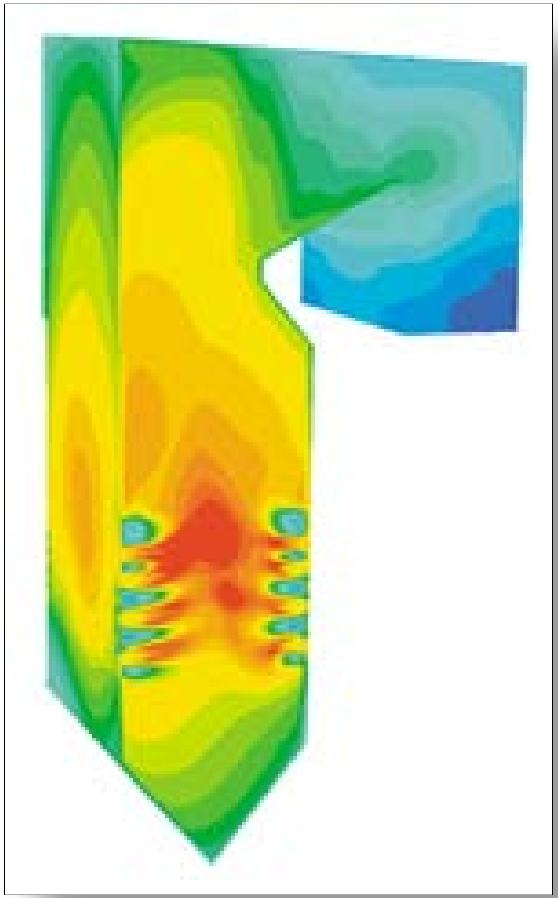
Oxy-Fuel Char Combustion – Extended Single-Film Model

Predictions of Best-Fit Oxidation/Gasification Model



Oxy-Fuel Char Combustion Fundamentals – Extension to Applied Programs

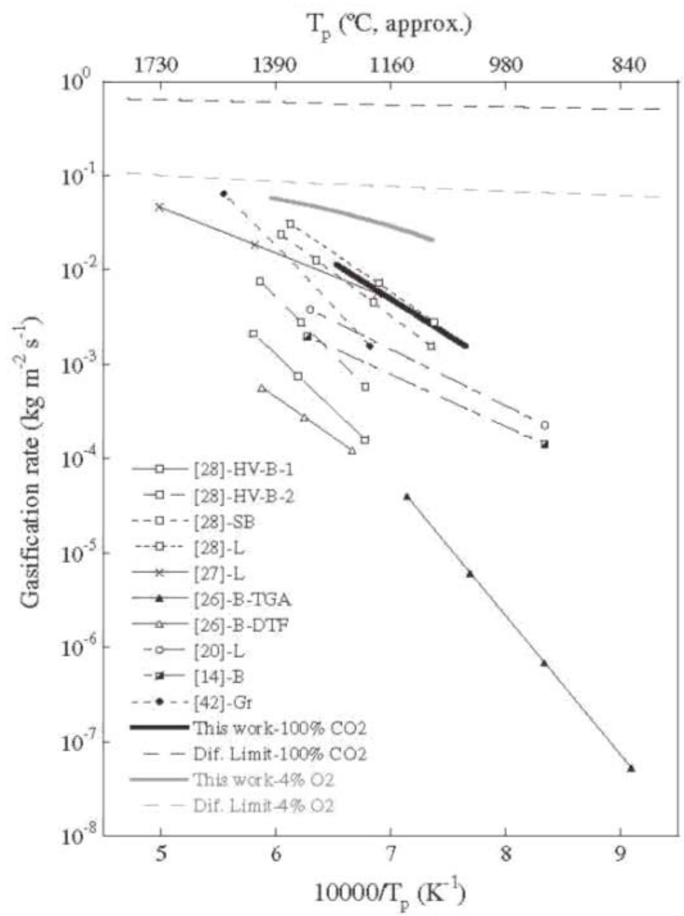
- Collaborated with Reaction Engineering International (REI) to implement extended single-film kinetic model to CFD modeling of full-scale oxy-fuel boiler retrofit (FE Carbon Capture Program, Tim Fouts)
- REI reports that extended single-film kinetic model has improved predictions of CO and LOI from *conventional* and oxy-fuel boilers



http://www.fluent.com

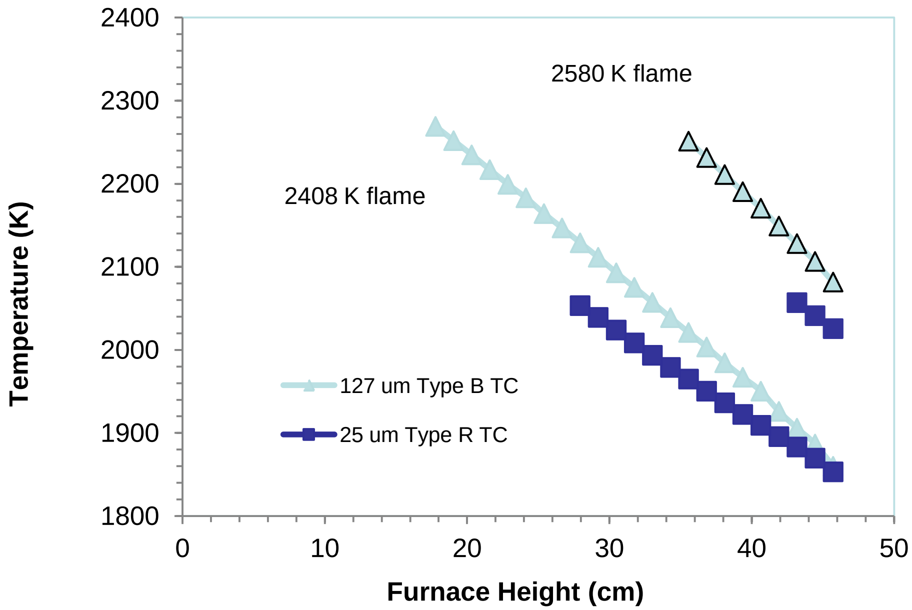
1 atm Char Gasification Kinetics in CO_2 – Previous High-T Measurements

- Gonzalo-Tirado, Jiménez, Ballester (Comb. Flame, 2011)
  - 1310 – 1570 K wall T
  - mass loss measurements
  - derived kinetics on high end of literature
- Hampsartsoumian et al. (Comb. Sci. Technol., 1993)
  - 1400 – 1800 K gas T
  - char particle T measured – up to 250 K lower than gas T

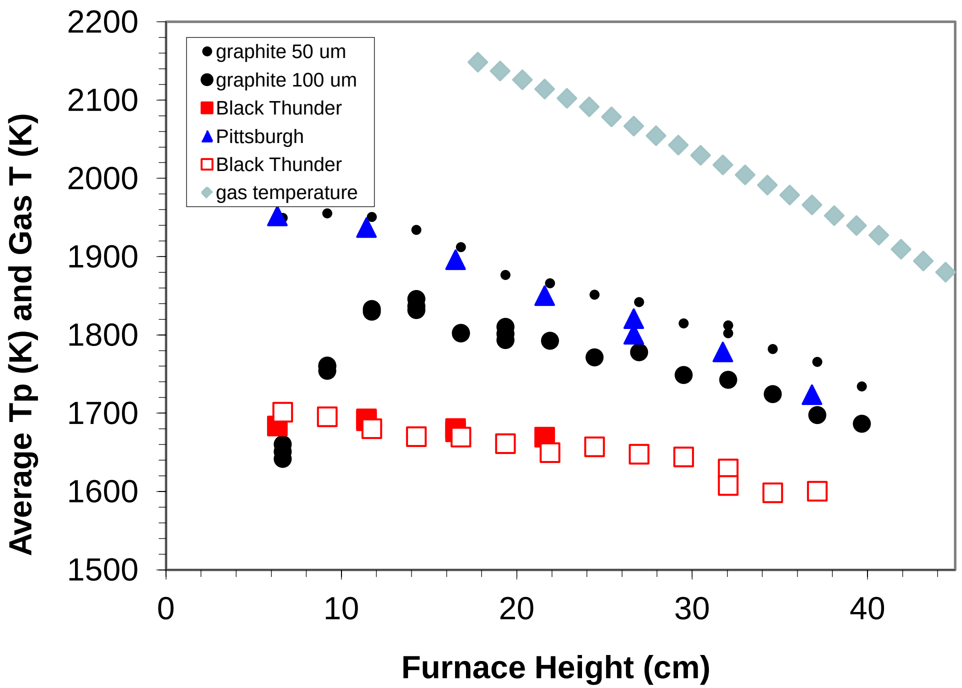


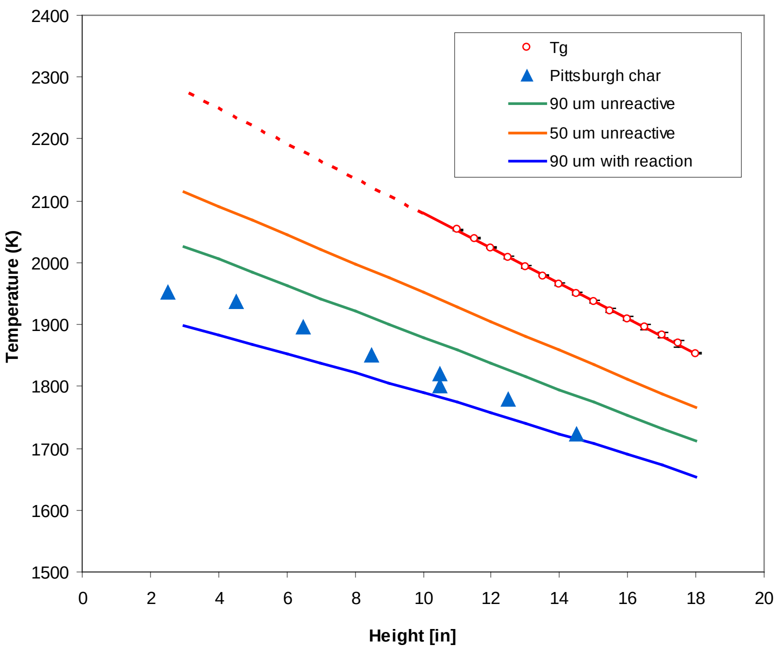
1 atm Char Gasification Kinetics in CO_2 – Experimental Method

- Generate chars in drop tube at 1200 °C, sieve to 75-105 μm
- Introduce chars into laminar EFR, with burner operated on CO fuel with CO_2 diluent
- Use gas T ~ 2200 K, so that chars react near 2000 K
- Difficult to measure gas T

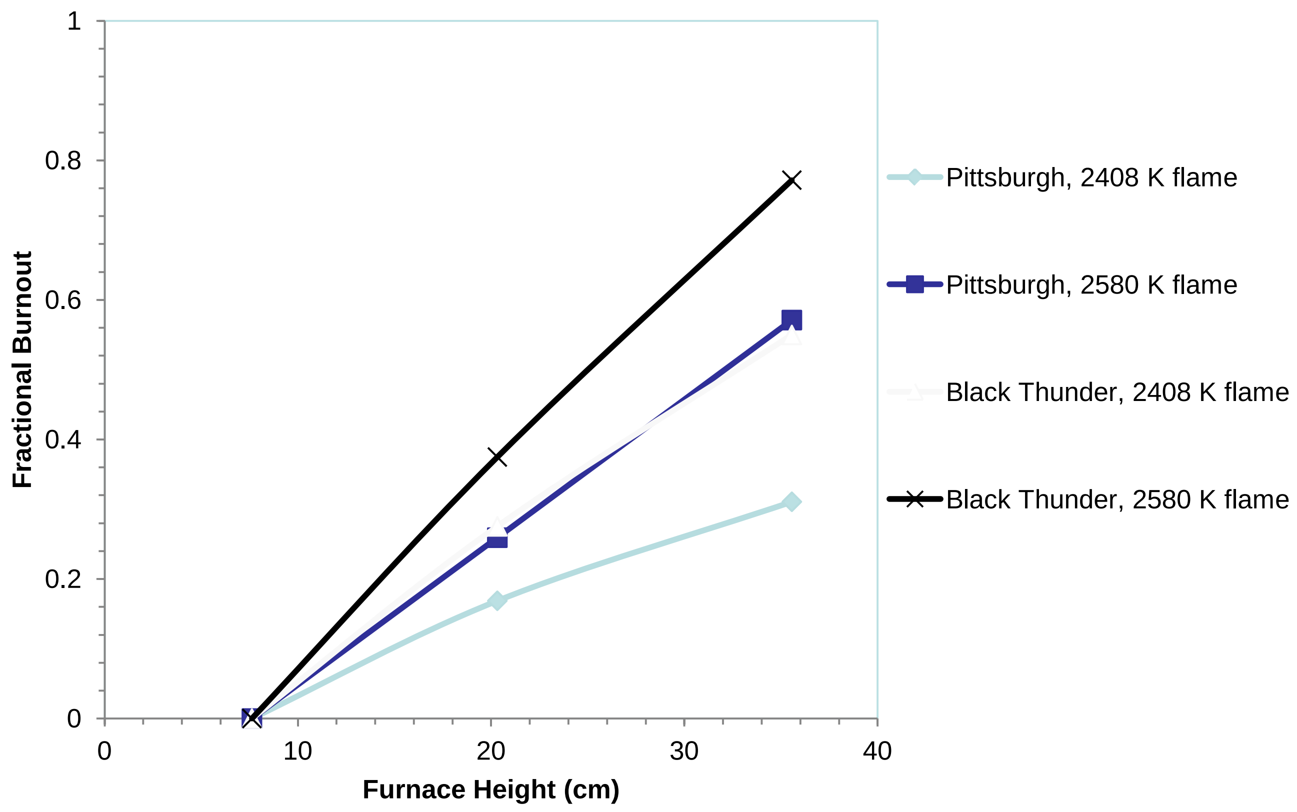


1 atm Char Gasification Kinetics in CO_2 – Particle T Measurements and Modeling





1 atm Char Gasification Kinetics in CO_2 – Char Burnout



Pressurized Char 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 is difficult (dangerous) to extrapolate rates from TGA measurements at 1000-1100 K
- Gasification kinetics are complicated at pressure, because of action of reverse reactions involving gasification products (CO and H_2) – need well-controlled, systematic study to deduce kinetic rates of each reaction step

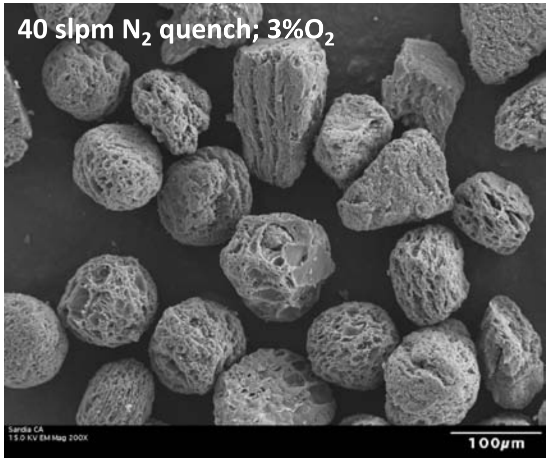
Pressurized Char Gasification Kinetics – Experimental Method

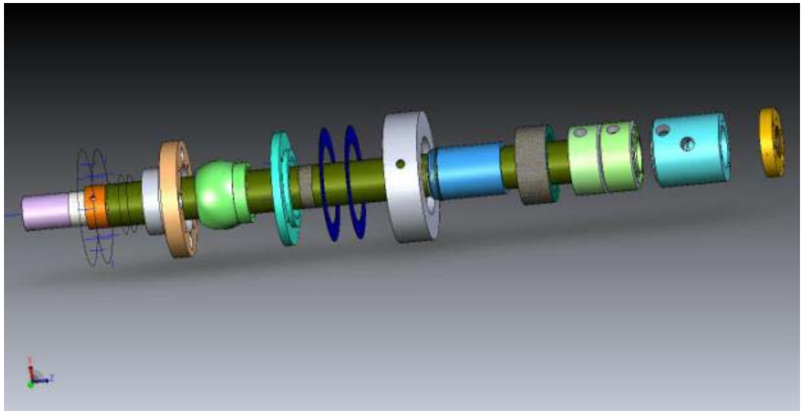
- Perform experiments in specially designed, turbulent entrained flow reactor – low particle loading, isothermal conditions
- Separate char formation step from char gasification, to clearly quantify rates – i.e. pre-form chars
- Begin by measuring char gasification in CO_2 only, and in H_2O only, then in mixtures of CO_2 and H_2O, then add in H_2 and CO, first separately, then together

Pressurized entrained flow reactor

Pressurized Char Gasification Kinetics – Results

- Developed procedure for generating high heating rate char – 1200 °C, 250 ms
- Designed fiber-optic probe for in situ particle T measurements – some parts fabricated
- Char gasification experiments performed in CO_2 and in H_2O up to 8 bar, but flow T dropped down the tube at p > 5 bar, and char conversion was minimal
- Fixes to internal heating are being worked on





Summary of Progress

- Ignition delay has been measured for first time for several U.S. and Chinese coals over range of O_2, T, particle size, particle loading, for both N_2 and CO_2 diluents
- SKIPPY particle simulation code has been used to evaluate role of CO_2 properties and CO_2 and steam gasification reactions on oxy-fuel char combustion – gasification reactions have small effect on char conversion (except for low O_2 environments), but have profound effect on char combustion T
- Extended single-film char combustion kinetic model with gasification reactions has been developed and fit to experimental oxy-fuel char combustion data, showing good agreement
- Experimental measurements have been completed on high-temperature CO_2 gasification of coal char at 1 atm

Continuing Work

- Measurement of gas temperature profile in very hot CO_2 environments – to complete quantification of char gasification kinetics at 1 atm
- Improvements in T profile in high-p entrained flow reactor, to quantify coal char gasification kinetics
- Oxy-fuel char combustion at elevated p

Acknowledgments

- Research collaborators Ethan Hecht, Manfred Geier (postdoc), Yinhe Liu (visitor), Alejandro Molina (visitor), and Brian Haynes
- Funding provided by Robert Romanosky through FE Power Systems Advanced Research Program and FE Cross-Cutting Research Program

- For more information . . .

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925-294-3840

Recent Publications

Journal articles

- 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," submitted to *Combustion and Flame*.
- M. Geier, C.R. Shaddix, F. Holzleithner, "Predicting the CO2/CO Production Ratio during Char Oxidation: Capturing the Oxygen Dependence with Semi-Global Intrinsic Kinetics Models," submitted to *Proceedings of the Combustion Institute.*
- A. Molina, C.R. Shaddix, B.S. Haynes, "Effect of Physical and Transport Properties of CO2 on Oxy-Fuel Pulverized Coal Char Combustion," submitted to *Proceedings of the Combustion Institute*.
- Y. Liu, M. Geier, A. Molina, C.R. Shaddix, "Pulverized coal stream ignition delay under conventional and oxy-fuel combustion conditions," *Int. J. Greenhouse Gas Control*, 5S (2011) S36-S46.
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