Improvements to a Detailed Fundamental Char Conversion Model for Oxy-Coal Combustion

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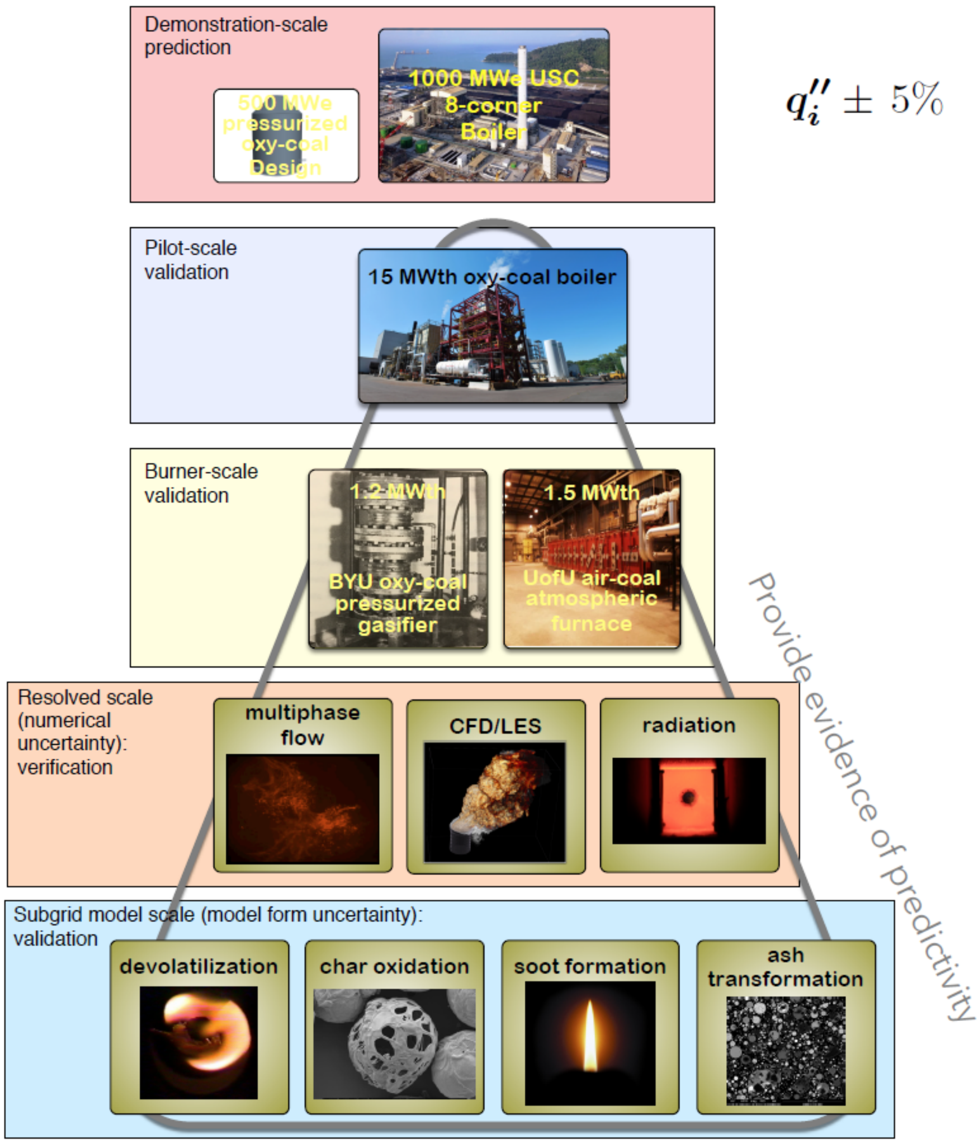
CCMSC Center



$$q_i'' \pm 5\%$$

objective
predictivity

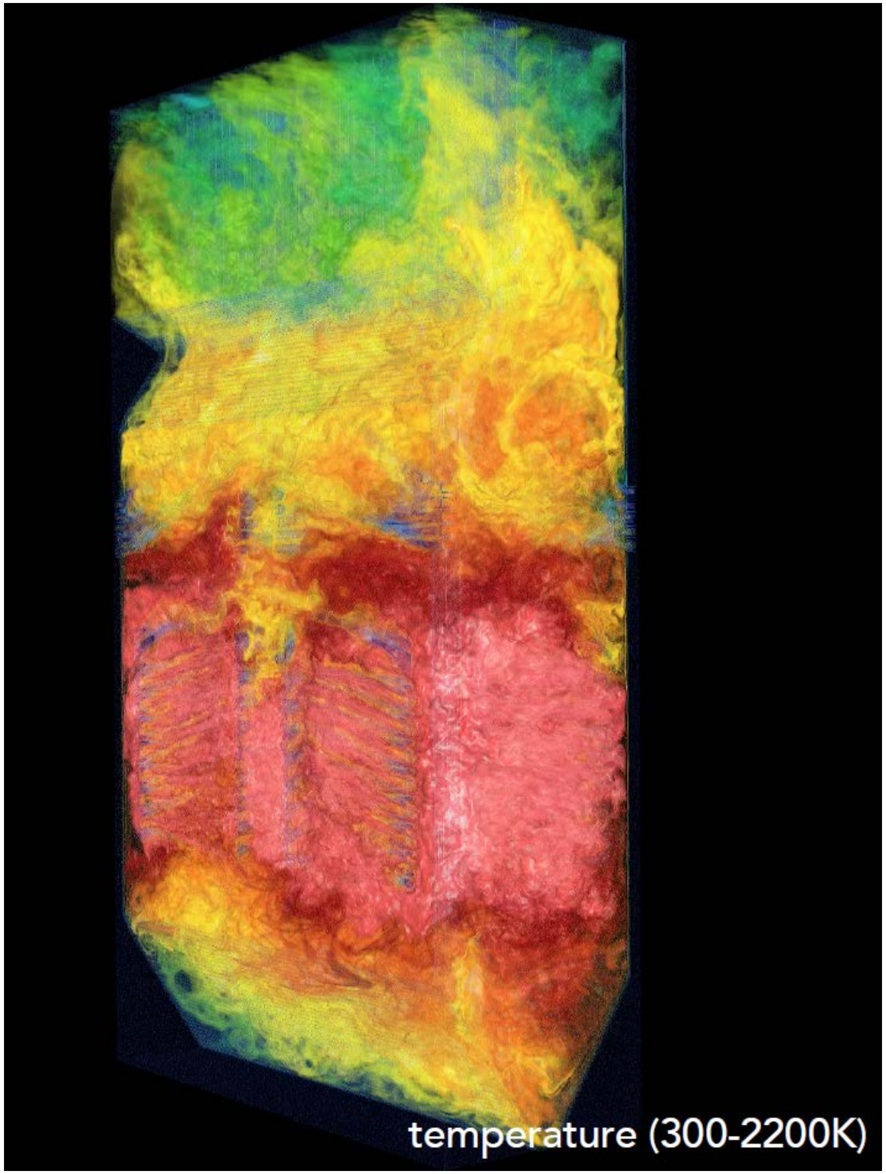
CARBON CAPTURE MULTIDISCIPLINARY SIMULATION CENTER

- PSAAPii:
  - *demonstrate positive societal impact of extreme computing*
  - *accelerate the deployment of a new technology: sCO_2 w CCUS (pressurized oxy-coal gasifier)*
  - ***demonstrate optimization of state-of-the-art coal boilers for global market demands (8-corner USC air-fired, 1GW)***
- GE:
  - *Model Form Uncertainty*
  - *Validation/UQ*
    - *expt. & sim. obtain predictivity*

$$y_e = y_m(x) + \epsilon + b$$

evidence: $$|\mathbb{E}(b)| \leq \sigma_e \qquad \forall e$$
$$|\overline{y_m(\mathbf{x})} - \overline{y_e}| \leq \sigma_e$$

1 GWe 8-corner GE Boiler



- LES, Eulerian-Eulerian
  - DQMOM for particle phase
  - Mixture fraction/equilibrium for gas phase
- 350 million core hours
- 4 simulations
- Each simulation:
  - 256,000 cores
  - 23days on MIRA
  - 8 days on TITAN
- Resolution:
  - 2.5 cm^3
  - 1 ms time step
  - 2 billion cells

Char Conversion

- Surface reactions (O_2, H_2O, CO_2)
  - Products include CO, CO_2, H_2
- Diffusion processes
  - Through external boundary layer
  - Through pores
- Changes in solid
  - Change in diameter, porosity, internal surface area
  - Change in reactivity
    - Annealing
    - Distribution of reactivity
  - Ash layer inhibition

Coal General Correlation?

- Coal general methods available for:
  - Coal pyrolysis (CPD, etc.)
  - Particle swelling
    - Empirical (Shurtz & Fletcher)
    - Detailed (Oh et al., Yang et al.)
  - Global char rate
    - Limited conditions only (Hurt & Mitchell)
- No coal general method available for char intrinsic rates
  - Ian Smith log-log plot
    - 5 orders of magnitude

Char Reaction Model Progress
(still not coal general)

- **CBK-E model** (Hurt & coworkers, 1998)
  - 3-step surface reaction
    - Changes effective reaction order with temperature
  - Thiele modulus for pore diffusion
  - Annealing, ash inhibition, (distributed E)
  - Crude swelling model
  - Empirical mode of burning (diameter/density change)
- **CBK-G model** (Niksa & coworkers, 2003-4)
  - Gasification by H_2O, CO_2, and H_2 (5-steps)
- **CCK model** (Shurtz & coworkers, 2011)
  - Combined CBK-E & CBK-G
- **CCK/oxy model** (Holland & Fletcher)
  - Improved CCK model applied to oxycoal combustion

Kinetic Parameters in CCK/Oxy

- 8-step system
- All steps tied to R3 and R7 via correlations
- For any given coal, 4 kinetic parameters contain plenty of flexibility (usually 2 are adequate)

$$2C + O_2 \rightarrow C(O)_\alpha + CO \quad \text{(R1)}$$

$$C + O_2 + C(O)_\alpha \rightarrow C(O)_\alpha + CO_2 \quad \text{(R2)}$$

$$C(O)_\alpha \rightarrow CO \quad \text{(R3)}$$

$$CO_2 + C \leftrightarrow C(O)_\delta + CO \quad \text{(R4)}$$

$$C(O)_\beta \rightarrow CO \quad \text{(R5)}$$

$$C + H_2O \leftrightarrow C(O)_\beta + H_2 \quad \text{(R6)}$$

$$C(O)_\beta \rightarrow CO \quad \text{(R7)}$$

$$C + 2H_2 \rightarrow CH_4 \quad \text{(R8)}$$

$$R_{C-O_2} = \frac{k_1 k_2 P_{O_2}^{(1+n_1)} + k_1 k_3 P_{O_2}}{k_1 P_{O_2} + \frac{k_3}{2}}$$

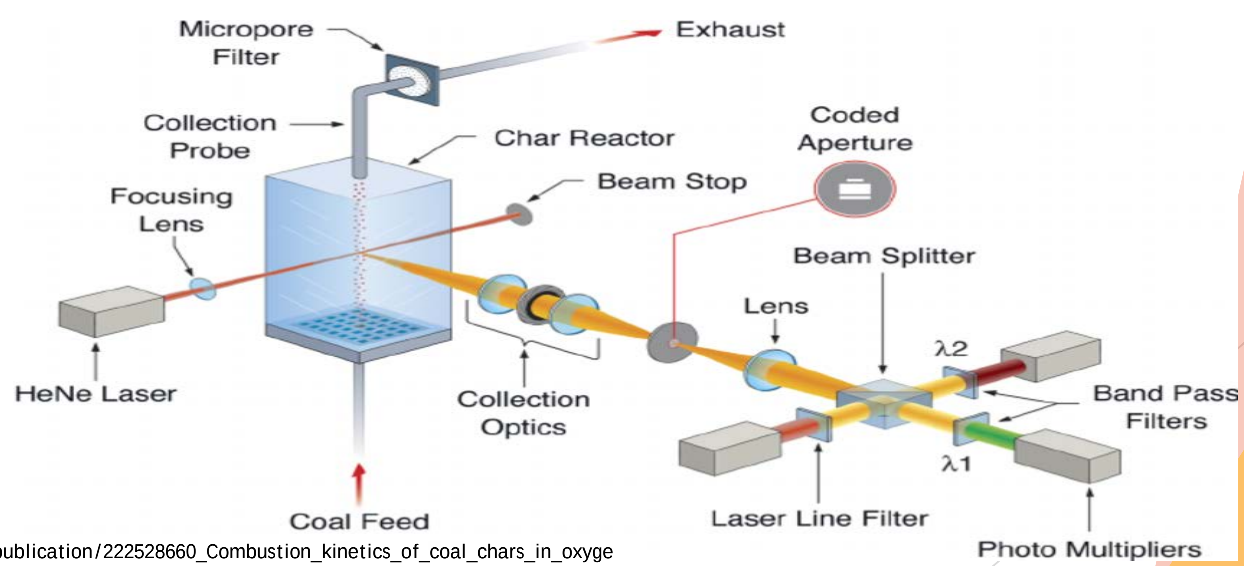
$$R_{C-CO_2} = \frac{k_4 P_{CO_2}}{1 + \frac{k_4}{k_5} P_{CO_2} + \frac{k_{4r}}{k_5} P_{CO} + \frac{k_6}{k_7} P_{H_2O} + \frac{k_{6r}}{k_7} P_{H_2}}$$

$$R_{C-H_2O} = \frac{k_8 P_{H_2O}}{1 + \frac{k_4}{k_5} P_{CO_2} + \frac{k_{4r}}{k_5} P_{CO} + \frac{k_6}{k_7} P_{H_2O} + \frac{k_{6r}}{k_7} P_{H_2}}$$

(Niksa et al., 2003; Liu and Niksa, 2004)
(Shurtz and Fletcher, 2013)

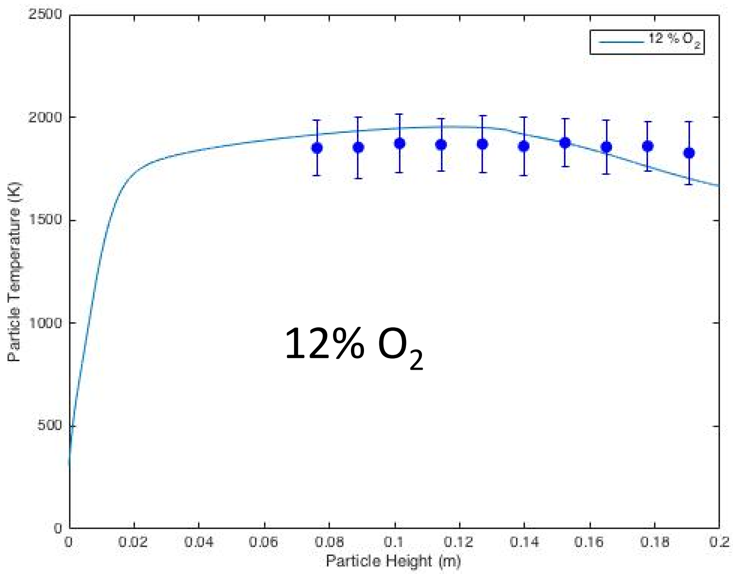
Sandia Oxy-coal Combustion Data

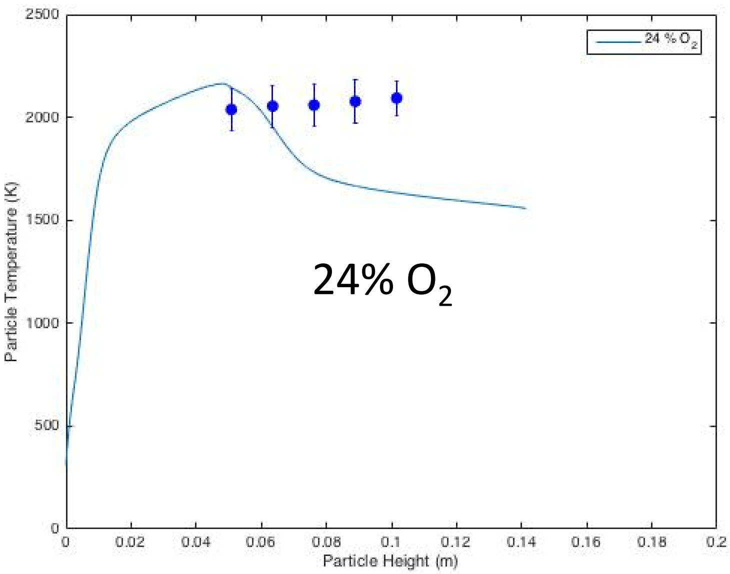
- Collected in a flat-flame burner at Sandia National Laboratory (Shaddix and Molina, 2009, 2011; Geier et al., 2012)
- Data points collected through 2-color pyrometery is used to collect particle temperature and diameter for thousands of individual particles at various heights above the burner
- T_g from 1400 to 1800°C, 12 to 36 mol% O_2 in post-flame gas
- In some setups, the char may be collected to measure degree of conversion
- The pyrometer is sensitive to total luminescent intensity
  - small, cool particles are not observed

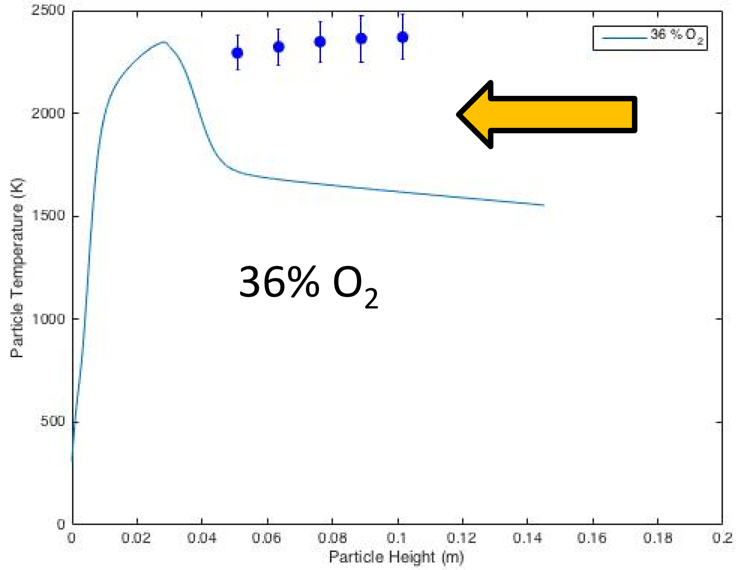


https://www.researchgate.net/publication/222528660_Combustion_kinetics_of_coal_chars_in_oxygen-enriched_environments

Best fit to Sandia T_p vs. z Data







Something wrong here!
Improvements needed!

Formal Sensitivity Analysis on CCK/Oxy Model Using the Shaddix Conditions

- Determine which submodels/ parameters are most important
- Global analysis varying all parameters simultaneously testing for both linear and non-linear sensitivity
- 27 parameters, 4 burn-out quartiles, 4 coals, 3 gas conditions, 2 quantities of interest, and 2 types of sensitivity analysis ≈5,000 measures of sensitivity extracted from 120,000 computational experiments
- Kinetic parameters most sensitive (obviously)
- Which submodels are most sensitive?

Parameter	Importance
$E_{Annealing}$	0.74
n_1 (reaction order)	0.51
d/d_0 (swelling)	0.27
α (mode of burning)	0.20
d_{grain} (ash grain size)	0.20
σ_{EA} (distribution of E_A)	0.18
$t_{residence}$ (which time quartile)	0.14

Holland and Fletcher, *Energy and Fuels*, 30, 9339–9350 (2016).

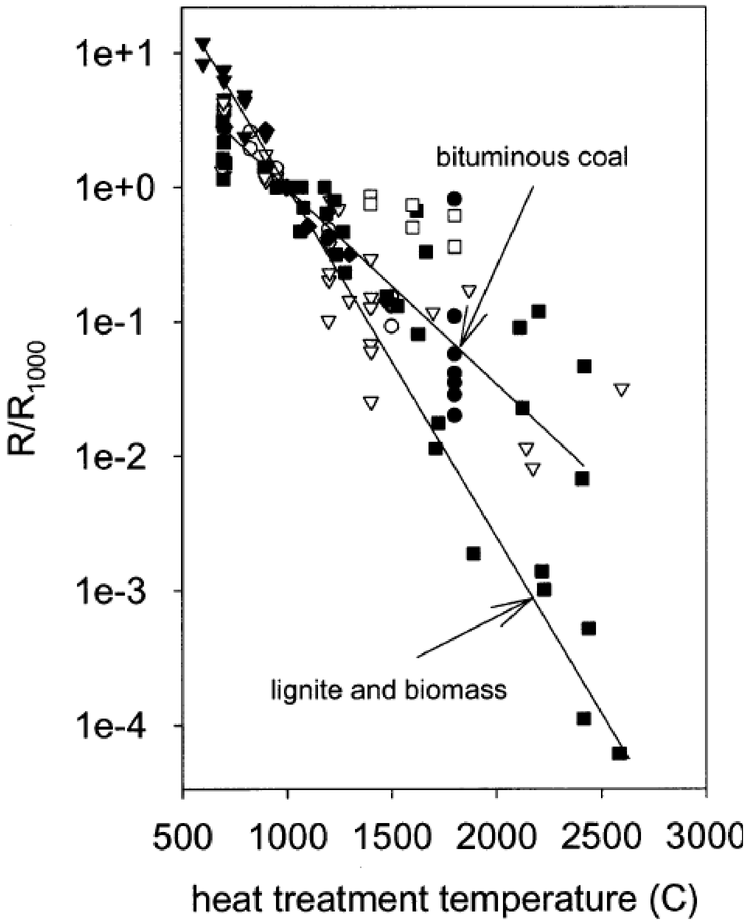
Char Annealing Introduction

- Initially observed decades ago
- Comprised of numerous activated processes beginning in initial heat-up and continuing throughout burnout
  - Pyrolysis (loss of heteroatoms and crosslinking)
  - Ash fusion (plugging pores and losing catalytic activity)
  - Changes in pore structure
  - Decrease in char structural defects
- May decrease char reactivity by orders of magnitude over a few ms
  - Shown to change reactivity by a factor of ~2-50 over as little as tens of ms at high T
- Occurs on widely varying time scales and to very different degree depending on coal type, heating rate, and peak temperature

Typical Annealing Data

- Generate a coal char at some specified residence time, temperature, and heating rate
- Measure a char reactivity in a TGA
- Compare different conditions

Example of Change in Reactivity Due to "Annealing"



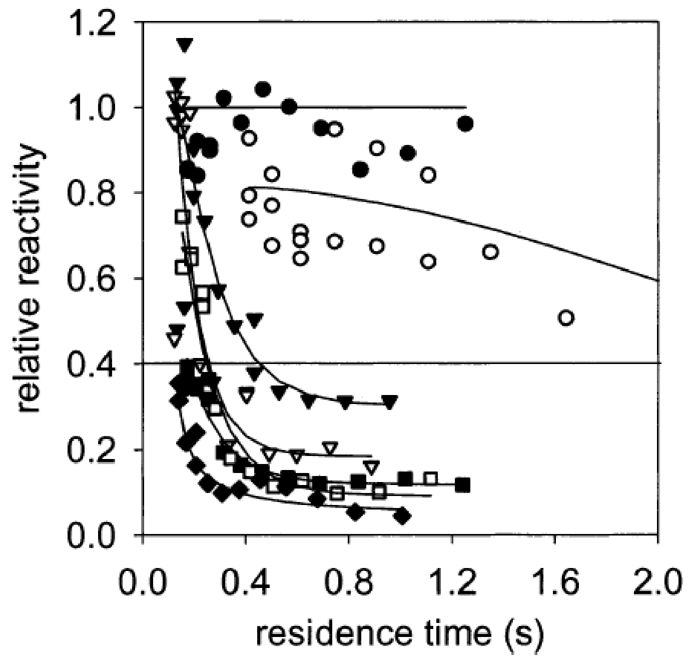


Figure 3. Reactivity of the Cerrejon coal chars after pyrolysis in the entrained flow reactor at various temperatures for various residence times. The relative reactivity is defined as the ratio of A_0 (see text) of any char to that of the char pyrolyzed at 700 °C for about 1 s. Points are experimental data and solid lines are fittings. The pyrolysis temperatures are (●) 700 °C. (○) 900 °C. (▼) 1000 °C. (▽) 1100 °C. (■) 1200 °C. (□) 1300 °C. (◆) 1475 °C.

Feng, et al., *Energy & Fuels*, 2003, 17, 399-404

Annealing Model
Starting Point (Hurt Model)

- Coal anneals as a series of first order kinetic reaction with a log-normal distributed activation energy
- All reactive sites have the same annealing activation energy
- Annealing affects only the preexponential factor of char conversion reactions

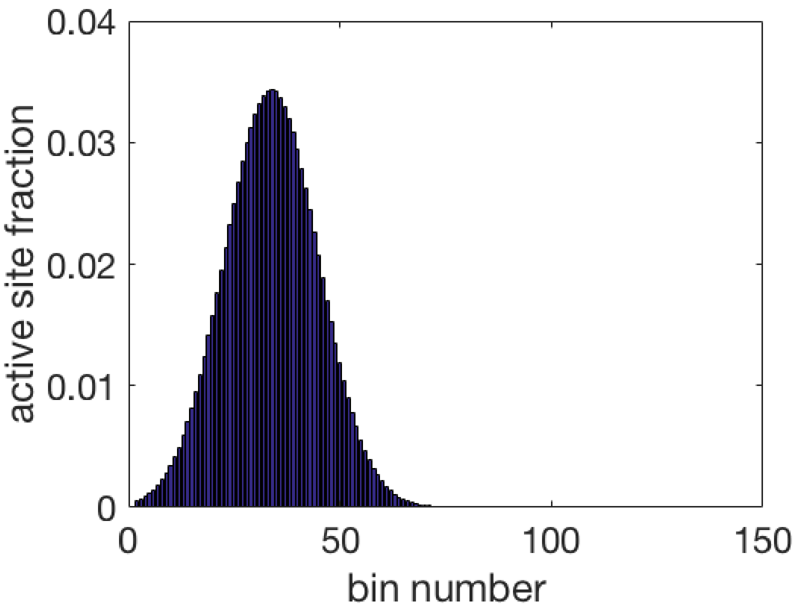
$$\frac{N_i(E_{d,i})}{N_0} = \frac{1}{\sigma_{E_d}\sqrt{2\pi}} \exp\left[-\frac{\left(\ln(E_{d,i}) - \mu_{E_d}\right)^2}{2\sigma_{E_d}{}^2}\right]$$

$$\sum_i \Delta E_d \left[\frac{N_i}{N_0}\right]_{initial} = \sim 1$$

$$\frac{df_i}{dt} = -A_d \exp\left(-E_{d,i}/(RT_p)\right) f_i$$

See Shurtz, R. C. and T. H. Fletcher, "Coal Char-CO_2 Gasification Measurements and Modeling in a Pressurized Flat-Flame Burner," *Energy & Fuels*, **27**, 3022-3038 (2013).

Log-Normal Distribution of E
(used in Hurt’s CBK model)



Log-normal distributed activation energy

- Initial annealing rate is very rapid
  - Changes rate by orders of magnitude in a few ms
- Pre-exponential factor for char oxidation rate must be increased substantially to compensate

How to Improve?

- Lots of data available since the Hurt model
- Lots of individual models, but no model has tried to explain <u>all</u> of the experiments (until now)
- Experiments performed at lots of different conditions

Impact of Preparation Conditions

- Heating Rate
  - Rapid loss of heteroatoms vs. cross linking
  - Degree of swelling and pore development
  - Annealing time scale compared to combustion time scale
- Peak Temperature
  - Fusion of potential catalysts (either for char conversion or carbon structural rearrangement)
  - Some changes in carbon turbostratic structure only occur as particles approach practical combustion regimes
  - Higher temperatures reduce the prevalence of O_2 complexes on the char surface

None of these effects are explicityly treated in the Hurt annealing model

Impact of Preparation Conditions (cont.)

- Coal type
  - Highly variable chemistry leads to radically different reactivity after char preparation
- Bulk Gas
  - CO_2 is not observed to hinder carbon structural rearrangements due to surface complexes in the same way as O_2
  - Different char conversion pathways imply the potential for differences in the relevant annealing pathway

Annealing Data in O_2

- Most literature data lack sufficient detail
  - proximate and ultimate analysis
  - definition of reactivity
  - an adequate time temperature profile
- Total of 167 data points

Coal Name	C	H	O	N	S	V_{ASTM}
Beulah Zap (Shim and Hurt, 2000)	73.2	4.4	20.6	1	0.8	42
Pocahontas (Shim and Hurt, 2000)	89.8	5	3.4	1.2	0.7	19.2
Illinois 6 (Shim and Hurt, 2000)	78.2	5.5	9.8	1.3	5.4	45.5
South African (Senneca et al., 2004)	80.6	4.51	12.6	1.4	0.7	27.4
Cerrejon (Feng et al., 2003b)	81.7	5.15	11.9	1.8	0.7	40.13
Pocahontas (Russell et al., 2000)	91.8	4.48	1.66	1.3	0.5	19.54
Pittsburgh 8 (Russell et al., 2000)	84.9	5.43	6.9	1.6	0.9	41.7
Tillmanstone (Cai et al., 1996)	91.4	4.4	2.2	1.3	0.7	18.1
Pittsburgh 8 (Cai et al., 1996)	83.2	5.3	9	1.6	0.9	41.7
Lindby (Cai et al., 1996)	81	5.3	11	1.7	1	37.5
Illinois 6 (APCS)(Cai et al., 1996)	77.7	5	13.5	1.4	2.4	47.4
Illinois 6 (SBN)(Cai et al., 1996)	75.6	5.8	14.5	1.4	2.7	47
South African (Bar-Ziv et al., 2000)	80.6	4.51	12.6	1.4	0.7	27.4
High Volatile Bituminous (Naredi and Pisupati, 2008)	80.3 3	5.95	10.9 7	1.4 4	0.9 6	44.43
Pittsburgh 8 (Gale, 1994; Gale et al., 1995,	84.9	5.43	6.9	1.6	0.9	41.7
Blind Canyon (Gale, 1994; Gale et al., 1995,	81.3	5.81	10.8	1.5	0.3	48.11
Beulah Zap (Gale, 1994; Gale et al., 1995,	74.0	4.9	19.1	1.1	0.7	49.78
South African (Senneca et al., 1997)	82.5	4.6	13.2	1.4	0.7	27.43
South African (Salatino et al., 1999)	82.6	4.51	12.6	1.4	0.7	27.4
Shenfu (Wu et al., 2008)	80.1	5.52	12.2	1.8	0.2	40.64
Rhur (Senneca et al., 1998)	81.0	5.03	10.4	2.1	1.2	32.91
South African (Bar-Ziv et al., 2000)	80.6	4.51	12.6	1.4	0.7	27.4
High Ash Indian (Jayaraman et al., 2015)	72.8	4.65	19.9	1.7	0.8	50.03

Annealing Data in CO_2

- Far less sufficiently detailed annealing data in CO_2 and virtually none in steam
- Total of 70 data points

Coal Name	Carbon %	Hydrogen %	Oxygen %	Nitrogen %	Sulfur %	ASTM Volatile %
South African (Senneca et al., 1997)	82.5	4.6	13.2	1.46	0.73	27.43
South African (Salatino et al., 1999)	82.66	4.51	12.69	1.46	0.73	27.4
Shenfu (Wu et al., 2008)	80.14	5.52	12.29	1.83	0.22	40.64
Rhur (Senneca et al., 1998)	81.03	5.03	10.48	2.1	1.2	32.91
South African (Bar-Ziv et al., 2000)	80.66	4.51	12.69	1.46	0.73	27.4
High Ash Indian (Jayaraman et al., 2015)	72.82	4.65	19.91	1.79	0.83	50.03

Annealing Model Extension

- The distribution (not just the reaction rate) depends on
  - coal particle heating rate
  - peak temperature, and
  - chemical structure

$$if\ HR < 10^4\ K/s \qquad A_d = \frac{p_0 * A_{d,0}}{\ln(HR + 2.7)}$$

$$if\ HR \geq 10^4\ K/s \qquad A_d = \frac{p_0 * A_{d,0}}{\ln(10^4)}$$

$$\ln(\sigma_{E_d}) = \frac{\ln(\sigma_0)}{p_0}$$

$$if\ T_p \leq 1500\ \mathrm{K} \qquad \ln(\mu_{E_d}) = \mathrm{a} * p_0 + \mathrm{b} + T_p * c/1000$$

$$if\ T_p > 1500\ \mathrm{K} \qquad \ln(\mu_{E_d}) = \mathrm{a} * p_0 + b$$

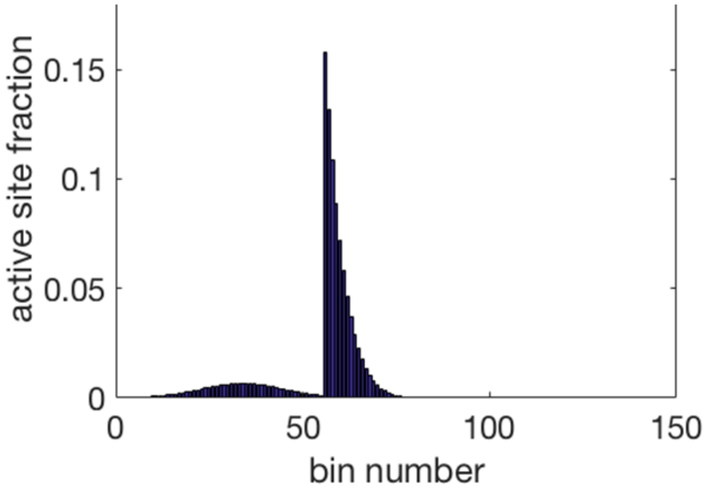
- O_2 char conversion may be impacted differently by annealing than CO_2 and H_2O char conversion

HR = particle heating rate
T_p = maximum temperature during heating
p_0 = coal type parameter from NMR

Holland, T., S. Bhat, P. Marcy, J. Gattiker, J. D. Kress, and T. H. Fletcher, "Modeling Effects of Annealing on Coal Char Reactivity to O_2 and CO_2 Based on Preparation Conditions," *Energy and Fuels*, **31**, 10727-10744 (2017).

Annealing Model Extension

- The distributed activation energy is bimodal and irregular
- First part is during pyrolysis
  - Accounts for heating rate
- Second part is during char oxidation
  - Temperature and residence time effects
- Method described to generate irregular (bimodal) distribution



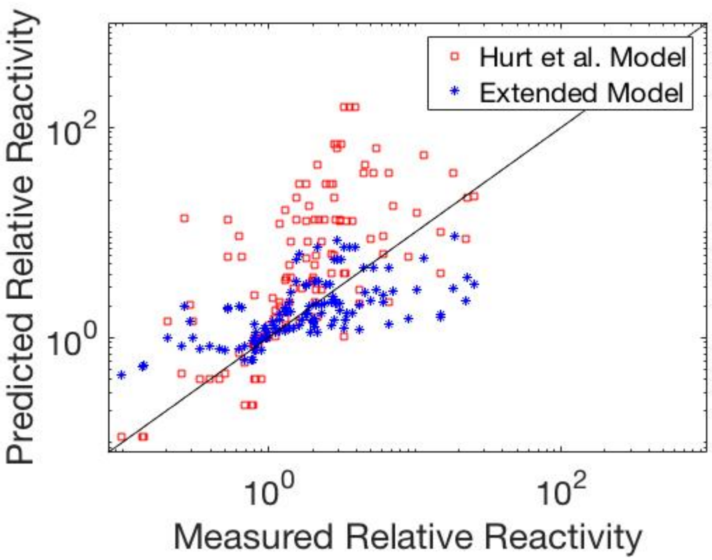
Irregular distributed activation energy

Holland, T., S. Bhat, P. Marcy, J. Gattiker, J. D. Kress, and T. H. Fletcher, "Modeling Effects of Annealing on Coal Char Reactivity to O_2 and CO_2 Based on Preparation Conditions," *Energy and Fuels*, **31**, 10727-10744 (2017).

Data Fitting

- Bayesian approach
- Sophisticated Uncertainty Quantification (UQ) codes at Los Alamos

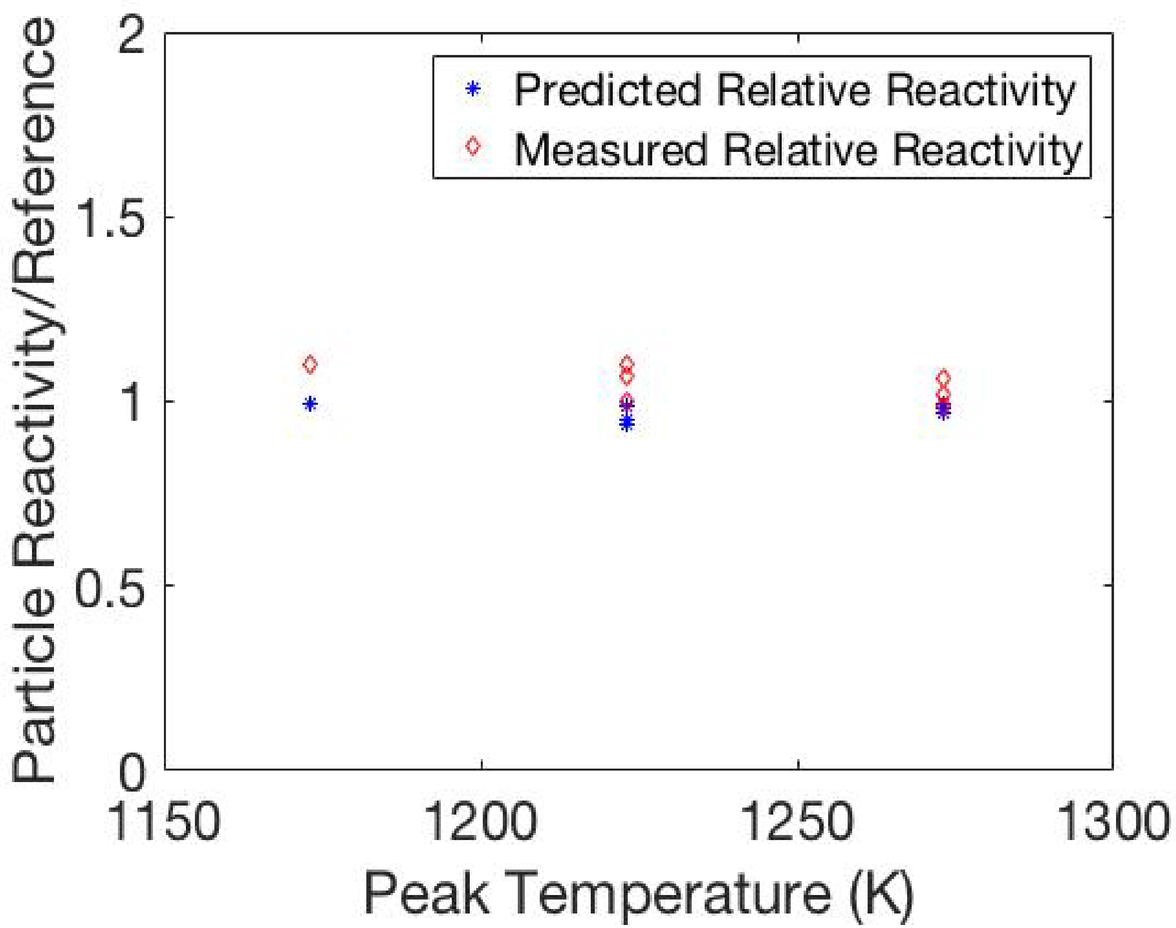
Annealing Model Results



	Hurt et al. Model			Extended Model		
Model Quantification	**Mean**	**Minimum**	**Maximum**	**Mean**	**Minimum**	**Maximum**
Sum Squared Error	1.45x10^{5*}	N/A	N/A	2.43x10^{3}*	N/A	N/A
Error Factor: All Points	**6.08**	**1.00**	**51.97**	**2.24**	**1.00**	**9.96**
Error Factor: Least Successful Quartile	17.28	7.00	51.97	4.44	2.30	9.96
Error Factor: Most Successful quartile	1.13	1.00	1.25	1.10	1.00	1.20
Error Factor: Central Quartiles	2.78	1.25	6.50	1.63	1.21	2.27

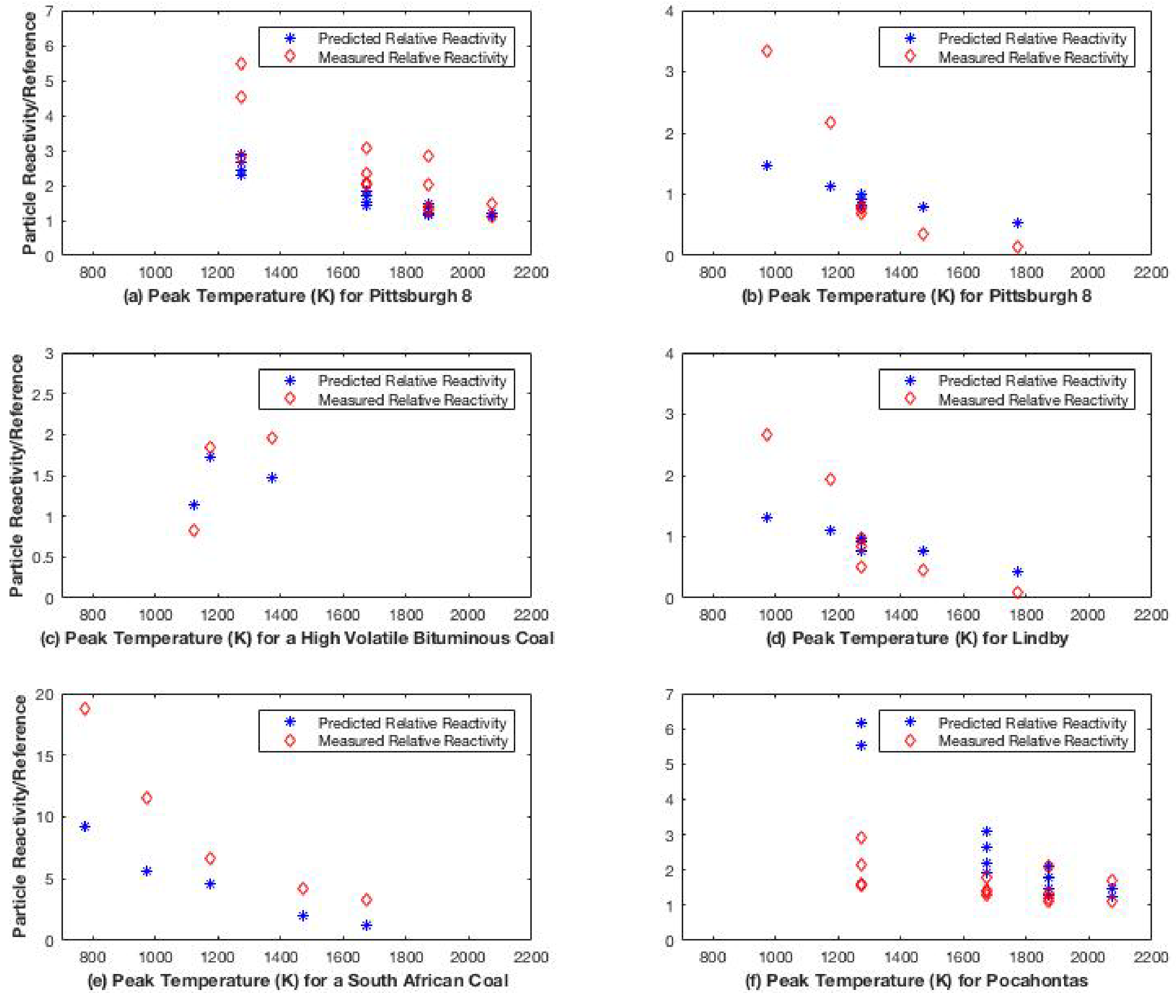
- Relative reactivity defined as the ratio of the reactivity at any time to some reactivity of that char at some standard time (initial, middle, or end)
- The log-log plot can be highly misleading, so an error factor is defined
  - Error factor = the greater of $r_{modeled}/r_{measured}$ and $r_{measured}/r_{modeled}$
- Mean error factor decreased from a factor of 6 to a factor of 2 with new model

Annealing Model Uncalibrated Results



Annealing model predictions with new data
(not used in the calibration)

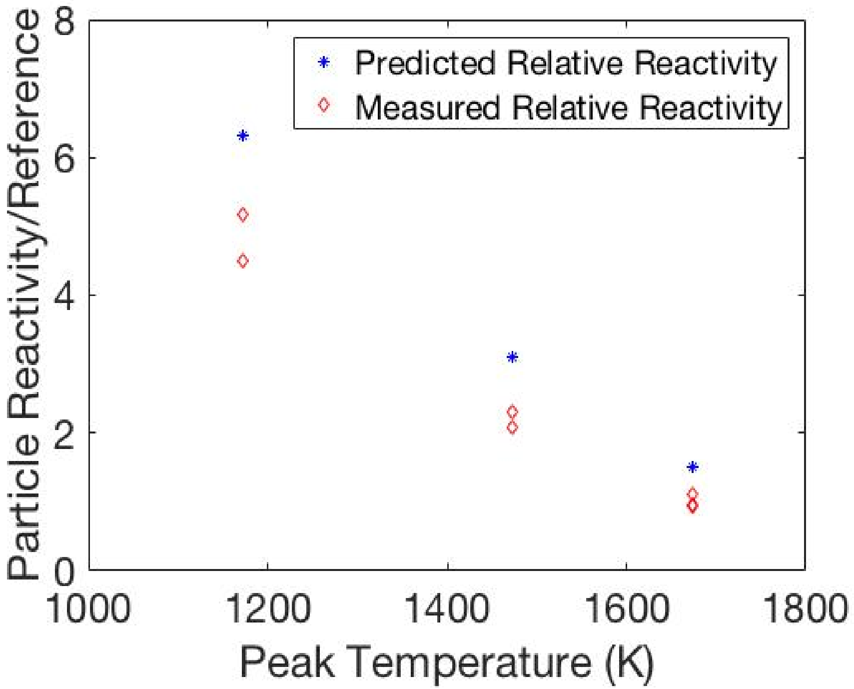
Annealing Model Results



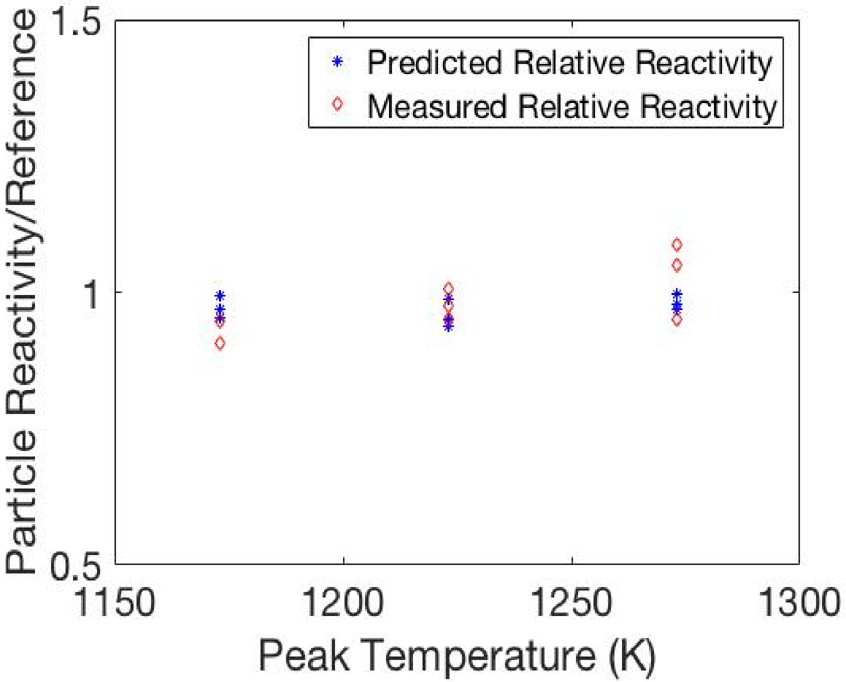
Results from several coals and experimental sources

Annealing Model Results

(vs. CO_2 and H_2O gasification data)



Sample CO_2 Data and Model Predictions

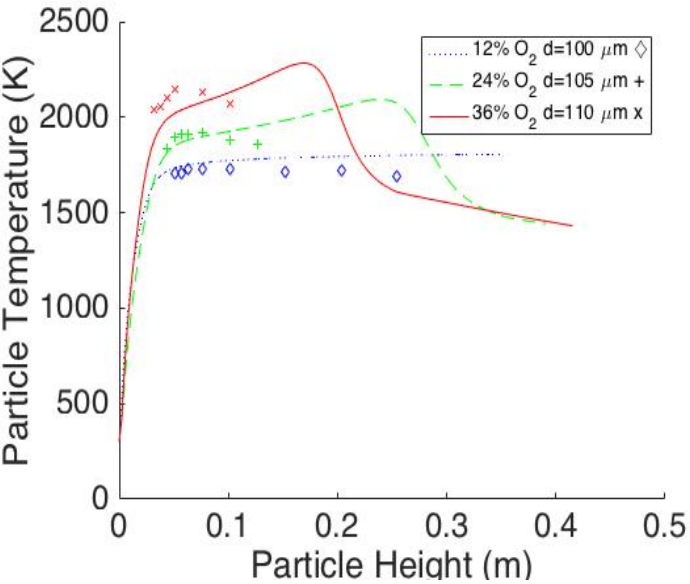


H_2O Data and Model Predictions

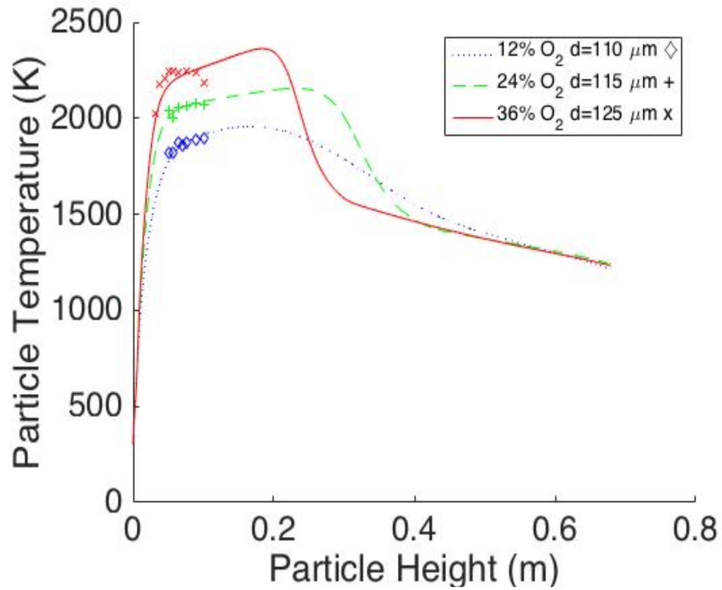
Summary of New CCK/oxy Model

- Used CPD model to predict starting char yield
- Used Shurtz swelling model to predict d_0
- Used Thiele modulus, mode of burning parameter from recent Mitchell paper based on Thiele modulus
- Used new annealing model
- Note that small particles burn out and their temperature is lower than optical measurement threshold
- Compare with Sandia optical temperature data (next few slides)
  - One diameter only
  - Two diameters

CCK/oxy Results:
Single Diameter Model



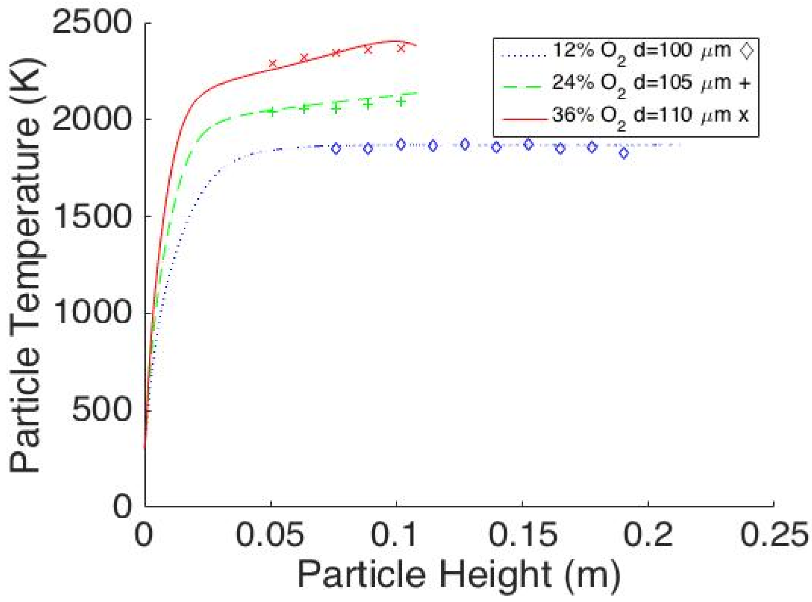
Black Thunder Coal



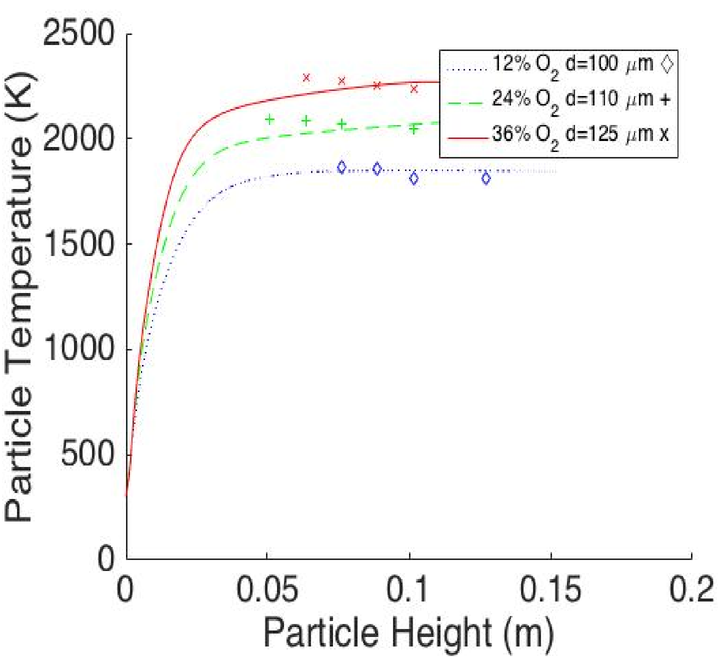
Pittsburgh 8 Coal

Holland, T. and T. H. Fletcher, “A Comprehensive Model of Single Particle Pulverized Coal Combustion Extended to Oxy-coal Conditions,” *Energy and Fuels*, **31**, 2722–2739 (2017).

CCK/oxy Results: Single Diameter Model



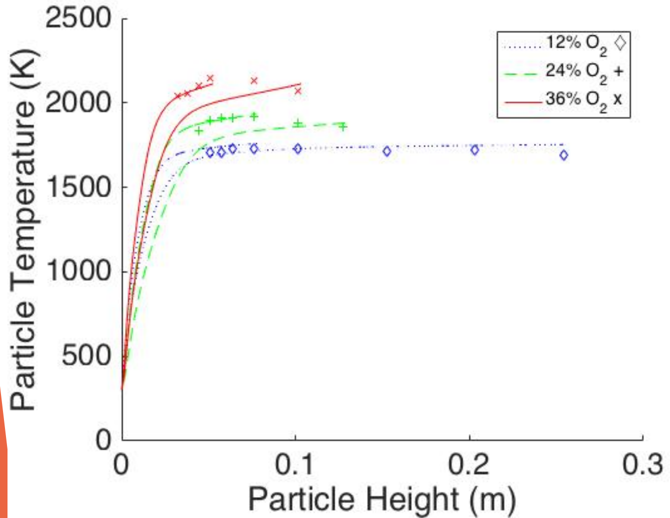
North Antelope



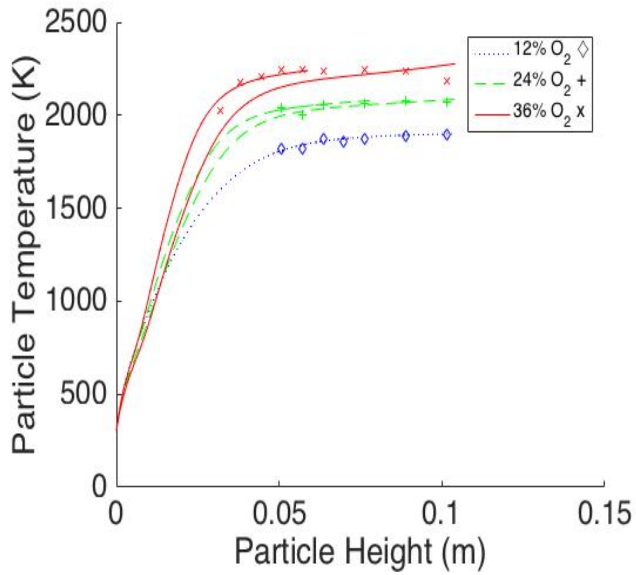
Utah Skyline

Holland, T. and T. H. Fletcher, "A Comprehensive Model of Single Particle Pulverized Coal Combustion Extended to Oxy-coal Conditions," *Energy and Fuels*, **31**, 2722–2739 (2017).

CCK/oxy Results:
Two Diameter Model



Black Thunder Coal



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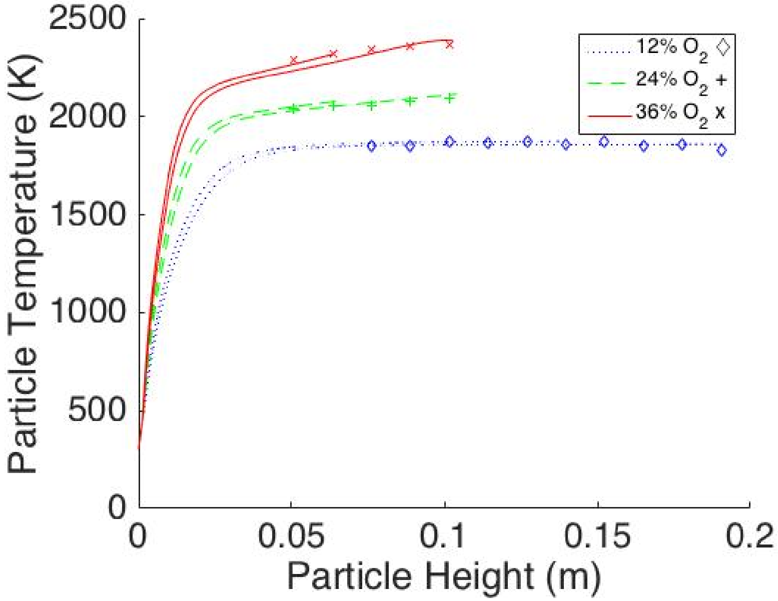
CCK/oxy Results: Two Diameter Model



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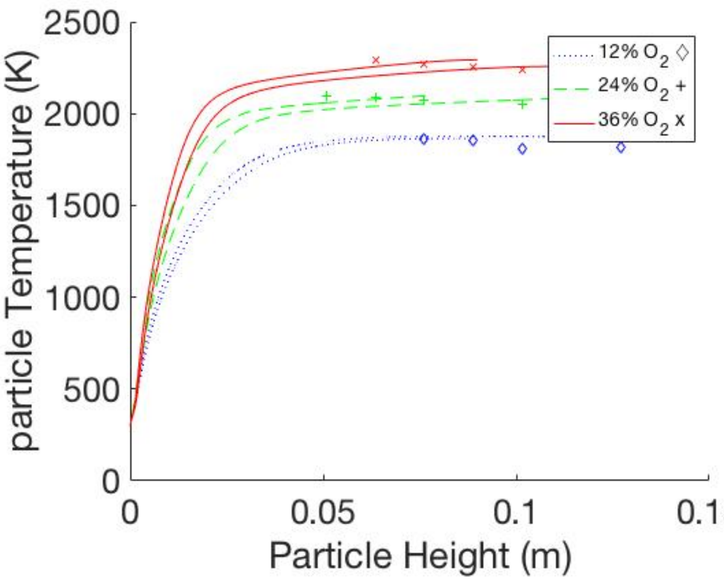

Utah Skyline

Holland, T. and T. H. Fletcher, "A Comprehensive Model of Single Particle Pulverized Coal Combustion Extended to Oxy-coal Conditions," *Energy and Fuels*, **31**, 2722–2739 (2017).

Summary & Conclusions

- A comprehensive, global sensitivity analysis was implemented for the first time on a comprehensive coal combustion code in oxy-fuel conditions
  - Annealing model identified as most sensitive
  - Particle diameter also very important
- The state of the art char conversion code (previously shown to be woefully inadequate in oxy-coal scenarios) was updated to be robust and auto-adaptive in far more extreme conditions
- Numerous sensitive submodels were updated based on literature observations, additional physics, and data collected over the past 20 years, including:
  - The CPD model
  - The Shurtz swelling model
  - An alternative mode of burning approach
  - An extended annealing model are of particular value.
- New submodels were guided by Bayesian uncertainty quantification and discrepancy analysis methods.

Summary & Conclusions

- The new annealing submodel decreased average error factor from 6 to 2, with terms to account for:
  - Coal type (char precursor) using p_0 (determined from NMR analysis)
  - Peak particle temperature (T_p)
  - Particle heating rate (HR)
- The annealing model, in conjunction with the other updated submodels, may enable a coal-general kinetic correlation (the elusive “Holy Grail” of coal combustion)
- The updated annealing model was shown to be effective (for the first time) in predicting CO_2 and H_2O reactivity loss as well as O_2 annealing
- Future annealing model work may include careful experiments at very short treatment times and a more thorough examination of coal ash chemistry.

Summary & Conclusions

- The final CCK/oxy model was validated against Shaddix data and shown to perform very well
- The CCK/oxy model was shown to perform reasonably well in extrapolation scenarios, which has enormous potential value in seeking a truly coal-general model
- Individual coal particle data are highly variable, and an accurate model must accept distributions in both particle diameter and particle composition (even within a single coal)
- Future work ideas:
  - Implementing high pressure functionality into CCK/oxy
  - General model updates as new data become available
  - A kinetic scheme that correlates a vast database of coal from practical combustion conditions to kinetic parameters via coal structure (NMR) parameters

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