Modeling Effects of Annealing on Coal Char Reactivity to O_2 and CO_2 Based on Preparation Conditions

Troy Holland[1] and Thomas H. Fletcher[2]

[1]Los Alamos National Laboratory, Los Alamos, NM
[2]Chemical Engineering Dept., Brigham Young University, Provo, UT

Western States Section of the Combustion Institute
University of Wyoming, Laramie, WY
Oct 2-3, 2017

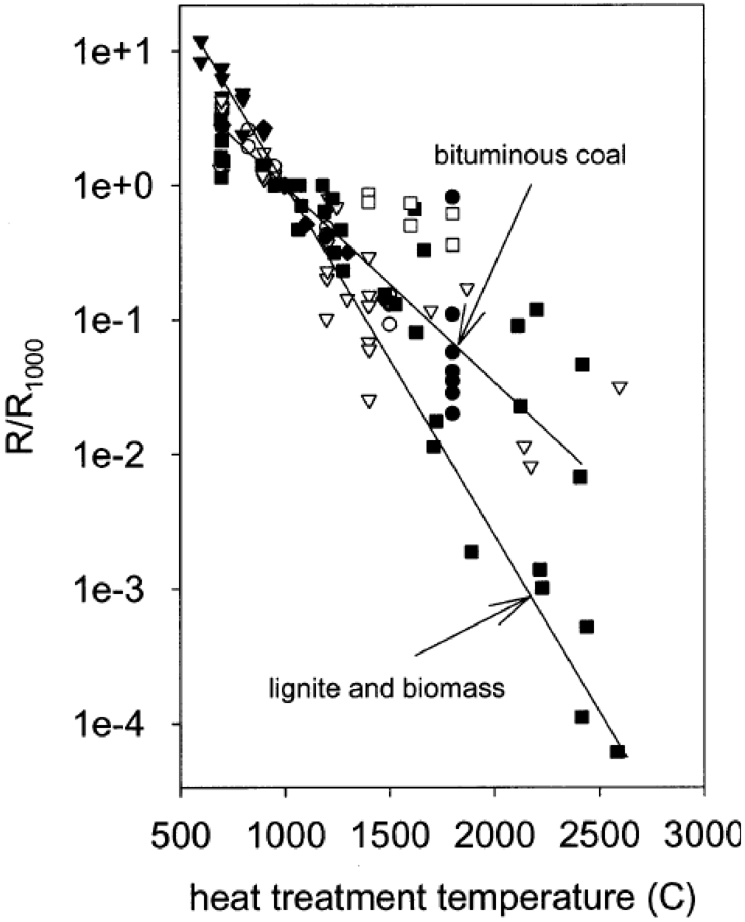
Char Annealing Introduction

- 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
- Can decrease char reactivity by orders of magnitude
- 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"



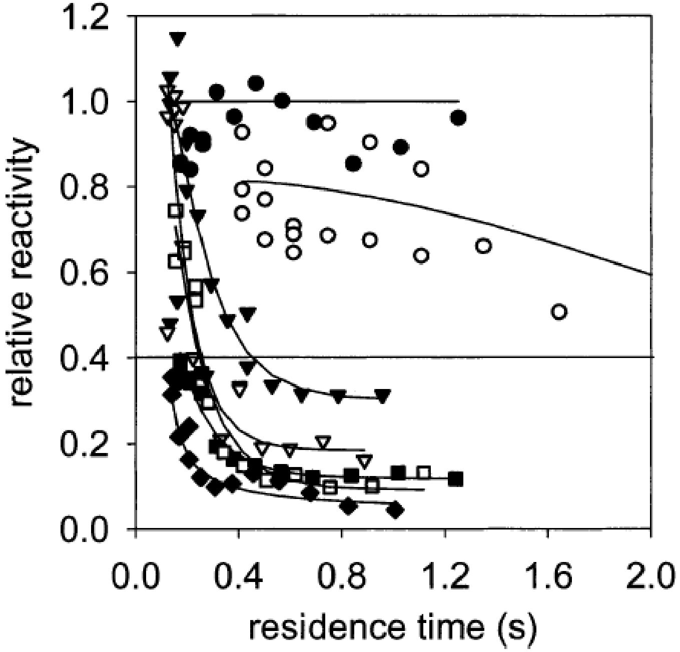


Figure 3. Reactivity of the Cerrejon coal chars after pyrolysis in the entrained flow reactor at various temperatures for various residence times. The relative reactivity is defined as the ratio of A_0 (see text) of any char to that of the char pyrolyzed at 700 °C for about 1 s. Points are experimental 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

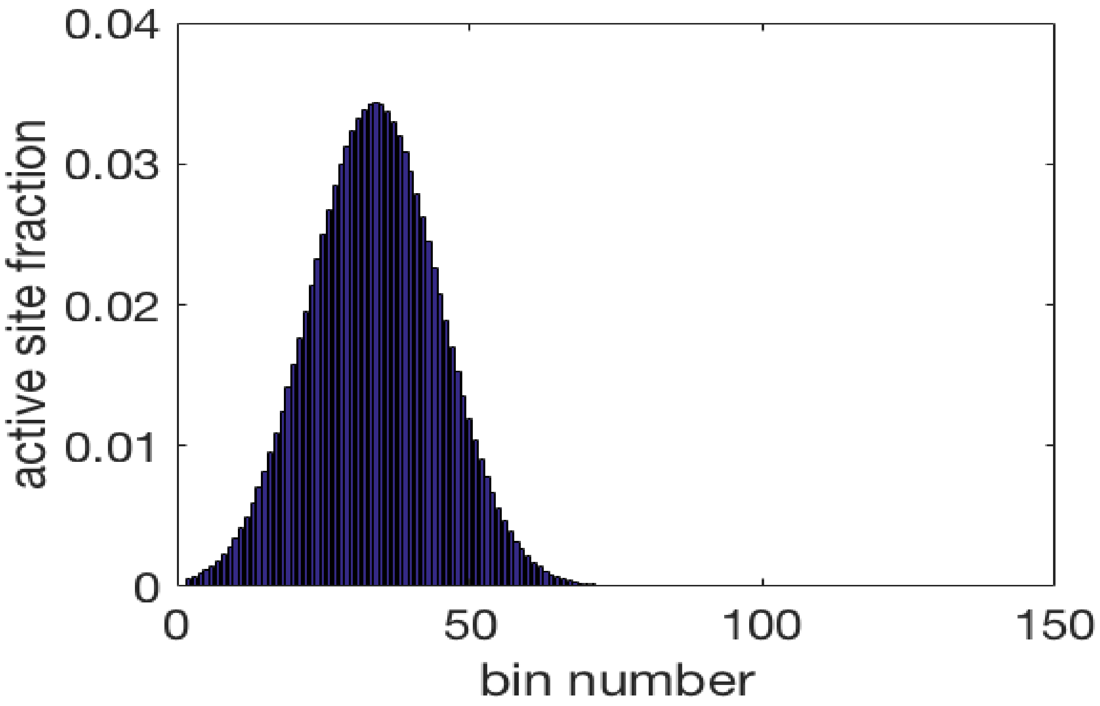
$$\frac{N_i(E_{d,i})}{N_0} = \frac{1}{\sigma_{E_d}\sqrt{2\pi}} \exp\left[-\frac{\left(\ln\left(E_{d,i}\right) - \mu_{E_d}\right)^2}{2{\sigma_{E_d}}^2}\right]$$

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

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

Log-Normal Distribution of E

(used in CBK model)



Log-normal distributed activation energy

Hurt Model

- 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 all 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 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)	80.33	5.95	10.97	1.44	0.96	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

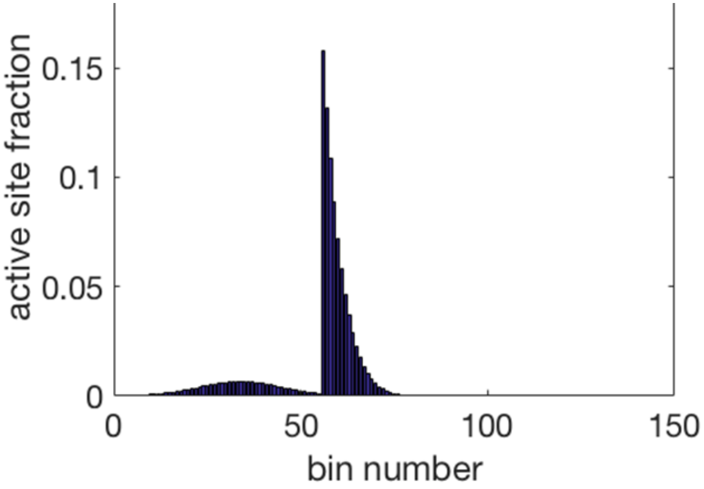
Annealing Data in CO_2

- 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 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



Irregular distributed activation energy

Annealing Model Extension
(cont.)

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

$$if\ HR < 10^4\ K/s \qquad A_d = \frac{p0 * A_{d,0}}{\ln(HR + 2.7)}$$

$$if\ HR \geq 10^4\ K/s \qquad A_d = \frac{p0 * A_{d,0}}{\ln\left(10^4\right)}$$

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

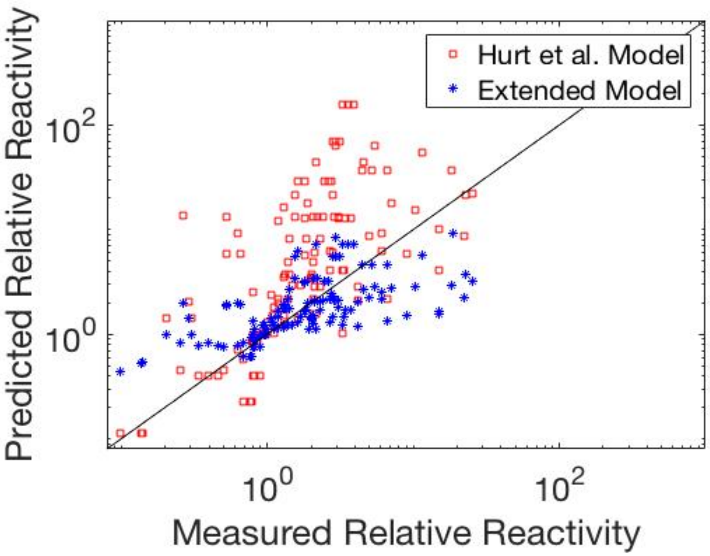
$$if\ T_p > 1500\ \mathrm{K} \qquad \ln\left(\mu_{E_d}\right) = \mathrm{a} * p_0 + b$$

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

Data Fitting

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

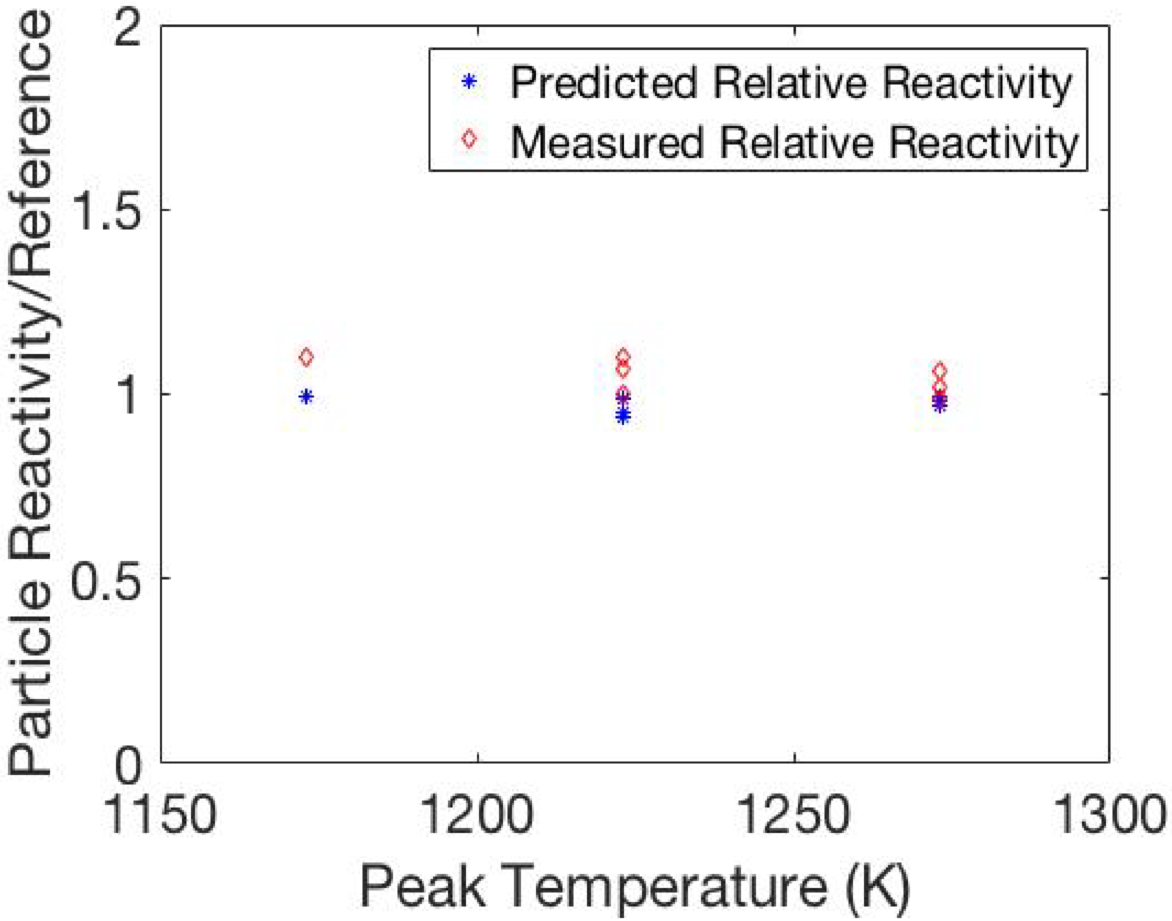
Annealing Model Results



	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

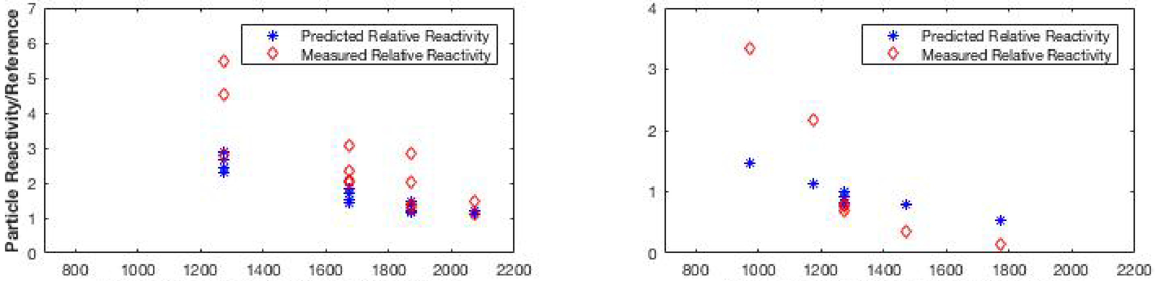
- **The log-log plot can be highly misleading, so an error factor is defined**
- **Mean Error factor decreased by a factor of 3 with new model**

Annealing Model Uncalibrated Results



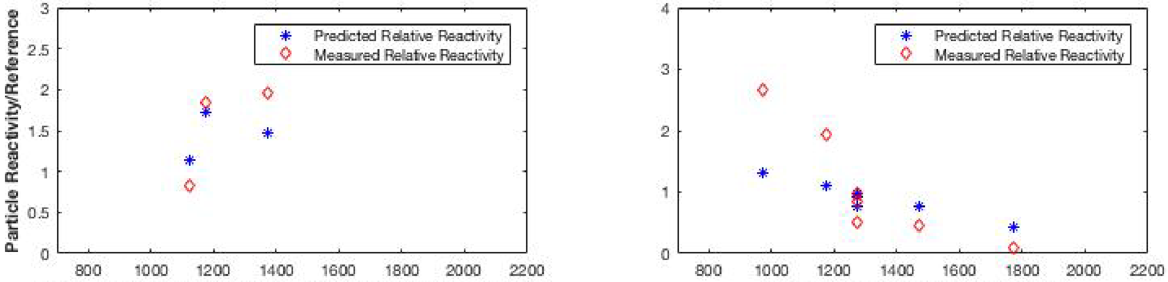
Annealing model predictions with new data
(not used in the calibration)

Annealing Model Results



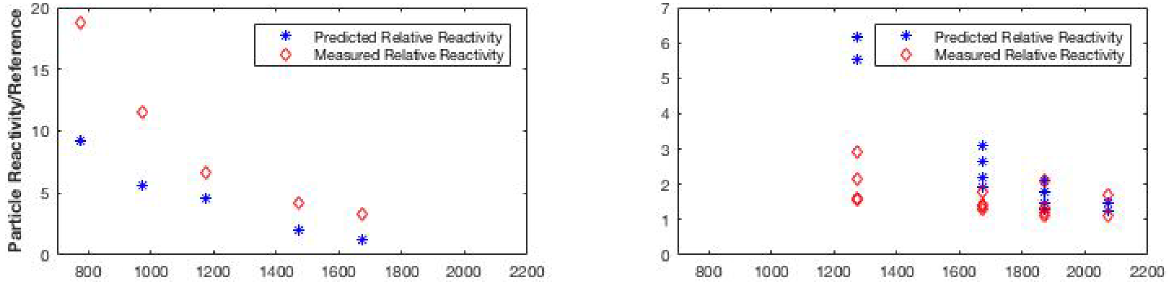
(a) Peak Temperature (K) for Pittsburgh 8

(b) Peak Temperature (K) for Pittsburgh 8



(c) Peak Temperature (K) for a High Volatile Bituminous Coal

(d) Peak Temperature (K) for Lindby

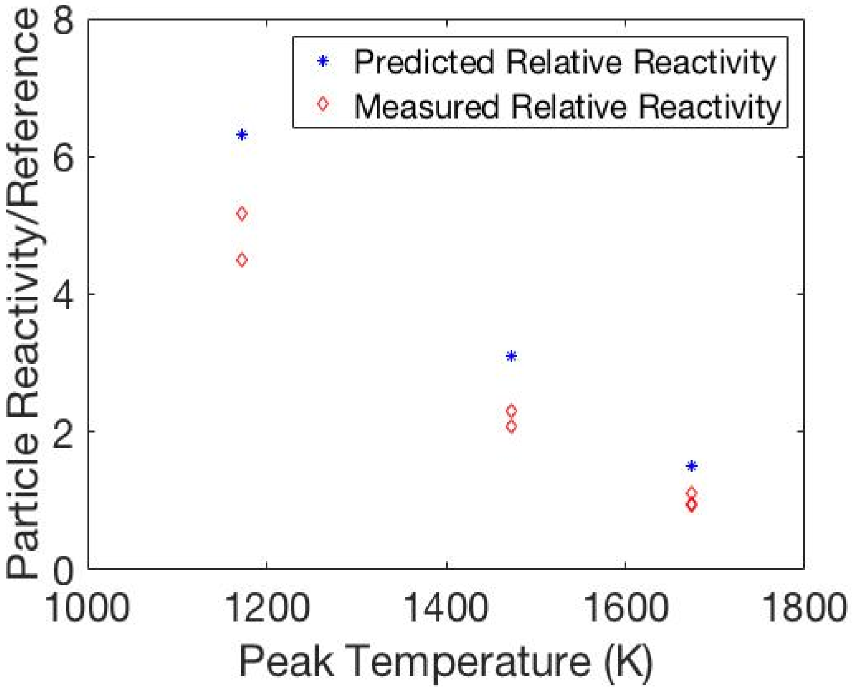


(e) Peak Temperature (K) for a South African Coal

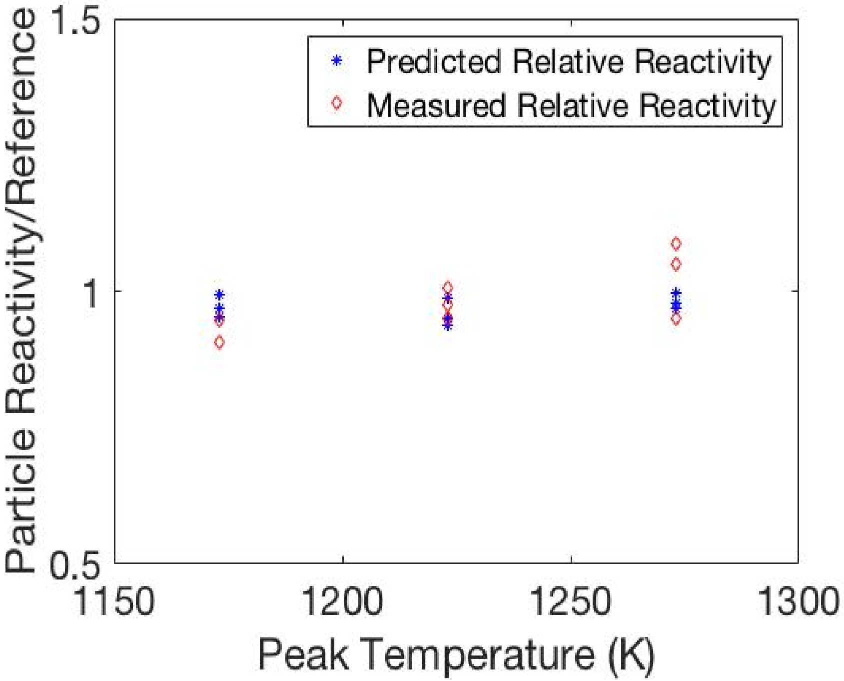
(f) Peak Temperature (K) for Pocahontas

Results from several coals and experimental sources

Annealing Model Results



Sample CO_2 Data and Model Predictions



H_2O Data and Model Predictions

Conclusions

- The resulting annealing model was shown to be a significant improvement
  - Average error decreased to roughly a factor of two
  - Hurt model had an average error of a factor of five Much of the error is found in low-temperature preparation condition experiments with high variance
- The annealing mode, when trained to *only* a subset of data taken in oxidative conditions, was successful in predicting
  - other data from oxidative conditions *and*
  - data taken in CO_2 or steam gasification conditions

Acknowledgements

This material is based upon work supported in part by the Department of Energy, National Nuclear Security Administration, under Award Number DE-NA0002375.

Funding for this work was provided by the Department of Energy through the Carbon Capture Simulation Initiative (CCSI) and the Carbon Capture Simulation for Industry Impact (CCSI^2) projects.

Los Alamos National Laboratory is operated by LANLS, LLC for the NNSA of the U.S. DoE under contract No. DE – AC52-06 NA 25396. Release No. LA-UR-17-24629

Disclaimer

Thank You!