# Calibration and Extension of a Coal Char Annealing Model

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# Synergistic Programs with a Carbon Capture goal

CARBON CAPTURE MULTIDISCIPLINARY SIMULATION CENTER

- **CCSMC**- Carbon Capture Simulation Multi-disciplinary Center
- Created by PSAAP II, an NNSA program
- Primary goal of promoting super computing in the community
- Secondary goal of enabling oxy-fuel combustion design for industry

CCSI Carbon Capture Simulation Initiative

- **CCSI I** (Carbon Capture Sequestration Initiative)
- DoE Office of Fossil Energy
- Primary goal of assisting industry in making carbon capture a feasible reality
- Provides tools for industry friendly (small cluster and desktop) models and simulation based design

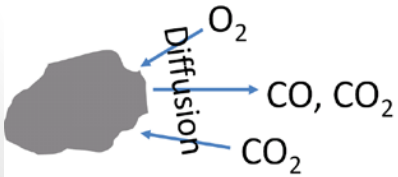
**Basic data models from CCSMC are improved via tools designed in CCSI.**

# Char Conversion (my work in Basic Data Models)

Raw coal heats and reacts in several steps:

- Particle heating (typical industrial heating rates at ~ $10^5$ K/s)
- Devolatilization/Swelling/Crosslinking
- Char conversion
  - Exothermic ($O_2$)
  - Endothermic ( $CO_2$ and $H_2O$)
  - Needs to be modeled with detailed submodels (kinetics, transport, etc.)
  - Current work is focused on the thermal annealing of coal char

**My work takes basic data submodels, builds basic data macro-models, and propagates the uncertainty. This presentation outlines the work is progress with a particularly useful calibration and uncertainty quantification method.**



# Calibration Step 1: Sensitivity Analysis

- Global sensitivity analysis of a comprehensive combustion code
- Should the annealing model be so sensitive, and if so, how can it be appropriately expressed?

**Table 1 – Total sensitivity measures for all $O_2$ conditions and each individual condition**

| Mean Sensitivity Measures | | Sensitivity for $O_2$ Mole Fraction=0.12 | | Sensitivity for $O_2$ Mole Fraction=0.24 | | Sensitivity for $O_2$ Mole Fraction=0.36 | |
|---|---|---|---|---|---|---|---|
| **Variable** | **Importance** | **Variable** | **Importance** | **Variable** | **Importance** | **Variable** | **Importance** |
| $E_A$ | 0.74 | $E_A$ | 0.76 | $E_A$ | 0.72 | $E_A$ | 0.75 |
| N | 0.51 | N | 0.55 | N | 0.51 | N | 0.48 |
| $\Omega$ | 0.27 | $\Omega$ | 0.40 | $\Omega$ | 0.22 | $\alpha$ | 0.22 |
| $\alpha$ | 0.20 | $g_d$ | 0.20 | $\alpha$ | 0.22 | $\sigma$ | 0.20 |
| $g_d$ | 0.20 | $t_r$ | 0.18 | $g_d$ | 0.21 | $g_d$ | 0.19 |
| $\sigma$ | 0.18 | $\alpha$ | 0.18 | $\sigma$ | 0.17 | $\Omega$ | 0.17 |
| $t_r$ | 0.14 | $\sigma$ | 0.17 | $t_r$ | 0.12 | $t_r$ | 0.11 |

# Coal Char Annealing

- An umbrella term to describe the physical and chemical changes in coal particles
  - Definition sometimes includes pyrolysis
  - Physical changes to the morphology of the coal and the ash
  - Chemical changes to the organics via crosslinking, ash-catalyzed rearrangement, devolatilization, and graphitization
  - Past models typically model the various chemical and physical processes with some sort of distributed activation energy

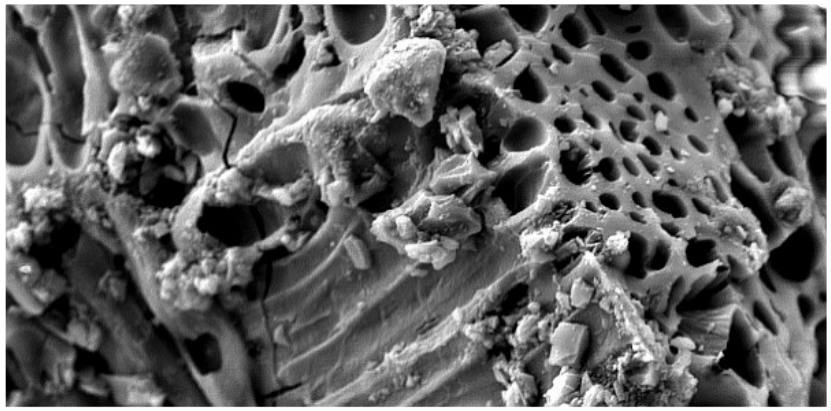


Figure 1- Pyrolyzed char

# Sample data

- The body of literature data shows that annealing depends on many things, but most especially on
  - Heating rate
  - Soak time
  - Peak particle temperature
  - Coal precursor

This sample shows that annealing conditions (or pyrolysis conditions) DO in fact have an enormous impact.

**Sample raw data used in the calibration (from a South African bituminous coal, Senneca et al. 1999 )**

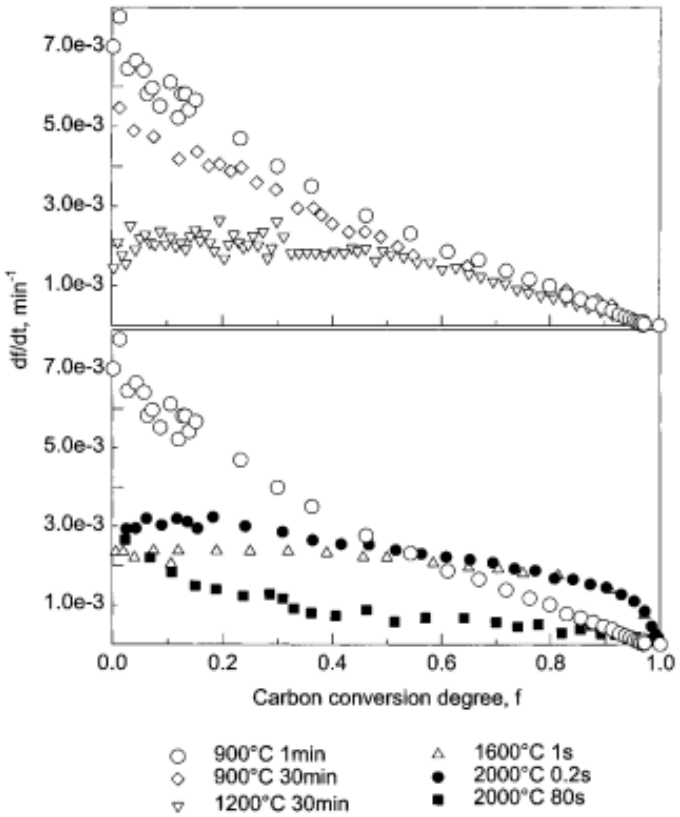



**Figure 3.** Typical gasification-rate profiles of heat-treated samples.

# Ideal Approach

- Ideal Approach: "[A] number of people . . . have applied char annealing models back into the late stages of devolatilization when active carbon structure arrangements are still taking place according to both chemical and thermal drivers. To me, it would make more sense to have a separate model of char formation (ideally tied to the devolatilization model) that accounts for those sorts of major bond rearrangements and a true annealing model that accounts for the smaller rearrangements that occur during active char combustion after the base char structure has been established." (Dr. Christopher Shaddix, Sandia National Laboratories)

- While ideal, the literature does not contain the data necessary to attack this problem in a coal general approach.
  - Data are confounded (i.e., different effects are impossible to distinguish)
  - Some data and rate estimates show that certain devolatilization conditions are concurrent with annealing, and impossible to deconvolute
  - The distributed activation energy approach with small modifications potentially allows us to capture a significant portion of the ideal approach mentioned above

# Calibration Step 2: Choose a Model, Parameters, and Priors

- Choose the parameters and their priors
- Parameters: σ, μ, and k ($E_a$=logN(μ,σ))
  - Priors limited by the activation energy of amorphous carbon reordering to crystalline graphite (~800 kJ/mol) and observed rates of activity decrease

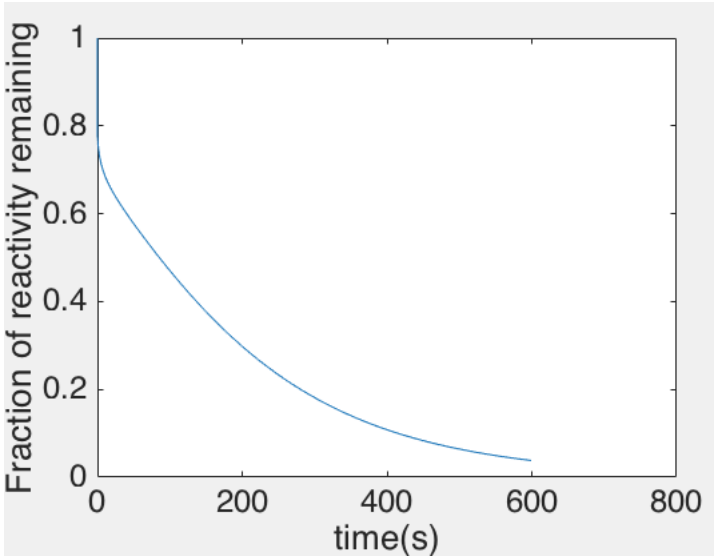
**Original CBK model**

$$\frac{df_i}{dt} = -k * exp(\frac{-E_{A\_anneal,i}}{R * T}) * f_i$$

Annealing data varies greatly with coal precursor and apparatus type, especially because of changes in heating rate, and Tpeak. What if $E_A$ could incorporate pyrolysis conditions, swelling, and coal precursor?

# Uncertainty Quantification – General Principles

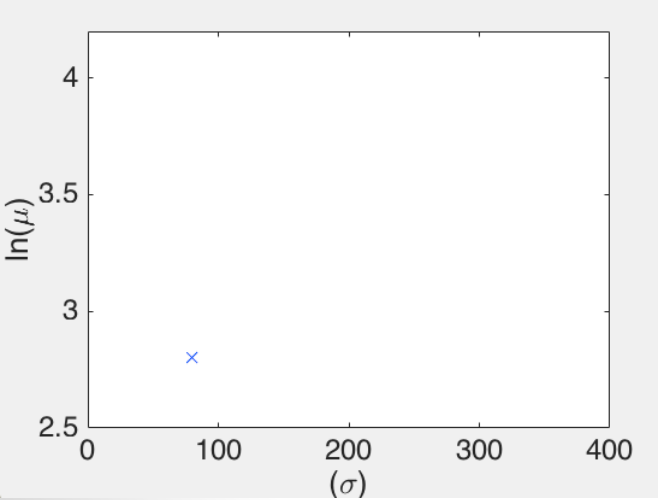
**Annealing sub-model curve**



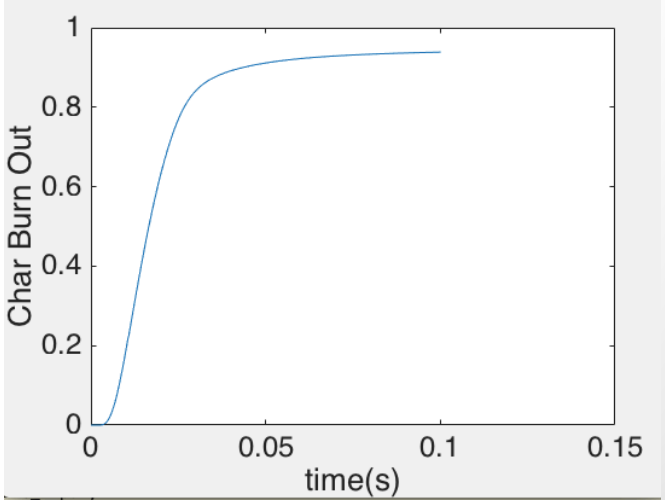

Basic Data Model

Macro Model

**Single best fit point**

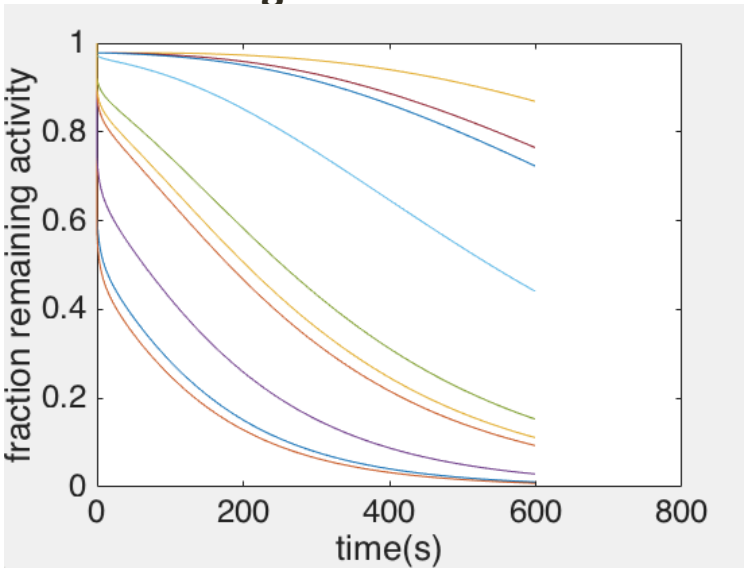



**Char burnout from comprehensive code**



# Uncertainty Quantification – General Principles

**Annealing sub-model curve**




Basic Data Model

Macro Model

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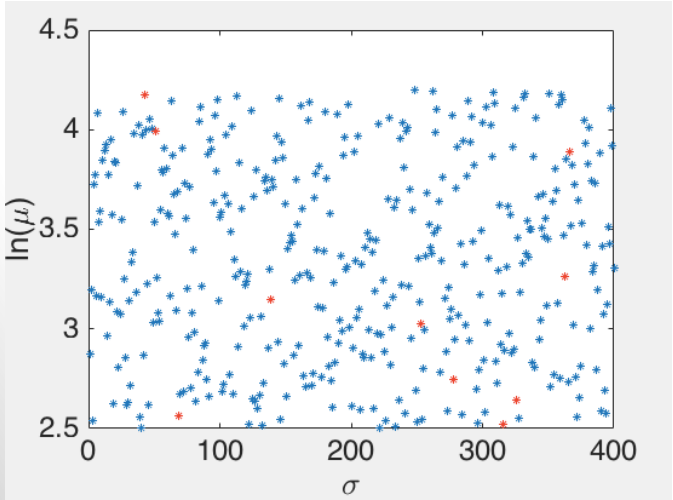
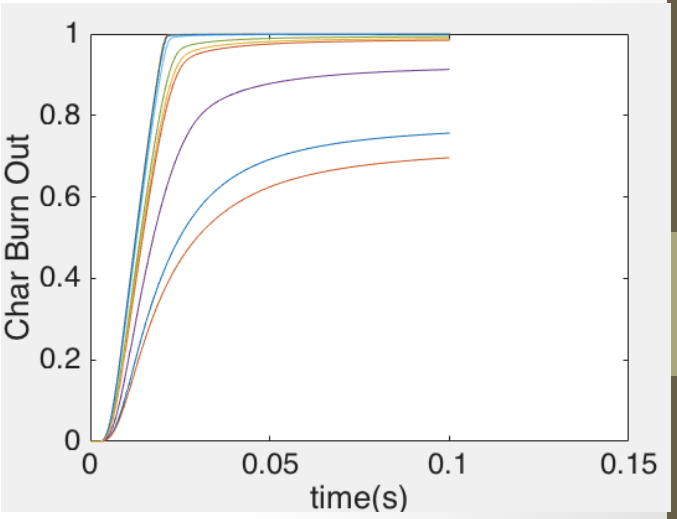
**Single best fit point**

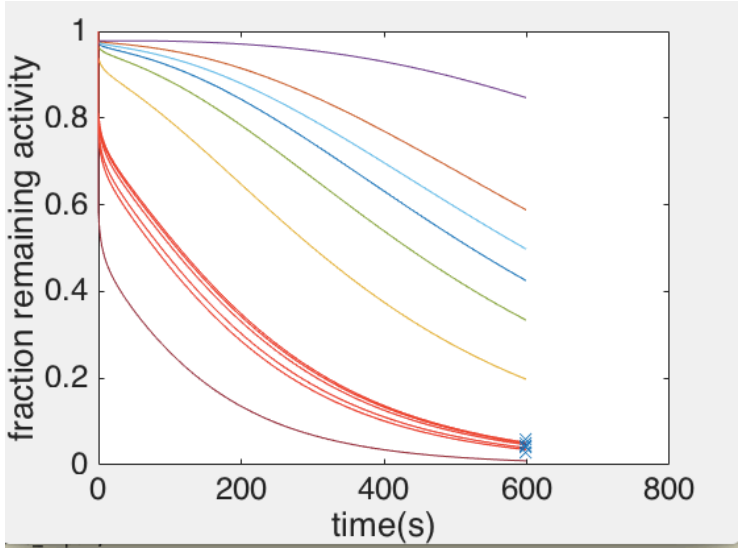


# Uncertainty Quantification – General Principles

Any calibration method accomplishes something similar, but the paradigm used here has particular advantages.

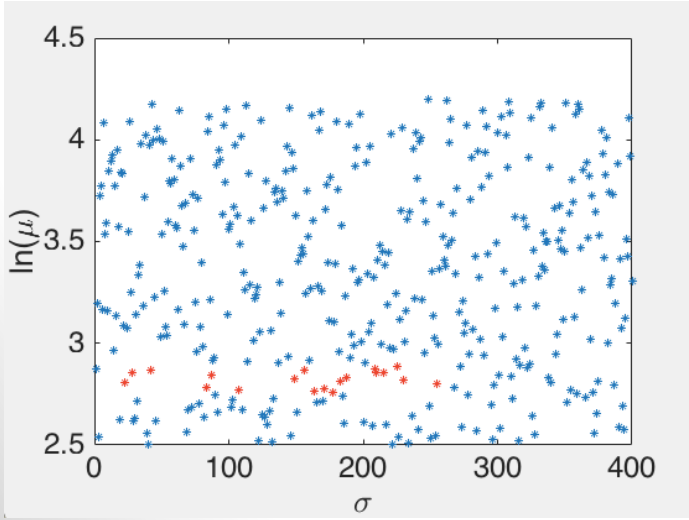
**Annealing sub-model curve**



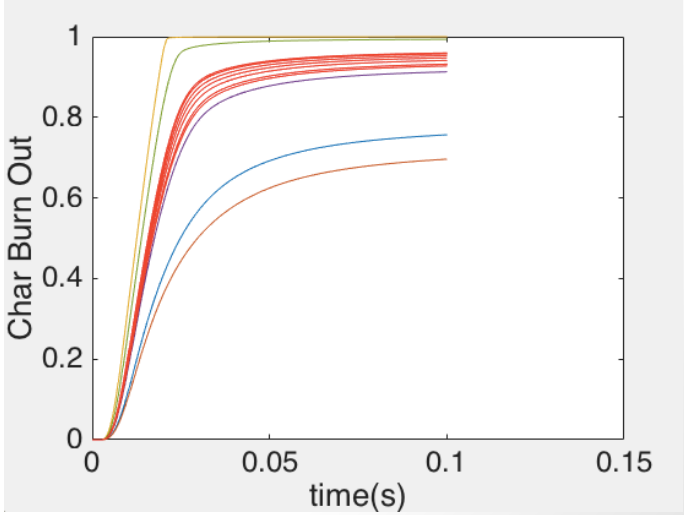

Basic Data Model

Macro Model

**Single best fit point**



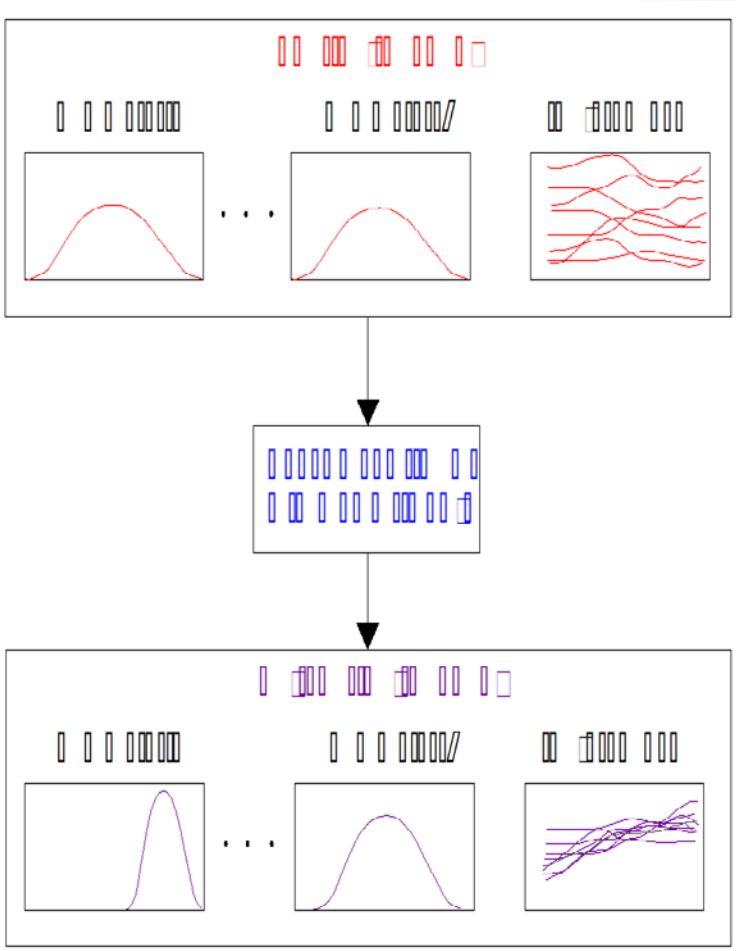

**Char burnout from comprehensive code**



# CCSI Calibration/UQ Paradigm

- **General UQ:** Find a plausible set of model parameter values (θ) that best produce the reality of experimental data.
- **Bayesian paradigm:** put a prior distribution on θ and condition on the experimental data to refine this prior distribution.
- Represent the physical system as the model (η) plus discrepancy function (δ) plus the measurement error (ε)

$$y_i = \eta(\mathbf{x}_i, \boldsymbol{\theta}) + \delta(\mathbf{x}_i) + \varepsilon_i$$



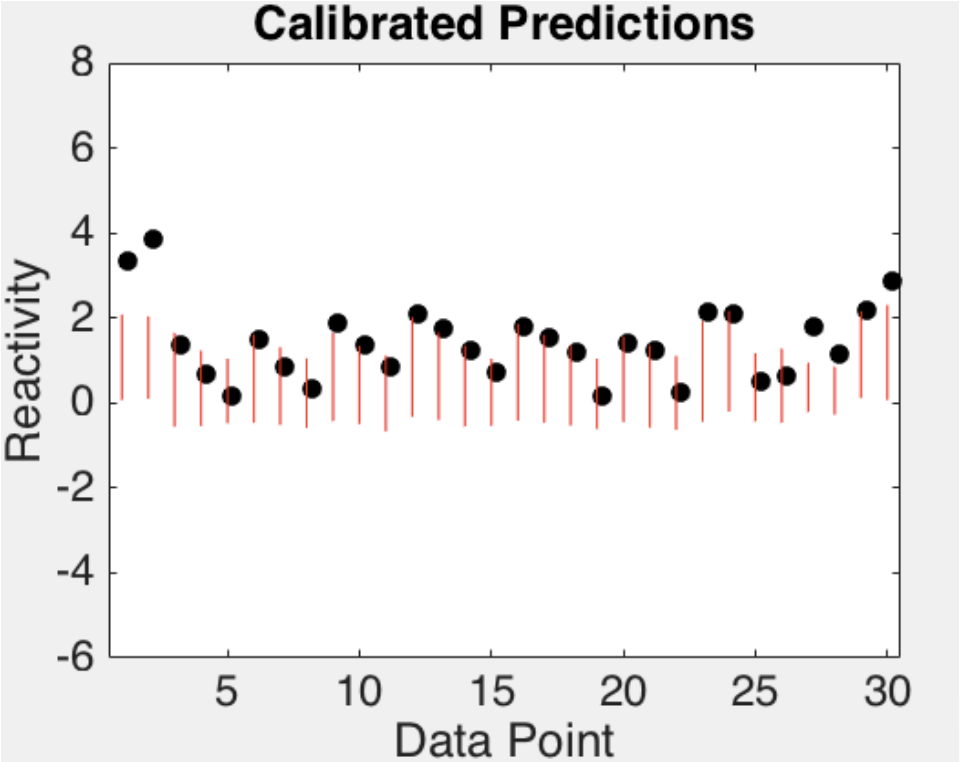
**Many traditional UQ methods substantially exaggerate the actual uncertainty, and those that don't inflate uncertainty typically fail to account for systematic model bias. This method is also particularly amenable to propagation.**

# Results:
# Original Annealing Model with Original Data

$$y_i = \eta(\mathbf{x}_i, \boldsymbol{\theta}) + \delta(\mathbf{x}_i) + \varepsilon_i$$

Red lines: η only

Black Dots: data points




Several data points are not within the uncertainty of the model, and most are on the extreme edges.

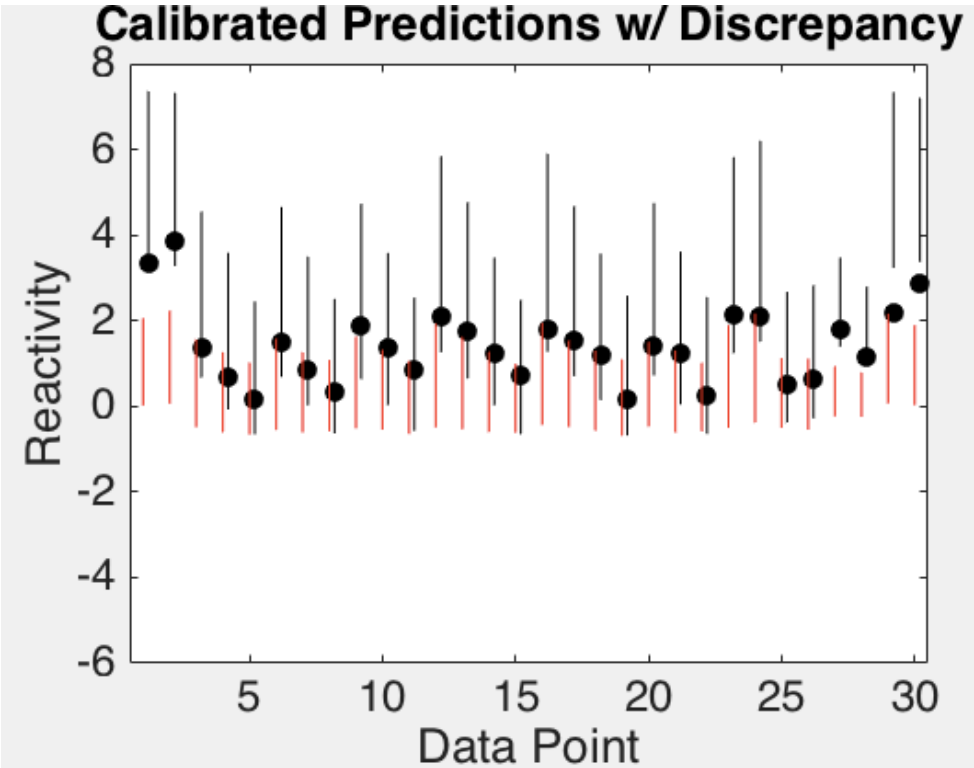
# Results:
# Original Annealing Model with Original Data

$$y_i = \eta(\mathbf{x}_i, \boldsymbol{\theta}) + \delta(\mathbf{x}_i) + \varepsilon_i$$

Red lines: η only

Black Dots: data points

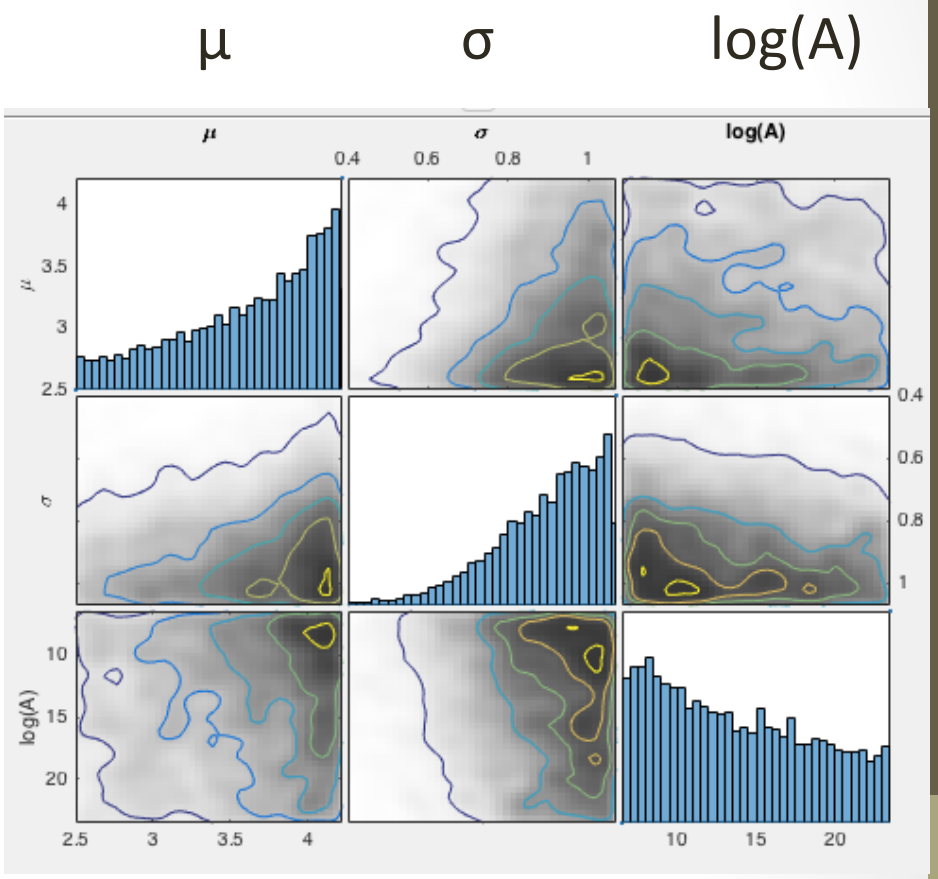
Black Lines: η+δ+ε




The discrepancy and model together do a much better job, but an accurate model functions without additional discrepancy.

# Results:
# Original Annealing Model with Original Data

- Diagonals are 1-dimensional marginal posterior distributions
- **When the majority of the probability density is piled up on a boundary, the model is very likely deficient.**

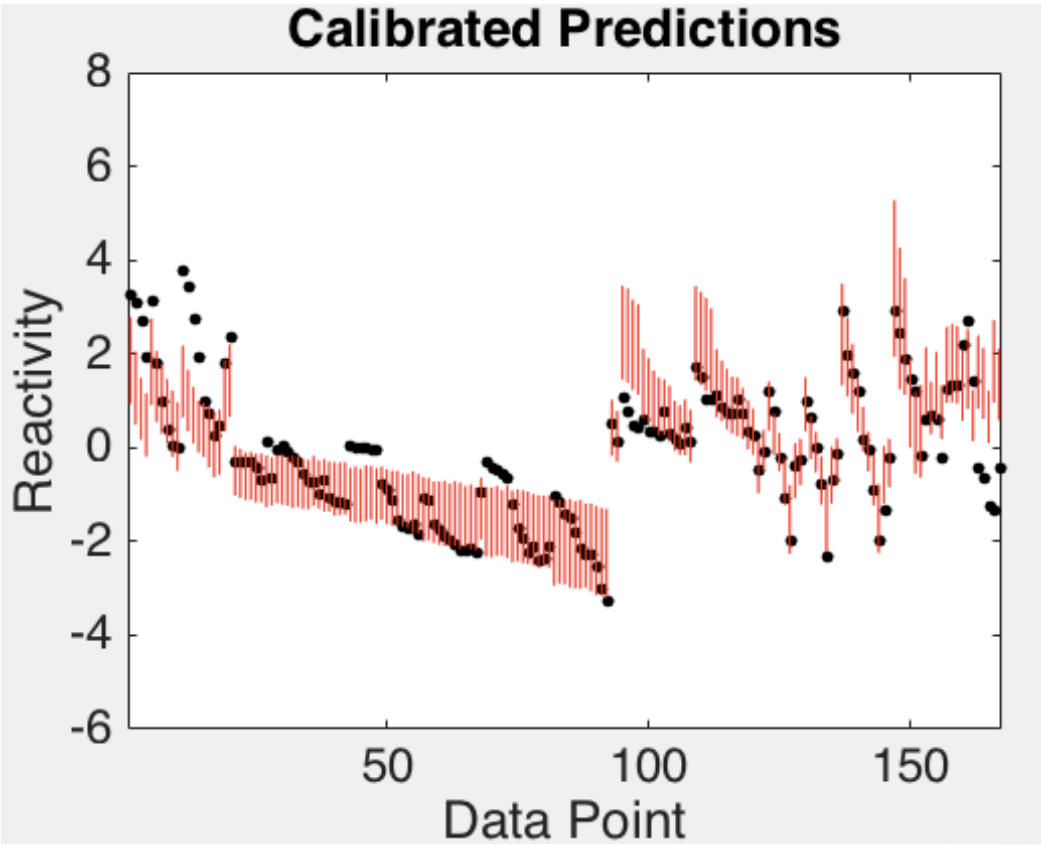


# Results:
# Original Annealing Model with Expanded Data

$$y_i = \eta(\mathbf{x}_i, \boldsymbol{\theta}) + \delta(\mathbf{x}_i) + \varepsilon_i$$

Red lines: η only

Black Dots: data points




**More data (and better quality) improves the fraction of points that the model can capture, but still fails to capture about 1/3 of the data.**

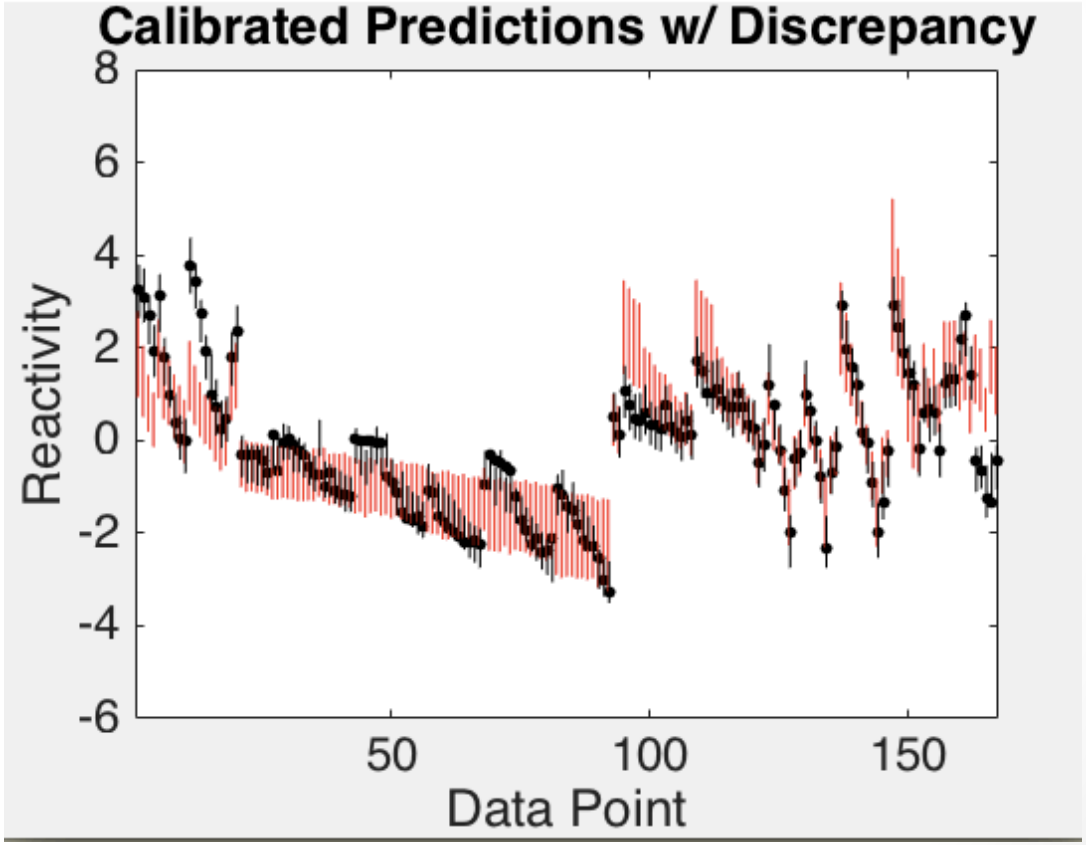
# Results:
# Original Annealing Model with Expanded Data

$$y_i = \eta(\mathbf{x}_i, \boldsymbol{\theta}) + \delta(\mathbf{x}_i) + \varepsilon_i$$

Red lines: η only

Black Dots: data points

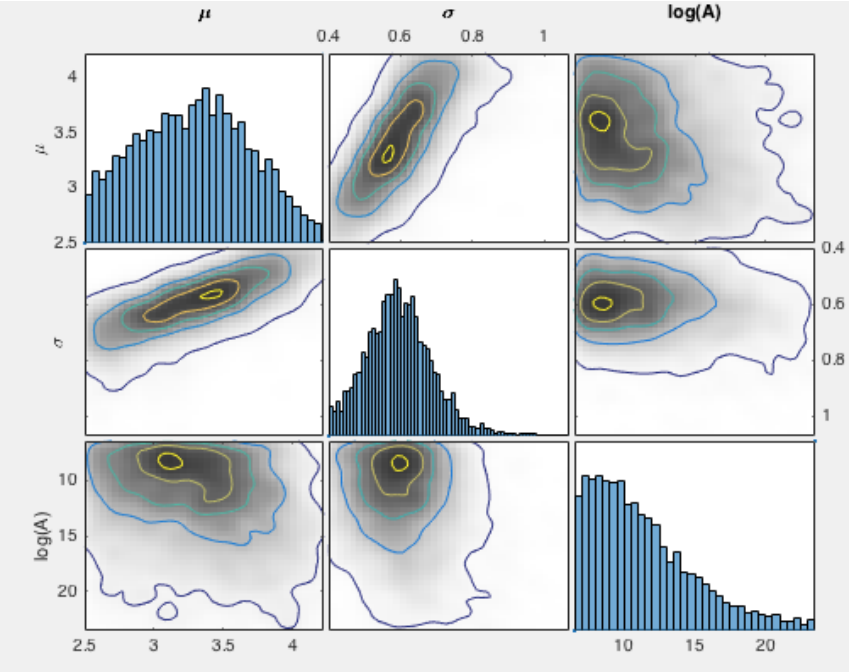
Black Lines: η+δ+ε




**Discrepancies can now capture all the data, and are greatly reduced, but are still far from 0.**

# Results:
# Original Annealing Model with Expanded Data

μ σ log(A)




**More and better data sharpen the peaks and narrow the parameter space, but no amount of data can overcome a model that has inadequate physics.**

# Conclusions and Future Work

- The current annealing model is unable to explain all the data.
- Additional data gives more information about model parameters, but not enough. Additional physics are needed.
- In this case, the activation energy curve should become a function of coal type, heating rate, and peak temperature
- $E_a = \log N(\mu,\sigma) = f(\text{heating rate, coal type, and } T_{peak})$
- The primary advantages of the uncertainty quantification used here are:
  1. The outputs include discrepancy to show where and how physics need to be improved
  2. The outputs are in the form of probability distributions, which is conducive to uncertainty propagation
  3. The method reduces uncertainty to as low as it can be given the data and the model physics (traditional methods often artificially inflate sensitivity)

# Disclaimer

# Acknowledgements

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# Figure references

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- Senneca, Salatino, and Masi; *Energy and Fuels*, 1999