A Comprehensive Model for Predicting Elemental Composition of Coal Pyrolysis Products

Andrew P Richards, Tim Shutt, Thomas H Fletcher

Chemical Engineering Department

Brigham Young University

10th U.S. National Combustion Meeting

April 23-26, 2017

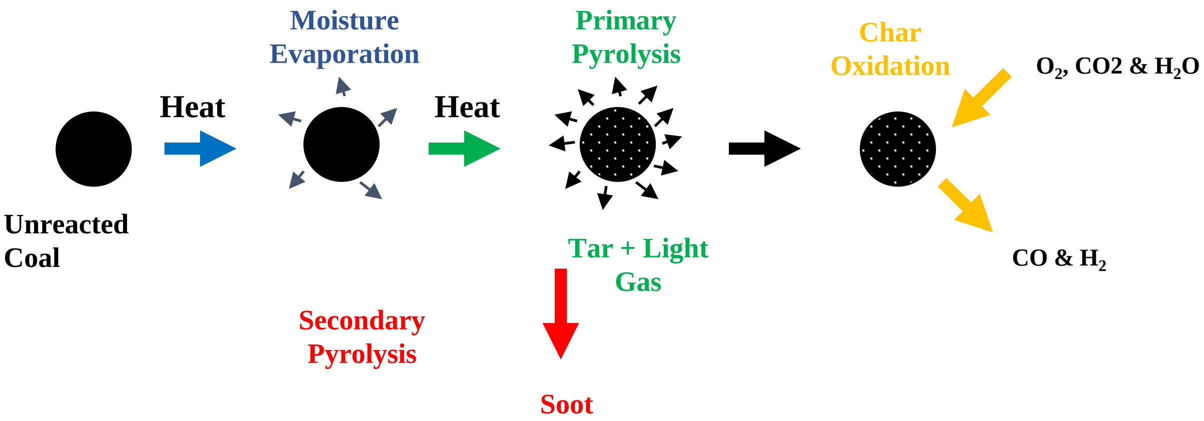
PSAAP Project

- Simulate coal combustion on industrial level
- Model several lab and pilot scale reactors
- Design and simulate an industrial coal power plant not yet built
- Project steps
  - Physics
    - Reactions (devolatilization, char reactions, soot reactions)
    - Particle and fluid flow
    - Heat transfer (radiative, convective, and conductive)
  - Verification, Validation, and Uncertainty Quantification
  - Exascale Computing

Why Coal?

- Many industries depend on coal
  - Energy (38% of U.S. electricity)
  - Steel and other metal production facilities
- Great potential for research areas
  - Kinetics
  - Heat transfer (convection and radiation)
  - Mass transfer
  - Microscopic (molecular and particle) and macroscopic (boiler) properties

Coal Combustion



Char: solid particle remaining after devolatilization
Tar: part of the volatile gases that condense to a viscous liquid at room temperature
Light gases: part of the volatile gases that remain as a gas at room temperature

Goals

- Develop set of correlations predicting the elemental composition of primary pyrolysis products (char and tar) at a variety of conditions and for a variety of coals
- Introduce this in a two mixture fraction description for coal gas in large-scale simulations
- Current simulations define only one mixture fraction for the coal gas based on **local gas phase equilibrium**
  - **Composition**
  - Energy Level
  - Pressure
- Single mixture fraction methods set equivalent compositions for char and gas phases

Approach

- Experimental data from various sources
  - Focused on elemental composition of coal tar
- Simple least sum squared error comparison
  - Correlate with $T_{gas,max}$, $x_{i,coal,0}$, t_{res}, d_p, V/V_∞
- Optimization to minimize sum squared error
  - Various optimizer algorithms to ensure optimal solution (Matlab based)
    - Unconstrained optimizer (*fminunc*), constrained optimizer (*fmincon*), Multi-Start algorithm (using both *fminunc* and *fmincon*, separately), and Global Search algorithm (using *fmincon*)
    - All similar optimizations use the same starting value
  - Optimizations for each element (C, H, N, S, O) in each of two states (coal char and coal tar)
    - 10 different model forms
    - 50 total optimizations

Approach – Experimental Data

Author(s)	Institution	Experimental Apparatus	T_{gas} Range (K)	Coal Ranks
Freihaut et al. [1]	United Technologies Research Center	Entrained-flow reactor	780-1326	hvA, sub, lvb
Hambly [2,3]	Brigham Young University	Drop tube reactor and flat-flame burner (methane)	Drop: 820-1220 FFB: 1650	ligA, subC, subA, hvC, hvB, hvA, lvb, mvb, an
Perry [4,5]	Brigham Young University	Drop tube reactor and flat-flame burner (methane)	895-1640	brown, sub, hvb, mvb, lvb
Fletcher and Hardesty [6]	Sandia National Laboratories	Entrained-flow reactor	1050-1250	lig, sub, hvB, hvA, lvb
Watt [7,8]	Brigham Young University	Drop tube reactor and flat-flame burner (methane)	Drop: 850-1220 FFB: 1650	ligA, subC, subB, hvC, hvB, hvA, mvb, lvb, an

Gathering more elemental tar composition data as well from literature

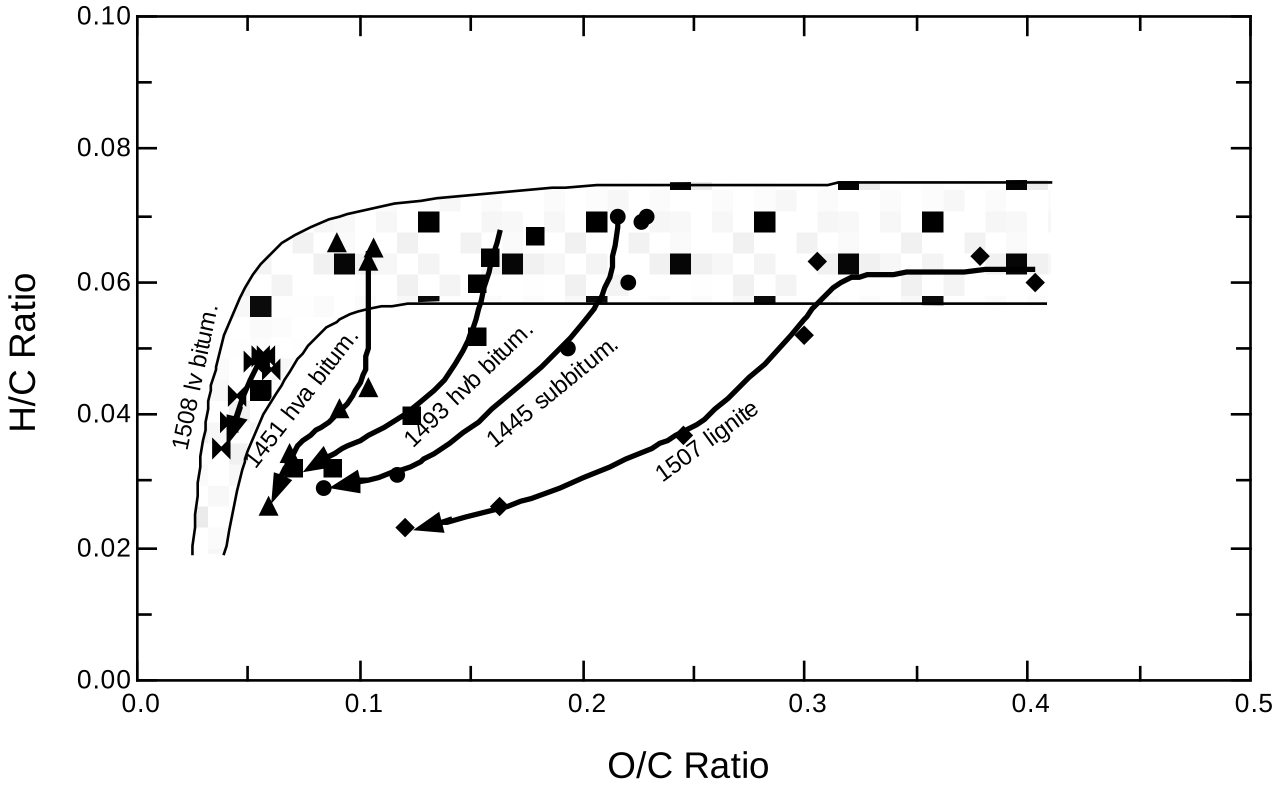
Correlation Model Form

- Simple polynomial form
- $EC \equiv aT_{gas,max}^{\alpha} + bx_{i,coal,0}^{\beta} + ct_{res}^{\gamma} + dd_p^{\delta} + eV_{norm}^{\varepsilon} + f$
- Variable descriptions in table to the right
- 10 total equations
- Measure goodness of fit: Root mean squared error (RMSE)

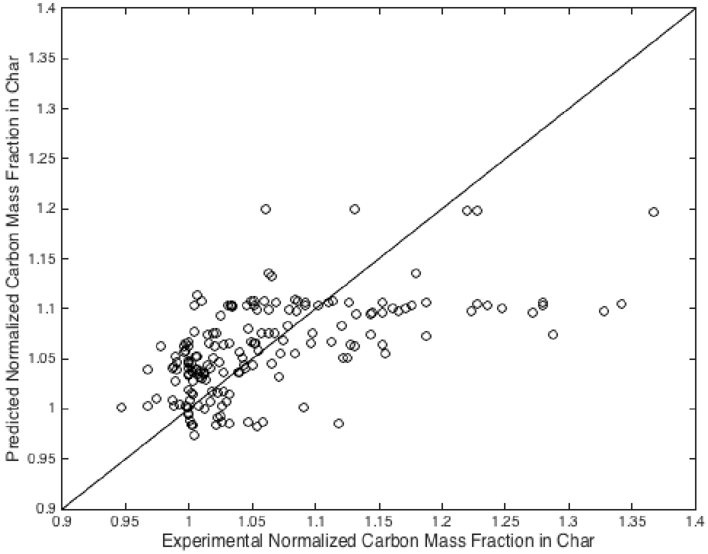
$$RMSE = \sqrt{\frac{SSE}{n}}$$

Variable	Meaning
EC	Normalized mass fraction of each element (C, H, O, N, S)
$T_{gas,max}$	Maximum gas temperature (K)
$x_{i,coal,0}$	Parent coal composition of element of interest (percent, on dry, ash-free basis)
t_{res}	Residence time (ms)
d_p	Particle size (average, in μm)
V_{norm}	Normalized total volatiles mass fraction (V/V_{∞})
a-f, α, β, γ, δ, ε	Fit parameters

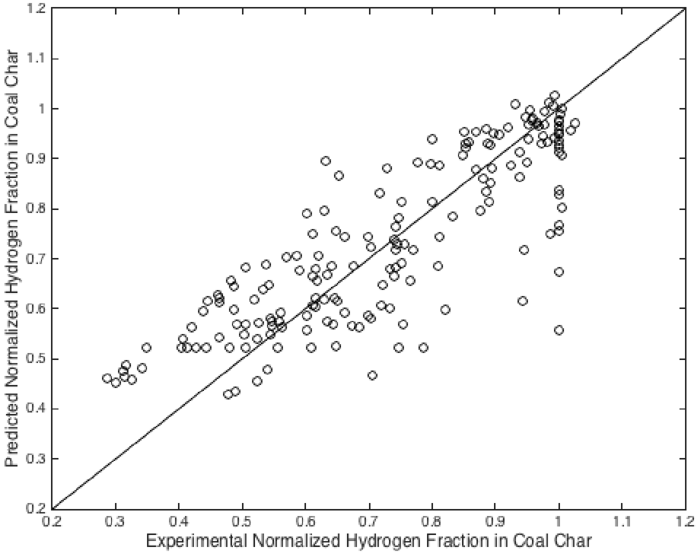
Char Composition Changes during Pyrolysis



Char Results - Carbon and Hydrogen

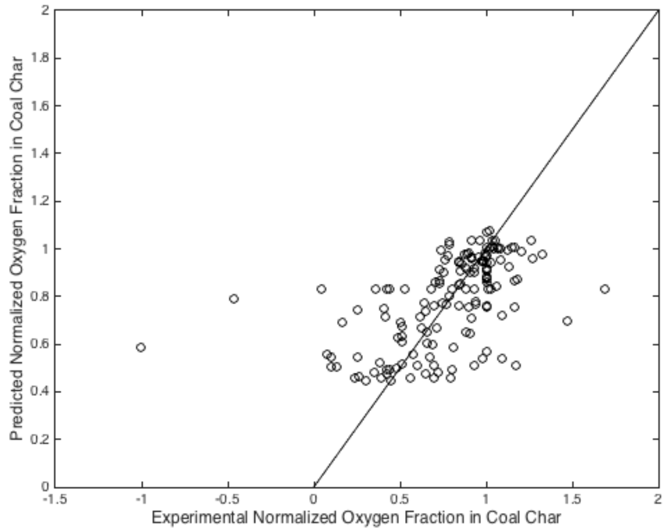


Carbon RMSE = 0.0632

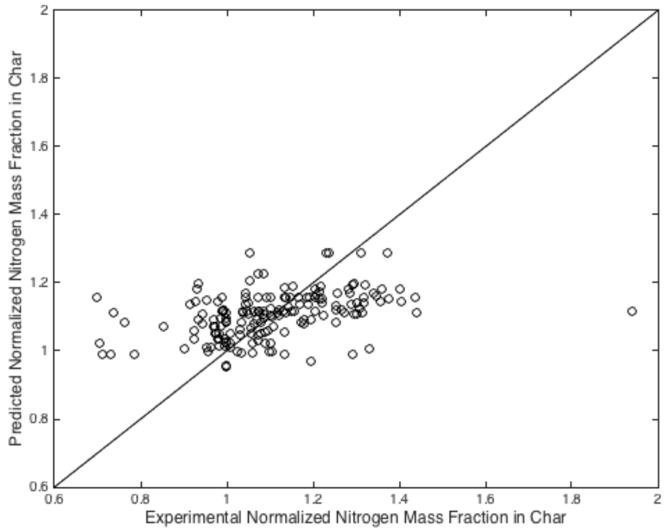


Hydrogen RMSE = 0.1138

Char Results – Oxygen and Nitrogen

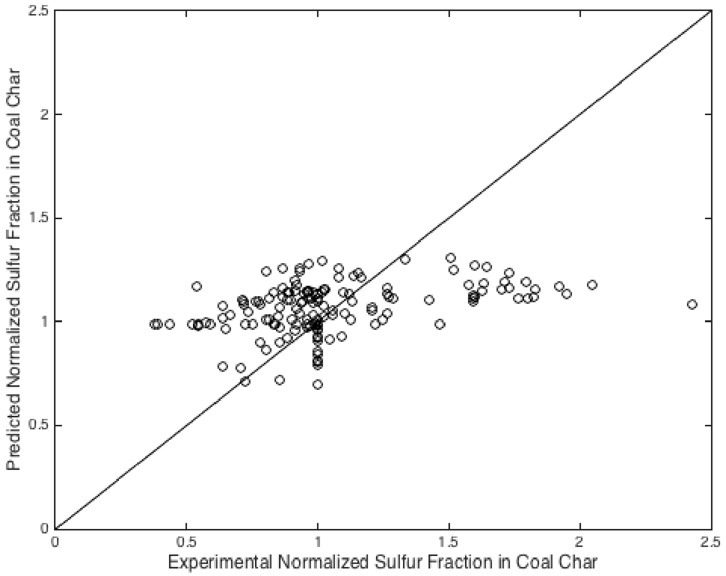


Oxygen RMSE = 0.2814



Nitrogen RMSE = 0.1423

Char Results – Sulfur

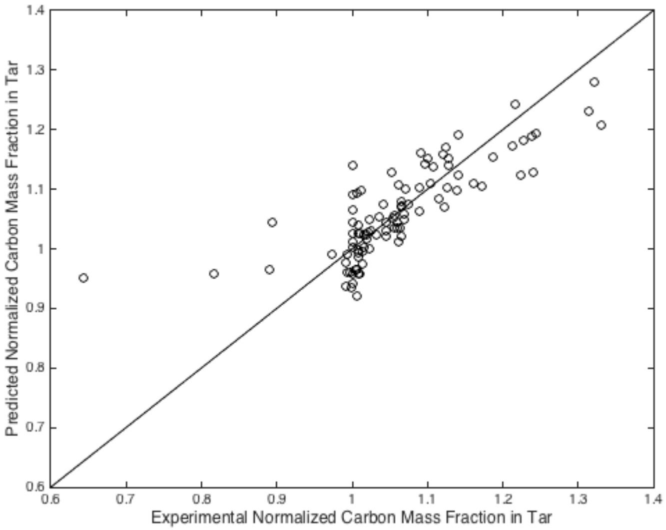


Sulfur RMSE = 0.3232

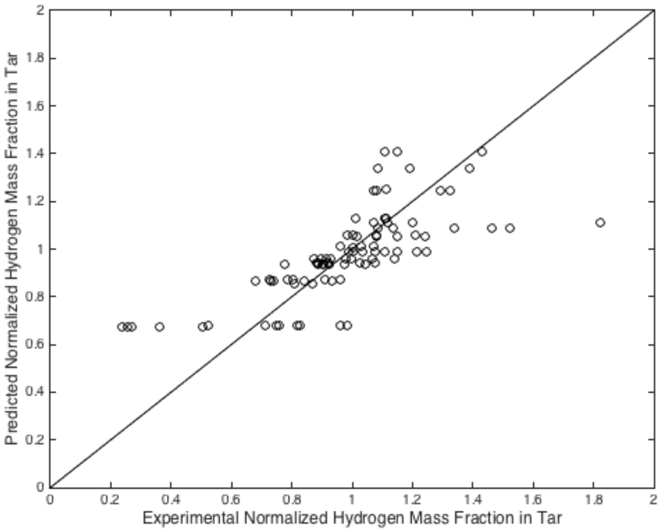
Tar Results

- As much as 30% of parent daf coal
- Important precursor for soot
- Contains most of the N released during pyrolysis for most coals
- Correlating primary tar composition (not secondary tar)

Tar Results – Carbon and Hydrogen

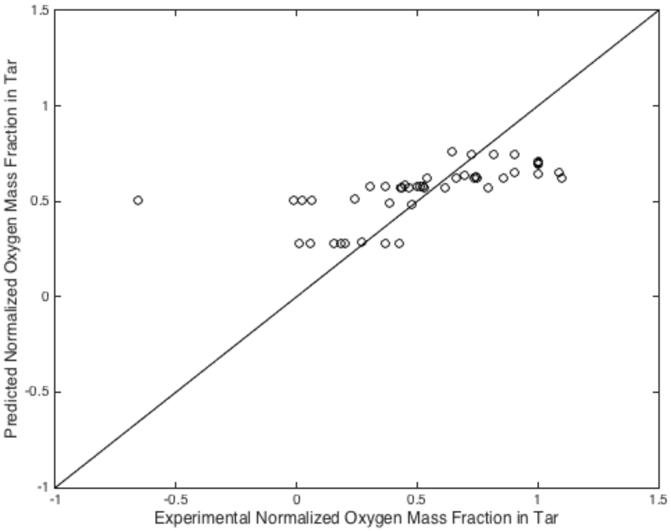


Carbon RMSE = 0.0560

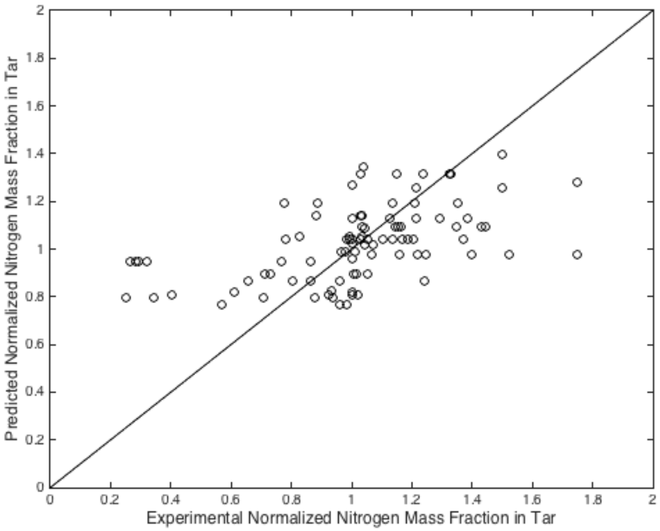


Hydrogen RMSE = 0.1614

Tar Results – Oxygen and Nitrogen

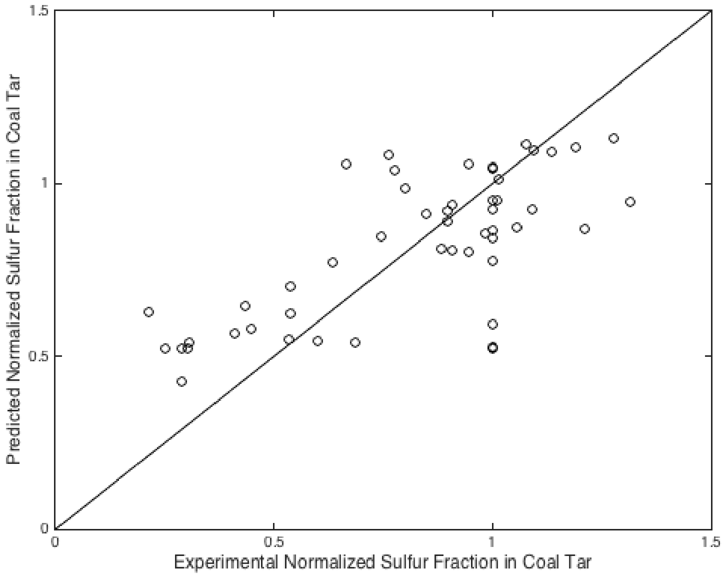


Oxygen RMSE = 0.2615



Nitrogen RMSE = 0.2382

Tar Results – Sulfur



Sulfur RMSE = 0.1886

Correlation Summary

State	Element	Correlation
Char	Carbon	$C_{char} = 0.1845T_{gas,max}^{0.2342} - 0.1021x_{C,coal,0}^{-0.1508} + 9.42 \times 10^{-6}t^{1.6226} + 0.1553d_p^{-0.161} + 0.0338$
	Hydrogen	$H_{char} = 0.1178T_{gas,max}^{-1.0165} + 2.4334x_{H,coal,0}^{-0.08} + 3.39 \times 10^{-4}t^{1.0253} - 0.4378d_p^{-0.3124} - 0.4694V_{norm}^{2.0306} - 1.0851$
	Oxygen	$O_{char} = -0.0444T_{gas,max}^{-0.0781} + 0.4436x_{O,coal,0}^{-0.1841} + 0.0631t^{9.10\times10^{-6}}0.0922d_p^{0.1028} - 0.4909V_{norm}^{4.6044} + 0.5173$
	Nitrogen	$N_{char} = 0.1623T_{gas,max}^{0.2973} - 0.4265x_{N,coal,0}^{0.0115} + 0.0019t^{0.8288} - 0.6898d_p^{-2.7568} + 0.1005$
	Sulfur	$S_{char} = -22.577T_{gas,max}^{-50.414} + 76.282x_{S,coal,0}^{9.04\times10^{-4}} + 0.1593t^{0.1494} + 0.4387d_p^{0.2259} - 0.0809V_{norm}^{25.428} - 76.726$
Tar	Carbon	$C_{tar} = 1.59 \times 10^{-5}T_{gas,max}^{1.3092} + 6.523x_{C,coal,0}^{-0.2887} - 0.9424t^{-2.3854} - 4.5519d_p^{-7.9637} - 0.9284$
	Hydrogen	$H_{tar} = 28.188T_{gas,max}^{-0.0259} - 27.102x_{H,coal,0}^{-30.309} + 31.221t^{1.26\times10^{-4}} - 14.488d_p^{-27.166} - 53.818$
	Oxygen	$O_{tar} = 12.489T_{gas,max}^{-0.1816} + 1.52 \times 10^{-9}x_{O,coal,0}^{4.672} + 7.1707t^{0.0021} - 1.1986d_p^{-2.3618} - 10.195$
	Nitrogen	$N_{tar} = 0.0221T_{gas,max}^{0.5953} + 6.71 \times 10^{-6}x_{N,coal,0}^{-16.404} + 5.3997t^{0.0323} - 10.369d_p^{-3.797} - 6.7641$
	Sulfur	$S_{tar} = 8.0937T_{gas,max}^{-0.0254} + 12.282x_{S,coal,0}^{-0.0148} + 8.1655t^{-9.3034} - 13.499d_p^{-0.2331} + 0.1954V_{norm}^{7.8778} - 13.168$

Summary and Conclusions

- Developed correlations for predicting the elemental composition of coal char and tar
  - 5 sets of entrained flow data (Sandia, UTRC, BYU)
  - Wide range of coal rank
- Strongest correlations:
  - Carbon in char and tar
  - Hydrogen in char
  - Oxygen in char (excluding outliers)
- Elemental composition of primary pyrolysis products changes significantly with changing conditions

Future Work

- Search for and analyze additional experimental data
- Utilize more complex optimization methods for increased accuracy
- Validate the results and quantify uncertainty
- Evaluate outliers (especially for oxygen composition)
- Incorporate 2 (or 3) mixture fraction approach into large-scale simulations

Acknowledgements

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

Acknowledgements

- This material is based upon work supported by the Department of Energy, National Nuclear Security Administration, under Award Number(s) DE-NA0002375

- Project work is a tri-university effort with support from the University of Utah, Brigham Young University, and University of California- Berkeley

- Project oversite and guidance is provided from three national labs: Lawrence Livermore, Sandia, and Los Alamos National Laboratories

Future Work

- More formal fitting procedures (VUQ)
- Additional data sets
  - Not many people have elemental compositions of coal tar
- May need to back out tar composition from char and light gas composition
- Energy balance?