A Comprehensive Model for Predicting Elemental Composition of Coal Pyrolysis Products

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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 $T_{\text{gas, max}}$, $x_{\text{i, coal, 0}}$, $t_{\text{res}}$, $d_p$, $V/V_{\infty}$
- Optimization to minimize sum squared error
  - Various optimizer algorithms to ensure optimal solution (Matlab based)
    - Unconstrained optimizer ($f\text{minunc}$), constrained optimizer ($f\text{mincon}$), Multi-Start algorithm (using both $f\text{minunc}$ and $f\text{mincon}$, separately), and Global Search algorithm (using $f\text{mincon}$)
    - 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
<table>
<thead>
<tr>
<th>Author(s)</th>
<th>Institution</th>
<th>Experimental Apparatus</th>
<th>$T_{\text{gas}}$ Range (K)</th>
<th>Coal Ranks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freihaut et al. 1</td>
<td>United Technologies Research Center</td>
<td>Entrained-flow reactor</td>
<td>780-1326</td>
<td>hvA, sub, lvb</td>
</tr>
<tr>
<td>Hambly 2,3</td>
<td>Brigham Young University</td>
<td>Drop tube reactor and flat-flame burner (methane)</td>
<td>Drop: 820-1220 FFB: 1650</td>
<td>ligA, subC, subA, hvC, hvB, hvA, lvb, mvb, an</td>
</tr>
<tr>
<td>Perry 4,5</td>
<td>Brigham Young University</td>
<td>Drop tube reactor and flat-flame burner (methane)</td>
<td>895-1640</td>
<td>brown, sub, hvb, mvb, lvb</td>
</tr>
<tr>
<td>Fletcher and Hardesty 6</td>
<td>Sandia National Laboratories</td>
<td>Entrained-flow reactor</td>
<td>1050-1250</td>
<td>lig, sub, hvB, hvA, lvb</td>
</tr>
<tr>
<td>Watt 7,8</td>
<td>Brigham Young University</td>
<td>Drop tube reactor and flat-flame burner (methane)</td>
<td>Drop: 850-1220 FFB: 1650</td>
<td>ligA, subC, subB, hvC, hvB, hvA, mvb, lvb, an</td>
</tr>
</tbody>
</table>

Gathering more elemental tar composition data as well from literature
Correlation Model Form

- Simple polynomial form
  \[ EC \equiv aT_{gas,max}^\alpha + b x_{i,coal,0}^\beta + c t_{res}^\gamma + d d_p^\delta + e V_{norm}^\epsilon + f \]
- Variable descriptions in table to the right
- 10 total equations
- Measure goodness of fit: Root mean squared error (RMSE)
  \[ RMSE = \sqrt{\frac{SSE}{n}} \]

<table>
<thead>
<tr>
<th>Variable</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>( EC )</td>
<td>Normalized mass fraction of each element (C, H, O, N, S)</td>
</tr>
<tr>
<td>( T_{gas,max} )</td>
<td>Maximum gas temperature (K)</td>
</tr>
<tr>
<td>( x_{i,coal,0} )</td>
<td>Parent coal composition of element of interest (percent, on dry, ash-free basis)</td>
</tr>
<tr>
<td>( t_{res} )</td>
<td>Residence time (ms)</td>
</tr>
<tr>
<td>( d_p )</td>
<td>Particle size (average, in ( \mu )m)</td>
</tr>
<tr>
<td>( V_{norm} )</td>
<td>Normalized total volatiles mass fraction (V/V(_\infty))</td>
</tr>
<tr>
<td>( a-f, \alpha, \beta, \gamma, \delta, \epsilon )</td>
<td>Fit parameters</td>
</tr>
</tbody>
</table>
Char Composition Changes during Pyrolysis

![Graph showing changes in H/C and O/C ratios during pyrolysis.](image)
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

<table>
<thead>
<tr>
<th>State</th>
<th>Element</th>
<th>Correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Char</td>
<td>Carbon</td>
<td>( C_{char} = 0.1845 T_{gas,max}^{0.2342} - 0.1021 x_{C,coal,0}^{-0.1508} + 9.42 \times 10^{-6} t^{1.6226} + 0.1553 d_p^{-0.161} + 0.0338 )</td>
</tr>
<tr>
<td></td>
<td>Hydrogen</td>
<td>( H_{char} = 0.1178 T_{gas,max}^{-10.165} + 2.4334 x_{H,coal,0}^{-0.08} + 3.39 \times 10^{-4} t^{1.0253} - 0.4378 d_p^{-0.3124} - 0.4694 V_{norm}^{2.0306} - 1.0851 )</td>
</tr>
<tr>
<td></td>
<td>Oxygen</td>
<td>( O_{char} = -0.0444 T_{gas,max}^{-0.0781} + 0.4436 x_{O,coal,0}^{-0.1841} + 0.0631 t^{9.10 \times 10^{-6}} - 0.0922 d_p^{0.1028} - 0.4909 V_{norm}^{4.6044} + 0.5173 )</td>
</tr>
<tr>
<td></td>
<td>Nitrogen</td>
<td>( N_{char} = 0.1623 T_{gas,max}^{0.2973} - 0.4265 x_{N,coal,0}^{0.0115} + 0.0019 t^{0.8288} - 0.6898 d_p^{-2.7568} + 0.1005 )</td>
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<td></td>
<td>Sulfur</td>
<td>( S_{char} = -22.577 T_{gas,max}^{-50.414} + 76.282 x_{S,coal,0}^{9.04 \times 10^{-4}} + 0.1593 t^{0.1494} + 0.4387 d_p^{0.2259} - 0.0809 V_{norm}^{25.528} - 76.726 )</td>
</tr>
<tr>
<td>Tar</td>
<td>Carbon</td>
<td>( C_{tar} = 1.59 \times 10^{-5} T_{gas,max}^{1.3092} + 6.523 x_{C,coal,0}^{-0.2887} - 0.9424 t^{-2.3854} - 4.5519 d_p^{-7.9637} - 0.9284 )</td>
</tr>
<tr>
<td></td>
<td>Hydrogen</td>
<td>( H_{tar} = 28.188 T_{gas,max}^{-0.0259} - 27.102 x_{H,coal,0}^{-30.309} + 31.221 t^{1.26 \times 10^{-4}} - 14.488 d_p^{-27.166} - 53.818 )</td>
</tr>
<tr>
<td></td>
<td>Oxygen</td>
<td>( O_{tar} = 12.489 T_{gas,max}^{-0.1816} + 1.52 \times 10^{-9} x_{O,coal,0}^{4.672} + 7.1707 t^{0.0021} - 1.1986 d_p^{-2.3618} - 10.195 )</td>
</tr>
<tr>
<td></td>
<td>Nitrogen</td>
<td>( N_{tar} = 0.0221 T_{gas,max}^{0.5953} + 6.71 \times 10^{-6} x_{N,coal,0}^{16.404} + 5.3997 t^{0.0323} - 10.369 d_p^{-3.797} - 6.7641 )</td>
</tr>
<tr>
<td></td>
<td>Sulfur</td>
<td>( S_{tar} = 8.0937 T_{gas,max}^{-0.0254} + 12.282 x_{S,coal,0}^{-0.0148} + 8.1655 t^{-9.3034} - 13.499 d_p^{-0.2331} + 0.1954 V_{norm}^{7.8778} - 13.168 )</td>
</tr>
</tbody>
</table>
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
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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?