Detailed Modeling of Soot Formation from Solid Fuels

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\textbf{9\textsuperscript{th} FM Global Open Source CFD Fire Modeling Workshop}
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Norwood, Massachusetts
• Work began as part of the CCMSC’s PSAAP II project
  ▪ Demonstrate exascale computing with V&V/UQ to more rapidly deploy new technologies for providing low cost, low emission electric power generation
  ▪ Full-scale simulation of an oxy-coal boiler
  ▪ Work supported by the Department of Energy, National Nuclear Security Administration, under Award Number(s) DE-NA0002375

• Work continued through the EES division at LANL
  ▪ HIGRAD/FIRETEC- combines physics models that represent combustion, heat transfer, aerodynamic drag and turbulence. Designed to simulate the constantly changing, interactive relationship between fire and its environment.
  ▪ Predicting solid particle emissions from wildfires
  ▪ Work supported by
Soot Introduction

Soot

- Particles heavily impact radiative heat transfer
- Changes flame chemistry
- Health and environmental impacts

Gaseous Fuels

- Rate largely determined by formation of precursors and time in fuel-rich environment
- Soot precursors are PAHs

Solid Fuels

- Parent fuel gives off tar during primary pyrolysis
- Tar is primary soot precursor
Soot Challenges

Validation Data

- Difficulties in physical collections
- Optical measurements
- Very few standards in experimentation or data reporting

Particle Size Distributions

- Particles form a broad distribution with a very large number of particles
- Characterization of the distribution (assumed shape, method of moments, discrete bin, etc.)
  - Assumed shape:
    - Typical- mono-dispersed or log-normal distributions
  - Discrete bin
    - Possible distribution too broad
  - Method of moments
    - Closure
    - Configuring the PSD from the moments

\[
N_i(m) = \frac{1}{m\sigma\sqrt{2\pi}} \exp\left[\frac{-(\ln m - \mu)^2}{2\sigma^2}\right]
\]

\[
N = \sum_{k=0}^{n_i} \delta(m) N_i(m)
\]

\[
M_r = \int_0^\infty m_i^r N_i(m) dm
\]

Modeling

- Numerical stiffness and stability
- Chemistry complications (equilibrium vs flamelet)
- Particle morphology during agglomeration
- System priorities (particle and system composition)
# Model Overview

## PAH Molecules
- Transport PAH PSD using a discrete bin approach
- Bin sizes determined by CPD model (~6 bins)
- Transport includes 4 source terms:
  - PAH creation
  - Surface Reactions
  - Thermal Cracking
  - Soot Nucleation

### Bin Species Number Density
\[
\frac{\delta \rho N_i}{\delta t} + \nabla \cdot (\rho \bar{v} N_i) + \nabla \cdot (\rho \bar{v}'' N_i'') = S_{N_i}
\]

\[S_{N_i} = r_{create} + r_{growth} - r_{crack} - r_{nucl}\]

## Soot Particles
- Transport soot PSD using method of moments
- Interpolative closure for source terms

\[
M_r = \int_0^\infty m_i^r N_i(m)dm
\]

\[
M_p = L_p (M_0, M_1, \ldots M_r)
\]

- Transport includes 3 source terms:
  - Soot Nucleation
  - Particle Coagulation
  - Surface Reactions

### PSD Moment Density
\[
\frac{\delta \rho M_r}{\delta t} + \nabla \cdot (\rho \bar{v} M_r) + \nabla \cdot (\rho \bar{v}'' M_r'') = S_{M_r}
\]

\[S_{M_r} = r_{nucl} + r_{growth} + r_{coag} - r_{consume}\]
PAH Model - Creation

PAH molecules creation from two sources:

1. Release of tar molecules by parent fuel
   - Rate determined from results of CPD model (Fletcher, 1992)
   - PSD spans broad range (~150 kg/kmole – 3000 kg/kmole)
   - Lognormal PSD
     - Coal (median ~350 kg/kmole, small variance)
     - Biomass (median ~225 kg/kmole, larger variance)
     - Varies over time, shifts to higher MWs.

2. Formation of aromatic rings from the gas-phase
   - Rate determined by ABF mechanism (Appel, 2000)
   - Creation of pyrene added to the PAH bins
   - Usually insignificant source of PAH (But not always, Zeng, 2011)
PAH Model – Thermal Cracking

- Four types of PAH molecules
- Cracking reactions determine amount of mass lost
- All reactions are simple Arrhenius equations with fitted parameters
PAH Model – Thermal Cracking

- It is undesirable to transport four species for each PAH bin
- Fraction of each species assumed to be constant
- Fraction estimation
  - Maximum tar concentration used
  - Equal parts phenol, naphthalene, and toluene
  - Phenol and toluene branches established by CNMR and Elemental analyses of parent fuel
  - Cracking scheme applied over time with soot nucleation until 99% PAH consumed
  - Average species fraction computed and used as constants over long simulation
PAH/Soot Model – Soot Formation

Based on work presented in *Soot Formation in Combustion* (Bockhorn 1991)

**Change in PAH species**

\[
 r_i = \sum_{j=j_0}^{\infty} \beta_{i,j} N_i^{PAH} N_j^{PAH}
\]

**Change in soot moments**

\[
 r_r = \sum_{i=i_0}^{\infty} \sum_{j=i}^{\infty} \beta_{i,j} (m_i + m_j)^r N_i^{PAH} N_j^{PAH}
\]

\(\beta\) represents the frequency of collision between different PAH molecules computed using the kinetic theory of gases.
PAH/Soot Model – Gas Phase Kinetics

Growth of soot particles:

1. HACA (Frenklach, 1994)

2. PAH deposition onto particle surface (Frenklach, 1991)
Two mechanisms for consumption simplified: 

\[ r_{\text{consume}} = r_{\text{oxy}} + r_{\text{gas}} \]

\[ r_{\text{oxy}} = \frac{1}{T^{1/2}} \left( A_{O_2} P_{O_2} \exp \frac{-E_{O_2}}{RT} + A_{OH} P_{OH} \right) \]

\[ r_{\text{gas}} = A_{CO_2} P_{CO_2}^{1/2} T^2 \exp \frac{-E_{CO_2}}{RT} + A_{H_2O} P_{H_2O}^{1.21} T^{-1/2} \exp \frac{-E_{H_2O}}{RT} \]
PAH Model – Coagulation

- Based on work done by Frenklach (Frenklach 2002)
- Knudsen number defines continuum vs free molecular

\[ Kn = 2\lambda_f / d \]
\[ G_r = \frac{G_r^f}{1 + 1/Kn} + \frac{G_r^c}{1 + Kn} \]

- Continuum and free molecular rates are calculated as follows:

\[ G_r = \frac{1}{2} \sum_{k=1}^{r-1} \left( \begin{array}{c} r \end{array} \right) \left( \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} m_i^k m_j^{r-k} \beta_{ij} N_i N_j \right) \]

- \( \beta \) are calculated differently for free molecular vs continuum (Seinfeld 1998)

Note the temperature dependence
Coal Validation

- Experiment conducted by Jinliang Ma at BYU (Ma, 1998)
- Laminar flat flame burner
- Separation system collects soot, char and ash particles
- 6 coal types
- 3 flame temperatures
- Equilibrium chemistry profile ABF mechanism
Coal Validation (Soot Mass)

- Model predicts consistent results with the experimented data
- Model results ‘over predict’ experimental results
  - Experimental mass loses:
    - Soot not captured by suction probe
    - Deposits in collection system
    - Filter pore size 1 micron
    - Sieve loses
- Concentrations level off
  - Little to no gas phase reactions
Coal Validation (Particle Size)

- Better agreement with the particle sizes
- Needs some refinement
  - Morphology of the soot
Biomass Validation

- Experiment conducted in collaboration between Technical University of Denmark and Lulea University of Technology (Trubetskaya, 2016)
- Drop tube reactor
- Biomass gasification
- Soot collected as deposits from drop tube products
- 3 biomass types
- 2 reactor temperatures

## Biomass Validation (Soot Mass)

### Experiment Measured Yield

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Temperature (C)</th>
<th>Measured Yield (%)</th>
<th>Predicted Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pinewood</td>
<td>1250</td>
<td>8.3</td>
<td>4.8</td>
</tr>
<tr>
<td>Pinewood</td>
<td>1400</td>
<td>6.9</td>
<td>12.7</td>
</tr>
<tr>
<td>Beechwood</td>
<td>1250</td>
<td>5.9</td>
<td>7.7</td>
</tr>
<tr>
<td>Beechwood</td>
<td>1400</td>
<td>6.1</td>
<td>4.3</td>
</tr>
<tr>
<td>Wheat Straw</td>
<td>1250</td>
<td>2.8</td>
<td>8.1</td>
</tr>
<tr>
<td>Wheat Straw</td>
<td>1400</td>
<td>3.7</td>
<td>7.9</td>
</tr>
</tbody>
</table>

### Model Predicted Soot Yield

![Graph showing biomass validation results](image-url)
<table>
<thead>
<tr>
<th>Experiment</th>
<th>Model</th>
<th>Experiment</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>151 nm</td>
<td>73 nm</td>
<td>70 nm</td>
<td>108 nm</td>
</tr>
<tr>
<td>(a) Pinewood soot (1250°C)</td>
<td>(b) Pinewood soot (1400°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>61 nm</td>
<td>23 nm</td>
<td>61 nm</td>
<td>62 nm</td>
</tr>
<tr>
<td>(c) Beechwood soot (1250°C)</td>
<td>(d) Beechwood soot (1400°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>63 nm</td>
<td>25 nm</td>
<td>45 nm</td>
<td>56 nm</td>
</tr>
<tr>
<td>(e) Wheat straw soot (1250°C)</td>
<td>(f) Wheat straw soot (1400°C)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Conclusions

• Detailed soot model for complex solid fuels presented
• Model evaluates evolution of two species: PAH and soot
• PAH PSD- discrete bin approach
• Soot PSD- method of moments with interpolative closure
• Validation work presented with good agreement for both coal and biomass systems

Ongoing Work

• Aggregate evaluation
• Surrogate model creation for use in computationally expensive systems