A fully coupled simulation of PAH and soot growth with a population balance model

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Outline

• Work flow
• The population balance model
  – Particle representation
  – Particle transformation
  – Model parameters
• Results
Work flow

Gas phase solver

Temperature profile & Fuel composition

Input

Laminar flame code

PREMIX

Output

Gas phase species profile

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Work flow: Continued

Population balance solver

Gas-phase profile

Input

Population balance model

Detailed particle representation

Kinetic Monte Carlo Method

Output

Simulated mass spectra and PSDFs
Detailed particle representation

Primary particle
\[ p_i = p_i(PAH_1, PAH_2, ..., PAH_j) \]

PAH molecule
\[ PAH_j = PAH_j(\eta_c, \eta_s) \]

Connectivity (C)

Soot particle
\[ P_q = P_q(p_1, ..., p_n, C) \]
Transformations

Inception:

Coagulation:

Condensation:
Transformations (surface reaction)

Surface reactions:

- Describe the evolution of PAH as a series of 18 jump process
- Can be applied to the growth of PAH in both the gas and particle phase
- Reactions occur on specific sites
Transformations (surface reaction)

Examples:

AC ring growth: \[ \text{R5 to R6 conversion:} \]

\[
\begin{array}{c}
\text{C}_2\text{H}_2 \quad \text{(R5 to R6 conversion)} \\
\text{(-2H)} \\
\text{R6 oxidation by oxygen:} \\
\text{O}_2 \quad \text{(-2CO)}
\end{array}
\]

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Particle rounding:

Two mechanisms for particle rounding:
- Mass addition incl. condensation and surface reaction
- Sintering
  Rearrangement of molecules in adjacent primary particles
Rounding level: \[ R(p_i, p_j) = \frac{S_{\text{sph}}(p_i, p_j)}{C_{ij}} - 2^{-\frac{1}{3}} \]

\[ 1 - 2^{-\frac{1}{3}} \]

\( S_{\text{sph}}(p_i, p_j) \): Spherical equivalence surface area

\( C_{ij} \): Common surface area

If \( R(p_i, p_j) > 0.95 \)

The change in the \( C_{ij} \) due to the sintering process

\[ \frac{\Delta C_{ij}}{\Delta t} = -\frac{1}{\tau_s(p_i, p_j)} (C_{ij} - S_{\text{sph}}(p_i, p_j)) \]

A viscous flow model is adapted:

\[ \tau_s = A_s d_{i,j} \exp \left[ \frac{E_s}{RT} \left( 1 - \frac{d_{p, \text{crit}}}{d_{i,j}} \right) \right] \]
# Model parameters

<table>
<thead>
<tr>
<th>Name</th>
<th>Variable</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soot density</td>
<td>$\rho$</td>
</tr>
<tr>
<td>Smoothing factor</td>
<td>$s$</td>
</tr>
<tr>
<td>Growth factor</td>
<td>$g$</td>
</tr>
<tr>
<td>Pre-exponential factor of sintering</td>
<td>$A_s$</td>
</tr>
<tr>
<td>Activation energy of sintering</td>
<td>$E_s$</td>
</tr>
<tr>
<td>Critical diameter of sintering</td>
<td>$d_{p,\text{crit}}$</td>
</tr>
</tbody>
</table>
The median of the particle size distribution is optimised against experimental values by minimising the objective function:

Data points in the 5-dimensional parameter space are generated using a Sobol sequence.

### Parameter estimation

<table>
<thead>
<tr>
<th>Name</th>
<th>Variable</th>
<th>Value (unit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soot density</td>
<td>ρ</td>
<td>1.88 (g/cm³)</td>
</tr>
<tr>
<td>Smoothing factor</td>
<td>s</td>
<td>1.69 (-)</td>
</tr>
<tr>
<td>Growth factor</td>
<td>g</td>
<td>0.0263 (-)</td>
</tr>
<tr>
<td>Pre-exponential factor of sintering</td>
<td>Aₖ</td>
<td>1.1x10⁻¹⁴ (s/m)</td>
</tr>
<tr>
<td>Activation energy of sintering</td>
<td>Eₛ</td>
<td>9.61x10⁴ (K)</td>
</tr>
<tr>
<td>Critical diameter of sintering</td>
<td>dₚ,crit</td>
<td>1.58 (nm)</td>
</tr>
</tbody>
</table>

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Results (PSDFs)

Initial conditions of the flames

<table>
<thead>
<tr>
<th>Flame</th>
<th>C2H4 (mole fraction)</th>
<th>O2</th>
<th>Ar</th>
<th>Φ</th>
<th>Pressure (bar)</th>
<th>Inflow velocity (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A2</td>
<td>0.242</td>
<td>0.379</td>
<td>0.379</td>
<td>1.92</td>
<td>1</td>
<td>7.85</td>
</tr>
<tr>
<td>A3</td>
<td>0.242</td>
<td>0.379</td>
<td>0.379</td>
<td>1.92</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>B3</td>
<td>0.242</td>
<td>0.379</td>
<td>0.379</td>
<td>1.92</td>
<td>1</td>
<td>8</td>
</tr>
</tbody>
</table>

Results (PSDFs)

- Experiments

- Simulations

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A3

B3

Normalised number density

Diameter, nm

5 mm 8 mm 10 mm 12 mm

Increasing HAB

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The CE model determines the sticking likelihood of two gas-phase PAHs.

- Step function
  - Min mode
  - Max mode
  - Combined mode
  - Reduced mode
Results (mass spectra)

Initial conditions of the flames

<table>
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<th>Flame</th>
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<th>Pressure (bar)</th>
<th>Inflow velocity (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>0.5</td>
<td>3.0</td>
<td>0.08</td>
<td>54</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>0.5</td>
<td>3.0</td>
<td>0.12</td>
<td>54</td>
</tr>
<tr>
<td>3</td>
<td>0.5</td>
<td>0.5</td>
<td>3.0</td>
<td>0.15</td>
<td>54</td>
</tr>
<tr>
<td>4</td>
<td>0.5</td>
<td>0.5</td>
<td>3.0</td>
<td>0.18</td>
<td>54</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>0.5</td>
<td>3.0</td>
<td>0.22</td>
<td>54</td>
</tr>
</tbody>
</table>


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Results (mass spectra)

Mass spectrum of flame 2, HAB = 30 mm.

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Mass spectra continued

- Maximum dimer point, $D_m$
- Monomer decay point, $M_{decay}$
- Dimer spread point, $D_{spread}$
Mass spectra continued

Optimal CE model:
- Min-32
- Max-48
- Combined-36
- Reduced-32
Mass spectra continued

<table>
<thead>
<tr>
<th>Case</th>
<th>$D_m$</th>
<th>$D_{spread}$</th>
<th>$M_{decay}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment</td>
<td>950</td>
<td>1100</td>
<td>800</td>
</tr>
<tr>
<td>Direct simulation</td>
<td>992</td>
<td>n/a</td>
<td>n/a</td>
</tr>
</tbody>
</table>
Assuming x-mer fragmentation by laser ablation:
Mass spectra continued

Simulation

Experiment

Number density, cm\(^{-3}\)

Intensity (Counts)

PAH mass, u

PAH mass, u

120 mbar

CoMo GROUP

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Mass spectra continued

Hypo-5 represents the thresholds of the x-mer fragmentation is five PAHs
Conclusions

According to the preliminary results:

• Direct simulation fails to reproduce the experimental mass spectra
• A laser ablation hypothesis is tested and shows promising agreement
Thank you!

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