Urban Air Pollution from Ethanol (E85) in the Presence of Aqueous Aerosols and Fog

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Outline

• Model
  – Mechanisms
  – Solver Optimizations
• Ethanol (E85) vs. Gasoline – Gas Phase
  – Model Setup
  – Results
  – Conclusions
• With a Fog?
Model

• Master Chemical Mechanism (v. 3.1)  
  (Saunders and Jenkins et al. 2003)
  – Near-Explicit Organic Chemistry Mechanism
  – Over 4,600 Species and 13,500 Reactions

• CAPRAM 3.0  
  (Herrmann et al. 2005)
  – Chemical Aqueous Phase Radical Mechanism
  – Aqueous oxidation pathways of 34 chemical species, C1-C4
Model

- SMVGGEAR II
  (Jacobson 1998)
  - Ordinary Differential Equation solver
  - Gear solution mechanism – accurate
  - Sparse-matrix – fast
### SMVGEAR II with MCM 3.1 and CAPRAM 3.0

<table>
<thead>
<tr>
<th></th>
<th>Initial</th>
<th>Sparse-matrix</th>
<th>% Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Order of matrix</td>
<td><strong>4,649</strong></td>
<td><strong>4,649</strong></td>
<td>0</td>
</tr>
<tr>
<td>No. initial matrix spots filled</td>
<td>21,566,736</td>
<td>38,016</td>
<td>99.82</td>
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<td>No. final matrix spots filled</td>
<td>21,566,736</td>
<td>49,069</td>
<td>99.77</td>
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<tr>
<td>Decomposition 1</td>
<td><strong>33,374,524,734</strong></td>
<td><strong>446,030</strong></td>
<td><strong>99.9987</strong></td>
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<tr>
<td>Decomposition 2</td>
<td>10,781,046</td>
<td>25,412</td>
<td>99.76</td>
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<tr>
<td>Backsubstitution 1</td>
<td>10,781,046</td>
<td>25,412</td>
<td>99.76</td>
</tr>
<tr>
<td>Backsubstitution 2</td>
<td>10,781,046</td>
<td>19,013</td>
<td>99.82</td>
</tr>
</tbody>
</table>
Model

• SMVGGEAR II

(Jacobson 1998)

– > 99.999% reduction in required multiplications
  (6 orders of magnitude)

– ~ 8 hrs to run 24 hrs in a 3D model with 50,000 grid cells for MCM plus CAPRAM ( >5,000 species and >14,500 reactions)
E85 vs Gasoline

E85
Model Setup

- Box Model, South Coast Air Basin
Model Setup

• Box Height = 500 m
• 2 Days – daytime and nighttime chemistry
• Vehicle Emissions Decreased by 60% - 2020
• Two Data Sets Based on
  – 11 studies ~24 C
  – 1 vehicle at -7 C
• Tested sensitivity to box height, water vapor, initial concentrations, background emissions, toluene
Emissions Profile

Diurnal profile for urban vehicles

EMCTA (U.S. EPA)
2 Day Average Ozone Concentration and Difference

Average Ozone (ppbv) vs Temperature (°C)

- E85 (-7°C)
- Gasoline (-7°C)
- E85 (24°C)
- Gasoline (24°C)

Difference in Average Ozone (E85 - Gasoline) (ppbv)

Temperature (°C):
-37 -32 -26 -21 -15 -9 -4 2 7 13 18 24 29 35 41

Average Ozone (ppbv):
0 5 10 15 20 25 30 35 40 45

Difference (E85 - Gasoline) (ppbv):
0 5 10 15 20 25 30 35 40 45
Conclusions

- Results suggest that E85’s effect on health through ozone formation becomes increasingly more significant relative to gasoline at colder temperatures, even with the weaker winter sunshine.

- Both E85 and gasoline are harmful to human health – should concentrate on cleaner technologies.

(Ginnebaugh et. al 2010)
With a Fog?

- Ethanol, Acetaldehyde, Formaldehyde dissolve
  - Impacts gaseous species
  - Difference between gasoline and E85
  - Ozone formation and human health implications
Aqueous Ethanol Reactions

\[
\text{CH}_3\text{CH}_2\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{CH}_3\text{CHOH}
\]
\[k = 2.1 \times 10^9 \text{ M}^{-1}/\text{s}\]

\[
\text{CH}_3\text{CHOH} + \text{O}_2 \rightarrow \text{O}_2\text{CH}_3\text{CHOH}
\]
\[k = 4.6 \times 10^9 \text{ M}^{-1}/\text{s}\]

\[
\text{O}_2\text{CH}_3\text{CHOH} \rightarrow \text{CH}_3\text{CHO} + \text{HO}_2
\]
\[k = 52 \text{ 1/s}\]

T = 298 K
Aqueous Acetaldehyde Reactions

\[
\text{CH}_3\text{CHO} + \text{H}_2\text{O} \leftrightarrow \text{CH}_3\text{CH} (\text{OH})_2 \\
K = 0.0246 \text{ M}
\]

\[
\text{CH}_3\text{CH} (\text{OH})_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{CH}_3\text{C} (\text{OH})
\]

\[
k = 3.6 \times 10^9 \text{ M}^{-1}/\text{s}
\]

\[
\text{CH}_3\text{C} (\text{OH})_2 + \text{O}_2 \rightarrow \text{CH}_3\text{C} (\text{OH})_2\text{O}_2
\]

\[
k = 5 \times 10^4 \text{ M}^{-1}/\text{s}
\]

\[
\text{CH}_3\text{C} (\text{OH})_2\text{O}_2 \rightarrow \text{CH}_3\text{COOH} + \text{HO}_2
\]

\[
k = 1 \times 10^3 \text{ 1/s}
\]

\[T = 298 \text{ K}\]
## Henry’s Constants

<table>
<thead>
<tr>
<th></th>
<th>H(298) (M/atm)</th>
<th>H*(298) (M/atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>190</td>
<td>190</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>4.8</td>
<td>4.92</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>2.5</td>
<td>92.5</td>
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</tbody>
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