Modeling of Partial Oxidation of Acetaldehyde in Cool Flame

Alexandre V. Chirokov

- Description of Modeling Case
- Gas Dynamics Modeling
- Chemistry Kinetics Modeling
Physical Properties for Reacting flow

- Density
- Viscosity
- Formation Enthalpies
- Heat Capacity
- Thermal Conductivity
- Mass Diffusion Coefficient

13 Species → 5 Physical Properties → at 8 Temperature points

Piecewise-Linear Variation with Temperature

\[ F(T) = F_n + \frac{(T - T_n) (F_{n+1} - F_n)}{T_{n+1} - T_n} \]
We solve Gas Dynamics equations on 2D axial-symmetrical non-uniform Grid. We vary the following parameters:

- Gas Mixture inlet velocity: $0.2 \ldots 50$ [m/sec]
- Temperature boundary conditions on Tube walls: $600 \ldots 1200$ [K]

and we try adiabatic walls.

We kept constant the following parameters:

- Gas Mixture composition: 1:8 [O2:CH3CHO] molar fractions
- Gas Mixture inlet temperature: 300 [K]
Tube Parameters

- Length = 240 [mm]
- Inner diameter = 80 [mm]
- Outlet diameter = 80 [mm]
- Inlet diameter = 3 [mm]
Effective Viscosity of Gas Mixture: $1.8 \times 10^{-5} \ldots 0.35 \times 10^{-3}$ [KG/M-S]

Stream Function of Gas Mixture: $0.0 \ldots 2.65 \times 10^{-5}$ [M3/S]

Parameters:
- $U = 0.6$ [m/sec]
- $T_w = 600$ [K]
- $T_g = 300$ [K]
Gas Dynamics Modeling

\[ \Delta T = 3.5 \text{ sec} \]

\[ T_m = 0.5 \text{ sec} \]

\[ U = 50 \text{ m/sec} \]

\[ \Delta T = 0.0338 \text{ sec} \]
Temperature Distribution

U = 0.6 [m/sec]
Tw = 600 [K]
Tg = 300 [K]

Zoom region

Temperature distribution 300 .. 650 [K]
Chemistry Modeling with FLUENT

Reaction Rate $\text{CH}_3\text{CHO} + \text{O}_2 = \text{CH}_3\text{CO} + \text{HO}_2$

$-1.44E3 \ldots 0.0 \quad [\text{KG/M}^3/\text{S}]$

U = 0.6 [m/sec]
Tw = 600 [K]
Tg = 300 [K]

Blue – no reactions

Reaction Rate $\text{OH} + \text{CH}_3\text{CHO} = \text{CH}_3\text{CO} + \text{H}_2\text{O}$

$2288.179 \ldots 0.0$

Blue – no reactions
Effective Viscosity of Gas Mixture $1.6 \times 10^{-5} \ldots 0.5 \times 10^{-3}$ [KG/M-S]

Stream Function of Gas Mixture $0 \ldots 2.65 \times 10^{-4}$ [M3/S]

$U = 5$ [m/sec]
$T_w = \text{adiabatic}$
$T_g = 300$ [K]
Temperature distribution \(300 \ldots 635\) [K]

\[
U = 5 \text{ [m/sec]}
\]

\[
Tw = \text{adiabatic}
\]

\[
Tg = 300 \text{ [K]}
\]

Mole fraction of OH \(0 \ldots 1.66E-3\)
Mole Fractions of Species

Mole fraction of O₂  0.04 .. 0.1

Mole fraction of OH  0 .. 1.66E-3

U = 5  [ m/sec ]
Tw = adiabatic
Tg = 300  [ K ]
Chemistry modeling with FLUENT

\[
\text{CH}_3\text{CHO} + \text{O}_2 = \text{CH}_3\text{CO} + \text{HO}_2 \quad 0 \ldots 0.003342973 \text{[kg/m}^3\text{/s]} 
\]

\[
\text{CH}_3\text{CO}_3\text{H} + \text{O}_2 = \text{CH}_3 + \text{OH} + \text{CO}_2 \quad 0 \ldots 0.149 \text{[kg/m}^3\text{/s]} 
\]

\[
U = 5 \quad \text{[m/sec]} 
\]

\[
T_w = \text{adiabatic} 
\]

\[
T_g = 300 \quad \text{[K]} 
\]
CHEMKIN Framework

Gas-Phase Reactions
[ chem.inp ]

Thermodynamic Database
[ therm.dat ]

COOL Flame Input file
[ cool flame.inp ]

CHEMKIN Interpreter

CHEMKIN link file
[ chem.bin ]

CHEMKIN Gas-Phase Subroutine Library

ODE Solver

COOL Flame FORTRAN Program

Debug information output
Used for control precision of solution
[ debug.out ]

Digitally formatted output
Contain the same data as [ cool flame.out ] but in EXEL format
[ cool flame.ex ]

Text Formatted Output file
[ cool flame.out ]
Post Processing Framework

- **CHEMKN link file** [chem.bin]
- **SENKIN input file** [senkin.inp]
- **SENKIN**
- **SENKIN Binary file** [senkin.bin]
- **MECHMOD**
- **XSenkPlot**
- **KINALC**

**Post Processing** of results of Chemistry kinetics modeling. Used for:
- Proving and Enhancement
- Visualization
- Understanding
- Reducing
- Validation of Gas-Phase Reactions Mechanism

**Sensitivity analysis of Gas-Phase Reactions Mechanism**

- Processing sensitivity analysis results
- Extracting information from reaction rates and stoichiometry
- Redundant species and QSSA species

**Modification and transformation of mechanism files**

- Reactions Paths Net Rate and Reaction Flux integration
## Version info of used Software

<table>
<thead>
<tr>
<th></th>
<th>Description</th>
<th>Version</th>
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<tbody>
<tr>
<td>1</td>
<td>CHEMKIN Gas-Phase Subroutine Library CHEMKIN-II</td>
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<td>5</td>
<td>KINALC</td>
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<td>6</td>
<td>MECHMOD</td>
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<tr>
<td>7</td>
<td>SENKIN</td>
<td>3.1</td>
</tr>
<tr>
<td>8</td>
<td>LSODE Livermore solver for ODE march 30, 1987</td>
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</tr>
<tr>
<td>9</td>
<td>XSenkPlot</td>
<td>1.2</td>
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</table>
Gas-Phase Reactions Mechanism

(k = A T**b exp(-E/RT))

<table>
<thead>
<tr>
<th>REACTIONS CONSIDERED</th>
<th>A</th>
<th>b</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. CH3CHO+O2=&gt;CH3CO+HO2</td>
<td>3.00E+12</td>
<td>0.0</td>
<td>25237.1</td>
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<tr>
<td>2. CH3CO+O2=&gt;CH3CO3</td>
<td>2.00E+11</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>3. CH3CO3+CH3CHO=&gt;CH3CO3H+CH3CO</td>
<td>1.00E+13</td>
<td>0.0</td>
<td>10139.0</td>
</tr>
<tr>
<td>4. CH3CO3H=&gt;CH3+OH+CO2</td>
<td>2.00E+14</td>
<td>0.0</td>
<td>40170.3</td>
</tr>
<tr>
<td>5. CH3CO+M=&gt;CH3+CO+M</td>
<td>3.00E+12</td>
<td>0.0</td>
<td>16722.0</td>
</tr>
<tr>
<td>6. CH3+O2=&gt;CH3O2</td>
<td>1.00E+12</td>
<td>0.0</td>
<td>15065.4</td>
</tr>
<tr>
<td>7. CH3O2=&gt;CH3+O2</td>
<td>1.00E+14</td>
<td>0.0</td>
<td>27641.7</td>
</tr>
<tr>
<td>8. 2CH3=&gt;C2H6</td>
<td>2.50E+13</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>9. CH3O2+CH3O2=&gt;CH3O+CH3O+O2</td>
<td>1.00E+12</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>10. CH3O+CH3O=&gt;CH2O+CH3OH</td>
<td>1.00E+12</td>
<td>0.0</td>
<td>0.0</td>
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<tr>
<td>11. CH3O2+CH3CHO=&gt;CH3O2H+CH3CO</td>
<td>1.00E+12</td>
<td>0.0</td>
<td>10329.8</td>
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<tr>
<td>12. CH3O2H=&gt;CH3O+OH</td>
<td>2.00E+15</td>
<td>0.0</td>
<td>40649.4</td>
</tr>
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</table>

NOTE: A units mole-cm-sec-K, E units cal/mole

Gas-Phase Reactions Mechanism

\( (k = A \ T^{b} \ \exp(-E/RT)) \)

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<th>b</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>13. OH+CH3CHO=&gt;CH3CO+H2O</td>
<td>1.00E+12</td>
<td>0.0</td>
<td>2391.6</td>
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<tr>
<td>14. CH3O+O2=&gt;CH2O+HO2</td>
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<td>15. OH+CH2O=&gt;HCO+H2O</td>
<td>6.00E+11</td>
<td>0.0</td>
<td>0.0</td>
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<tr>
<td>16. HCO+M=&gt;H+CO+M</td>
<td>1.50E+14</td>
<td>0.0</td>
<td>18991.7</td>
</tr>
<tr>
<td>17. HCO+O2=&gt;CO+HO2</td>
<td>1.00E+12</td>
<td>0.0</td>
<td>5978.0</td>
</tr>
<tr>
<td>18. OH+CO=&gt;H+CO2</td>
<td>3.00E+11</td>
<td>0.0</td>
<td>600.4</td>
</tr>
<tr>
<td>19. H+O2=&gt;OH+O</td>
<td>2.00E+14</td>
<td>0.0</td>
<td>16492.8</td>
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<tr>
<td>20. H+O2+M=&gt;HO2+M</td>
<td>5.00E+09</td>
<td>0.0</td>
<td>-1300.2</td>
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<tr>
<td>21. O+CH2O=&gt;HCO+OH</td>
<td>5.00E+13</td>
<td>0.0</td>
<td>4598.3</td>
</tr>
<tr>
<td>22. HO2+CH2O=&gt;HCO+H2O2</td>
<td>1.00E+12</td>
<td>0.0</td>
<td>7995.9</td>
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<tr>
<td>23. 2HO2=&gt;H2O2+O2</td>
<td>1.80E+12</td>
<td>0.0</td>
<td>0.0</td>
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<tr>
<td>24. H2O2+M=&gt;2OH+M</td>
<td>3.10E+17</td>
<td>0.0</td>
<td>46977.3</td>
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<tr>
<td>25. OH+H2O2=&gt;HO2+H2O</td>
<td>3.60E+12</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

NOTE: A units mole-cm-sec-K, E units cal/mole
We Solve:
\[
\frac{dY_i(x)}{dx} = F_i(x; y_1 \ldots Y_N); \quad i = 1 \ldots N
\]

In *initial value problems* all the \(Y_i\) are given at some starting value \(X_s\), and it is desired to find the \(Y_i\)'s at some final point \(X_f\), or at some discrete list of points (for example, at tabulated intervals).

We use:

*Predictor-corrector* methods store the solution along the way, and use those results to extrapolate the solution one step advanced; they then correct the extrapolation using derivative information at the new point. Ideal for high-precision solution of *smooth equations* with complicated right-hand sides.

Implementation:

“LSODE” Livermore solver for ordinary differential equations that use Adams-Bashforth-Moulton method.
Adams-Bashforth-Moulton method

The Adams-Bashforth part is the predictor. For example, the third-order case is

predictor: \[ y_{n+1} = y_n + \frac{h}{12}(23y'_n - 16y'_{n-1} + 5y'_{n-2}) + O(h^4) \]

Here information at the current point \( X_n \), together with the two previous points \( X_{n-1} \) and \( X_{n-2} \) (assumed equally spaced), is used to predict the value \( Y_{n+1} \) at the next point, \( X_{n+1} \). The Adams-Moulton part is the corrector. The third-order case is

corrector: \[ y_{n+1} = y_n + \frac{h}{12}(5y'_{n+1} + 8y'_n - y'_{n-1}) + O(h^4) \]

Without the trial value of \( Y_{n+1} \) from the predictor step to insert on the right-hand side, the corrector would be a nasty implicit equation for \( Y_{n+1} \).

The difference between the predicted and corrected function values supplies information on the local truncation error that can be used to control accuracy and to adjust stepsize.

\[ \text{RMS} \left( \frac{e(i)}{ewt(i)} \right) < 1, \text{ where } ewt(i) = rtol \cdot \text{abs}(y(i)) + atol; \]

All calculations were made with

\[ rtol=1.0\text{E}-8 \quad \text{relative tolerance} \]
\[ atol=1.0\text{E}-15 \quad \text{absolute tolerance} \]
Tolerance of *Predictor-Corrector*

The tolerance of *Predictor-corrector* is highly affected by the second derivative of solution. Because *Predictor* step performs extrapolation of solution, and when the second derivative is high this step leads to high local errors.

\[
F(x) = \frac{f(x_{i+1}) - 2 R(x_i) + R(x_{i-1})}{x_i^2}
\]

\( R = 4.0 \text{ [1/sec]} \)
Description of Modeling Case

For example if we have $R = 4$ and $(T-T_x)$ is about 100 [K] and Heat Capacity $C_p$ is 1.7 [$J/(g*K)$] then 

$$\text{Power} = 680 \ [J/(g*sec)]$$

Units of $R$ is [1/sec]

if $R=0$ then adiabatic reactor case
Ignition time of gas mixture

$\text{Ti} = 360 \, [\text{K}]$

$\text{Tf} = 1010 \, [\text{K}]$

ign. time $= 5160 \, [\text{sec}]$

O$_2$:CH$_3$CHO$=1:8$

Adiabatic case
Ignition time of gas mixture

O2:CH3CHO=1:8

Ignition time = 0.24/0.8 sec

Ti = 570 [ K ]
Tf = 1120 [ K ]
ign. time = 0.24/0.8 [ sec ]

Adiabatic case
Ignition time of gas mixture

O_2 : CH_3CHO = 1 : 8

ign. time = 4.4/4.8 [sec]

Ti = 480 [K]
T_f = 1074 [K]

Adiabatic case
Ignition time of gas mixture

\( \text{O}_2: \text{CH}_3\text{CHO} = 1:8 \)

Ignition time vs. initial gas mixture temperature

\[ y = 2 \times 10^e^{-0.0451x} \]

\( R^2 = 0.9672 \)

Adiabatic case
Ignition time of gas mixture

Ignition time vs. initial gas mixture temperature

O₂:CH₃CHO = 1:8
Temperature vs. time

O₂:CH₃CHO=1:8

Ti = 570 [K]
R = 0.3 [1/sec] Blue line
R = 0.0 [1/sec] Red line
Temperature vs. time

\[ \text{O}_2 : \text{CH}_3\text{CHO} = 1 : 8 \]

- \( T_i = 570 \) [K]
- \( R = 0.3 \) [1/sec] Blue
- \( R = 0.5 \) [1/sec] Yellow
- \( R = 1.0 \) [1/sec] Magenta
- \( R = 2.0 \) [1/sec] Aquamarine
Temperature vs. time

$O_2 : CH_3CHO = 1 : 8$

$T_i = 570 \ [\ K]\$

$R = 4.0 \ [\ 1/sec] \ \text{Magenta}$

$R = 5.0 \ [\ 1/sec] \ \text{Blue}$

$R = 6.0 \ [\ 1/sec] \ \text{Yellow}$

$R = 7.0 \ [\ 1/sec] \ \text{Aquamarine}$
Temperature vs. time

$O_2:CH_3CHO=1:8$

$T_i = 570 \text{ [ K ]}$

$R = 9.0 \text{ [ 1/sec ] Blue}$

$R = 10.0 \text{ [ 1/sec ] Magenta}$

$R = 20.0 \text{ [ 1/sec ] Yellow}$

$R = 25.0 \text{ [ 1/sec ] Aquamarine}$
Reactions, denoted by * below a reaction time number are important at this reaction time. Reactions, denoted by * below letter S are important at least at one reaction time.
Mole fraction of CH$_3$CO

O$_2$:CH$_3$CHO = 1:8

Ti = 570 [K]
R = 0.5 [1/sec]

CH$_3$CO [mole fractions]
Mole fraction

\[ \text{O}_2 : \text{CH}_3\text{CHO} = 1 : 8 \]

\[ T_i = 570 \, \text{[K]} \]
\[ R = 0.5 \, \text{[1/sec]} \]

\[ \text{CH}_3\text{CO}_3\text{H} \, \text{[mole fractions]} \]
\[ \text{CH}_3\text{CO} \, \text{[mole fractions]} \]
\[ \text{CH}_3\text{CO}_3 \, \text{[mole fractions]} \]
Mole fraction of Products

\[ \text{O}_2: \text{CH}_3\text{CHO} = 1:8 \]

\[ T_i = 570 \ [ \text{K} ] \]
\[ R = 0.5 \ [ \text{1/sec} ] \]

- \( \text{C}_2\text{H}_6 \) [mole fractions]
- \( \text{H}_2\text{O} \) [mole fractions]
- \( \text{CO}_2 \) [mole fractions]
Comparison of Products

O₂:CH₃CHO = 1:7

Ti = 470 [ K ]
R = 2.5 [ 1/sec ]
R = 0.0 [ 1/sec ]
Comparison of Products

O$_2$ : CH$_3$CHO = 1 : 7

Ti = 470 [ K ]
R = 2.5 [ 1/sec ]
R = 0.0 [ 1/sec ]

Cool flame

Ordinary flame
Comparison of Products

$O_2:CH_3CHO = 1:8$

$T_i = 570 [K]$  
$R = 0.5 \frac{1}{sec}$  
$R = 4.0 \frac{1}{sec}$  
$R = 25 \frac{1}{sec}$
Region of Cool Flame

\[ Ti = 550 \ [K] \]

\[ 5O_2 + 2CH_3CHO \rightarrow 4CO_2 + 4H_2O \]

\[ O_2 : CH_3CHO = 1 : 0.4 \]
Physical Properties for Reacting flow

- Density
- Viscosity
- Formation Enthalpies
- Heat Capacity
- Thermal Conductivity
- Mass Diffusion Coefficient

13 Species → 5 Physical Properties → at 8 Temperature points

Piecewise-Linear Variation with Temperature

\[ F(T) = F_n + \frac{(T - T_n)(F_{n+1} - F_n)}{T_n + 1 - T_n} \]
We solve Gas Dynamics equations on 2D axial-symmetrical non-uniform Grid. We vary the following parameters:

- Gas Mixture inlet velocity $0.2 \ldots 50$ [m/sec]
- Temperature boundary conditions on Tube walls $600 \ldots 1200$ [K]

and we try adiabatic walls.

We kept constant the following parameters:

- Gas Mixture composition $1:8$ [O₂:CH₃CHO] molar fractions
- Gas Mixture inlet temperature $300$ [K]
Tube Parameters

Length = 240 [mm]
Inner diameter = 80 [mm]
Outlet diameter = 80 [mm]
Inlet diameter = 3 [mm]
Gas Dynamics Modeling

Effective Viscosity of Gas Mixture  $1.8\times10^{-5} \ldots 0.35\times10^{-3}$ [kg/m-s]

Stream Function of Gas Mixture  $0.0 \ldots 2.65\times10^{-5}$ [m$^3$/s]

$U = 0.6$ [m/sec]

$T_w = 600$ [K]

$T_g = 300$ [K]
Gas Dynamics Modeling

$\Delta T = 3.5 \text{ sec}$

$T_m = 0.5 \text{ sec}$

$U = 50 \text{ m/sec}$

$\Delta T = 0.0338 \text{ sec}$
Temperature Distribution

$U = 0.6 \ [ m/sec ]$

$T_w = 600 \ [ K ]$

$T_g = 300 \ [ K ]$

Zoom region

Temperature distribution $300 \ldots 650 \ [ K ]$
Temperature + OH [600K..650K]

0.001 ... 0.0031

0.0005 ... 0.0031
Chemistry Modeling with FLUENT

Reaction Rate $\text{CH}_3\text{CHO} + \text{O}_2 = \text{CH}_3\text{CO} + \text{HO}_2$ $-1.44\times10^3 \ldots 0.0$ [KG/M$^3$/S]

U = 0.6 [m/sec]

Tw = 600 [K]

Tg = 300 [K]

Reaction Rate $\text{OH} + \text{CH}_3\text{CHO} = \text{CH}_3\text{CO} + \text{H}_2\text{O}$ $2288.179 \ldots 0.0$
Effective Viscosity of Gas Mixture 1.6E-05 .. 0.5E-3 [KG/M-S]

U = 5 [m/sec]
Tw = adiabatic
Tg = 300 [K]

Stream Function of Gas Mixture 0 .. 2.65E-04 [M3/S]
Temperature Distribution

Temperature distribution 300 .. 635 [ K ]

Mole fraction of OH 0 .. 1.66E-3
Mole Fractions of Species

Mole fraction of O₂: 0.04 .. 0.1

Mole fraction of OH: 0 .. 1.66E-3

U = 5 [ m/sec ]
Tw = adiabatic
Tg = 300 [ K ]
Chemistry modeling with FLUENT

CH₃CHO+O₂=CH₃CO+HO₂  0 .. 0.003342973 [KG/M³/S]

CH₃CO₃H+O₂=CH₃+OH+CO₂  0 .. 0.149 [KG/M³/S]

Red – no reactions

Blue – no reactions

U = 5  [ m/sec ]

Tw = adiabatic

Tg = 300  [ K ]