Improvements in the Modeling of the Self-ignition of Tetrafluoroethylene

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I. Introduction to topic and motivation

II. Numerical Model with REL and Comsol Multiphysics

III. Results of different numerical approaches

IV. Conclusion and outlook
Introduction to TFE

- Tetrafluoroethylene (TFE, $\text{C}_2\text{F}_4$) is monomer of Polytetrafluoroethylene (PTFE) and other copolymers (100.000 t/year)

- PTFE is resistant to most reactive and corrosive chemicals and has non-sticky properties
Motivation

- Several incidents in PTFE-production-plants in the last decades
- TFE is a decomposable gas → possibility of explosive decomposition
- Sources for ignition:
  - Spark ignition, electrostatic
  - Hot surfaces → content of this work
- Research project subsidized by PlasticsEurope to determine hazardous conditions, started 2007
- Exothermic Dimerization reaction of TFE to Octacyclofluorobutane can cause ignition

\[ 2C_2F_4 \leftrightarrow C - C_4F_8 \quad \Delta H_R = -103 \left( \frac{kJ}{mol_{TFE}} \right) \]
Reaktion Engineering Lab

- FEM simulation without fluid dynamic
- Easy integration of complex reaction kinetics
- Thermodynamic properties are calculated via the NASA polynomial coefficients
- Energy and mass balance are solved
Validation data base by experiments

3-dm³ autoclave

- thermocouple for gas temperature
- pressure transducer
- internal volume (cylindrical reaction chamber)

Steel vessel

Aluminium (with heating jacket)

0.2-dm³ autoclave
1st Model: Dimerization – Reaction

**Forward reaction**

\[ 2C_2F_4 \xrightarrow{f} c - C_4F_8 \]

2. order reaction

\[ k_f = 82800 \left[ \frac{m^3}{mol \cdot s} \right] \cdot \exp \left( \frac{-105200 [J/mol]}{RT} \right) \]

\[ r_f = \left( c_{C_2F_4} \right)^2 \cdot k_f \]

New 2-stage kinetics was determined

**Backward reaction**

\[ c - C_4F_8 \xrightarrow{b} 2C_2F_4 \]

1. order reaction

\[ k_f = 2.1 \cdot 10^{16} \left[ \frac{m^3}{mol \cdot s} \right] \cdot \exp \left( \frac{-310961 [J/mol]}{RT} \right) \]

\[ r_b = c_{c-C_4F_8} \cdot k_b \]
# Enhanced reaction net in REL and COMSOL CFD Model

<table>
<thead>
<tr>
<th>Reaction</th>
<th>RO</th>
<th>A0 in [m³ mol⁻¹ s⁻¹] bzw. [s⁻¹]</th>
<th>Ea in [J/mol]</th>
<th>$\Delta H_r^0$ acc. NIST [kJ/mol]</th>
<th>$\Delta H_r^0$ acc. REL (NASA Polynoms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂F₄ + C₂F₄ → C₄F₈</td>
<td>2</td>
<td>8.28E+04</td>
<td>105000</td>
<td>-166</td>
<td>-161,5</td>
</tr>
<tr>
<td>C₄F₈(c) → 2*C₂F₄</td>
<td>1</td>
<td>2.10E+16</td>
<td>310871</td>
<td>166</td>
<td>161,5</td>
</tr>
<tr>
<td>C₄F₈(c) → C₃F₆(e) + CF₂</td>
<td>1</td>
<td>1.58E+17</td>
<td>332580</td>
<td>154,3</td>
<td>164</td>
</tr>
<tr>
<td>C₃F₆(e) → C₂F₄ + CF₂</td>
<td>1</td>
<td>1.58E+13</td>
<td>346008</td>
<td>308,7</td>
<td>288</td>
</tr>
<tr>
<td>C₃F₆(c) → C₂F₄ + CF₂</td>
<td>1</td>
<td>1.78E+13</td>
<td>161501</td>
<td>308,7</td>
<td>288</td>
</tr>
<tr>
<td>C₃F₆(e) → C₃F₆(c)</td>
<td>1</td>
<td>1.00E+13</td>
<td>139767</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C₂F₄ → 2*CF₂</td>
<td>1</td>
<td>5.01E+16</td>
<td>301285</td>
<td>297</td>
<td>290,6</td>
</tr>
<tr>
<td>C₄F₈(c) + CF₂ → C₃F₆(e) + C₂F₄</td>
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<td>1.00E+08</td>
<td>133032</td>
<td>-142,7</td>
<td>-126,5</td>
</tr>
<tr>
<td>C₄F₈(i) → 2*C₂F₄</td>
<td>1</td>
<td>1.00E+16</td>
<td>374070</td>
<td>309</td>
<td>-</td>
</tr>
<tr>
<td>C₄F₈(i) → C₃F₆(e) + CF₂</td>
<td>1</td>
<td>1.20E+16</td>
<td>384962</td>
<td>297,3</td>
<td>-</td>
</tr>
</tbody>
</table>
\[ V_r \cdot \sum (c_i \cdot c_{p_i}) \frac{dT}{dt} = Q_{\text{reaction}} + Q_{\text{loss}} + V_r \frac{dp}{dt} \]

Pressure work is considered

dynamic calculation of alpha, depending on T(t) is implemented

Input window of REL
Prediction of the MITD with the REL method

experimental MITD = 310 °C, 5 bar, 0.2-dm³
Comparison of REL results and experimental values

- Bisektor
- + 20%
- - 20%
- MITD 3-dm³ REL in °C
- MITD 0,2-dm³ REL in °C
- MITD Rohr REL in °C

Partially heated pipe
## Conclusions from REL method

### Pro
- Easy to calculate
- Volume of vessel is considered
- Height of vessel can be considered (via alpha)
- Complex reaction net possible
- All predicted MITD on the safe side

### Contra
- No fluid dynamic considered (buoyancy)
- Geometry specification can only be considered in calculation of alpha
- Prediction of MITD might be too conservative
Application modes in Multiphysics

Convection and diffusion mode: mass balance based on chemical reactions

Convection and conduction for heat transfer

Weakly compressible Navier-Stokes for impulse balance

\( R_{\text{TFE}}, R_{\text{Dimer}}, R \ldots \)

\( \Delta Q, c_p, \lambda, \rho \)

\( k_f, k_b \)

\( c_0, \rho, \eta, p \)

\( u, v \)

\( T(x) \)
FEM Model: Enhanced reaction net in COMSOL Multiphysics

additional reactions are important in the relevant temperature range (green)
Enhanced reaction net in COMSOL CFD Model

- 4 additional reactions and two additional species were integrated
- New reaction net shows very good numerical results
- Additional reactions prevent a too early runaway at lower temperatures
- At higher temperatures the primary dimerization reaction generates a runaway – ignition of decomposition reaction

\[
\begin{align*}
C_2F_4 + C_2F_4 & \leftrightarrow C_4F_8(c) \\
C_2F_4 & \rightarrow CF_2 + CF_2 \\
C_4F_8(c) + CF_2 & \rightarrow C_3F_6(e) + C_2F_4 \\
C_4F_8(c) & \rightarrow C_3F_6(e) + CF_2 \\
C_3F_6(e) & \rightarrow C_3F_6(c) \\
C_3F_6(c) & \rightarrow C_2F_4 + CF_2
\end{align*}
\]
Enhanced reaction net in COMSOL CFD Model

- New model shows for the volumes of 0.2-dm³ and 3-dm³ a maximal deviation of 10 K in the MITD
- For both volumes a pressure peak in the simulation could be observed and was taken as the ignition criterion

![Exponential pressure increase graph](image-url)
Comparison of CFD Simulation and experimental values, 0.2 dm³
Enhanced reaction net in COMSOL CFD Model - results

Comparison of CFD Simulation and experimental values, 3 dm³

MITD$_{\text{COMSOL}}$ in °C vs. MITD$_{\text{Experiment}}$ in °C

- Red dashed line: Bisektor
- Blue line: + 20%
- Black line: - 20%
- Green squares: MITD 3-dm³ COMSOL in °C
Conclusions from CFD method

**Pro**
- Most accurate prediction of MITD
- Complex geometries can be considered
- Complex fluid flow possible
- Complex reaction kinetics possible
- Partially heating possible

**Contra**
- Intense knowledge of software is necessary
- Long computational times
- Not applicable on standard PC
Outlook

Validation in larger volumes

- Tests in 100-dm³-vessel
- Vessel is fixed in rotational rack
- Tests for MITD in horizontal and vertical orientation will be carried out

- Prediction with COMSOL REL and Multiphysics was done
- MITD dependence on variation in geometry for similar volumes could be found when using COMSOL Multiphysics
100-dm³ vessel: construction

Permanent sealing with graphite gasket

Easy removable lid

From existing 6,5-dm³ autoclave

Trough put for 4 thermocouples, 90° offset
100-dm³ vessel:
Simulation of MITD, 5 bar TFE

Ignition criterion based on exponential pressure increase

Vertical orientation

\[ p \text{ in bar (260 °C)} \]

\[ p \text{ in bar (270 °C)} \]

COMSOL Conference, Paris, 17.11.2010 – 19.11.2010
100-dm³ vessel simulation: MITD dependence on geometry

Simplified geometry

real geometry

Temperature field at \( t(T_{\text{max}}) \) in °C

Max: 674.594

Max: 298.567

58 s

30 s

COMSOL Conference, Paris, 17.11.2010 – 19.11.2010
100-dm³ vessel simulation: MITD dependence on geometry

Comparison of p-t curves for different geometries (similar volume)

COMSOL Conference, Paris, 17.11.2010 – 19.11.2010
Prediction of MITD for 100-dm³-vessel
(simple geometry)

MITD dependence on pressure for 100-dm³-vessel

\[ \text{MITD (°C)} = -27.474 \times \ln(p) + 313.96 \]