Study of a Self Heating Process of Tetrafluoroethylene by the Exothermic Dimerization Reaction to Octafluorocyclobutane

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• Motivation

• Hazardous properties of Tetrafluoroethylene

• Experiments

• Geometric and numerical model

• Numerical simulation of self heating process
  - Feedback between model and experiments
  - New Kinetics for dimerization reaction
  - Measurement of more detailed temperature field

• Outlook
Motivation

• Tetrafluoroethylene (TFE, C₂F₄) 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
Hazardous properties

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

\[ 2C_2F_4 \leftrightarrow C - C_4F_8 \quad \Delta H_R = -103 \left( \frac{kJ}{mol_{TFE}} \right) \]
Experiments with 3-dm³ autoclave

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

Steel

Aluminium (with heating)
Outlook: 3D modeling

- 3D-geometry of 3-dm³ autoclave was transferred from a CAD software
- First calculations were carried out
- Very long solving times
- Transfer to 2D-model
Application modes

Application mode for reaction modeling

\[ R_{TFE}, \ R_{Dimer} \]

Application mode for modeling heat loss and heat production

\[ T(x) \]

Application mode for modeling Fluid Dynamics

\[ \rho, \ \eta, \ \rho \]

\[ u, \ v \]
numerical model: N-S-Approach

- Heat transfer by conduction and convection

$$\rho \cdot c_p \cdot \frac{\partial T}{\partial t} = \nabla (k \cdot \nabla T) + Q_{\text{production}} \cdot \rho \cdot c_p \cdot \mathbf{u} \cdot \nabla T$$

- Species transfer by diffusion and convection

$$\frac{\partial c_1}{\partial t} = \nabla (D \cdot \nabla c_1) + R - \mathbf{u} \cdot \nabla c_1$$

with \( R = \text{reaction rate } c_1 \)

- Impulse transport by Navier-Stokes approach

$$\rho \cdot \frac{\partial \mathbf{u}}{\partial t} + \rho \cdot \mathbf{u} \cdot \nabla \mathbf{u} = \nabla \left[ -\rho \mathbf{I} + \eta (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \left( \frac{2\eta}{3} - \kappa_{dv} \right) \cdot (\nabla \cdot \mathbf{u}) \cdot \mathbf{I} \right] + \mathbf{F}$$

with: \( \mathbf{u} \) is the velocity field

\( \mathbf{F} \) is the volume force field

\( \mathbf{I} \) is the identity matrix for the viscous stress tensor
Outlook: 3D modeling

Computational results for a 3-dm³- autoclave (300°C; 5,0 bara)
In 3D for 14 s, solving time about 28 hours

• First calculations were carried out

• Very long solving times

→

• Transfer to 2D-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

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

\[ r_b = C_{c - C_4F_8} \cdot k_b \]
Computational results for a 3-dm³ autoclave (300°C; 5,0 bara)

- Temperature: 300°C
- Maximum temperature: 436°C

Comsol Conference 2008, Hannover, 05.11.2008
• FEM - modeling showed thermal layering → even in a 0.2-dm³ autoclave, inner height of 120 mm

• Experiments with thin thermocouples were carried out
Feedback effects:
additional tests for temperature layering

test 5bara, 340°C, 0.2-dm³ autoclave

temperature in °C

- T middle
- T top
- pressure

Time in s

Pressure in bara

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Advantage of 2-stage-kinetics

100% TFE, 3-dm³, $t_{\text{wall}}=300^\circ\text{C}$, test TFEait70

- Experiment
- Comsol 2-stage kinetics_part1
- Comsol 1-stage kinetics

Graph showing pressure over time for the experiment and simulations.
Navier-Stokes approach

100% TFE, 3-dm³, \( t_{\text{wall}} = 300°C \), test TFEait70

![Graph showing the comparison of experimental and simulated pressures over time for a 100% TFE mixture in a 3-dm³ reactor with a wall temperature of 300°C. The graph includes data from experiments and simulations using the Comsol software for different parts of the reaction process.](image-url)
Outlook

• appliance of the numerical approach on other geometries
  - Vertical and horizontal pipes with different diameters
  - Big vessels
  - Influence of forced flow in pipes on self heating process

• Improvement of the used Kinetics approach
Thanks for your attention!