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

M. Beckmann-Kluge, H. Krause, V. Schröder, A. Acikalin and J. Steinbach

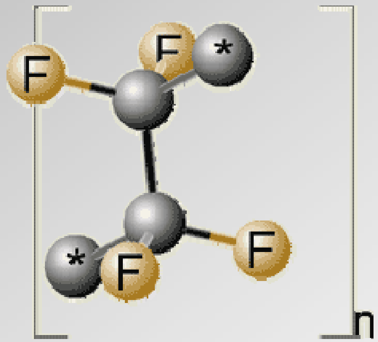
Federal Institute for Materials Research and Testing (BAM), Technical University Berlin

Content

- 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

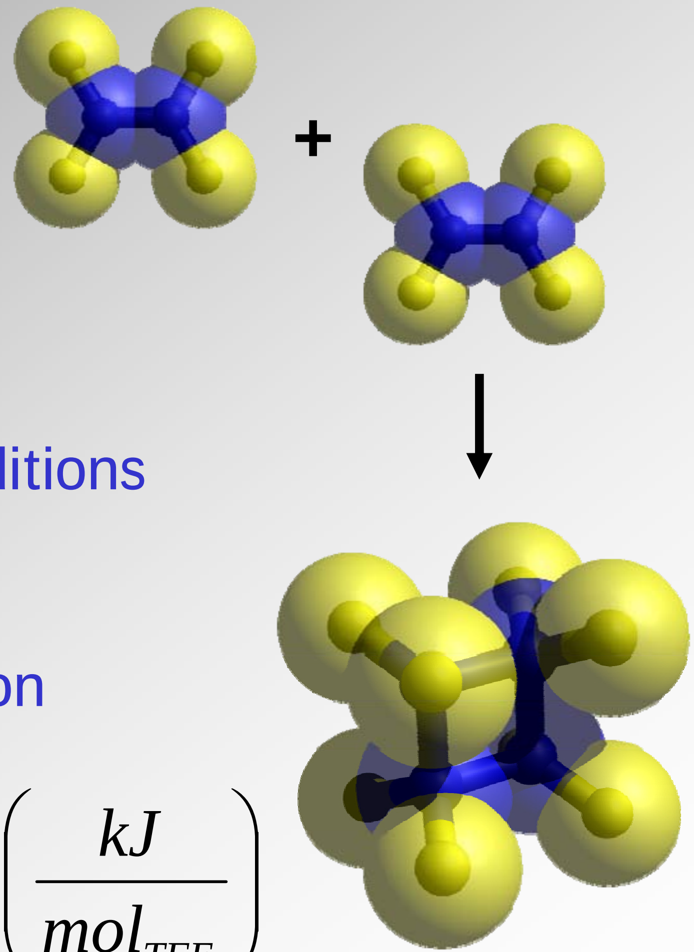
- Tetrafluoroethylene (TFE, C_2F_4) is monomer of Polytetrafluoroethylene (PTFE) and other copolymers (100.000 t/year)



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

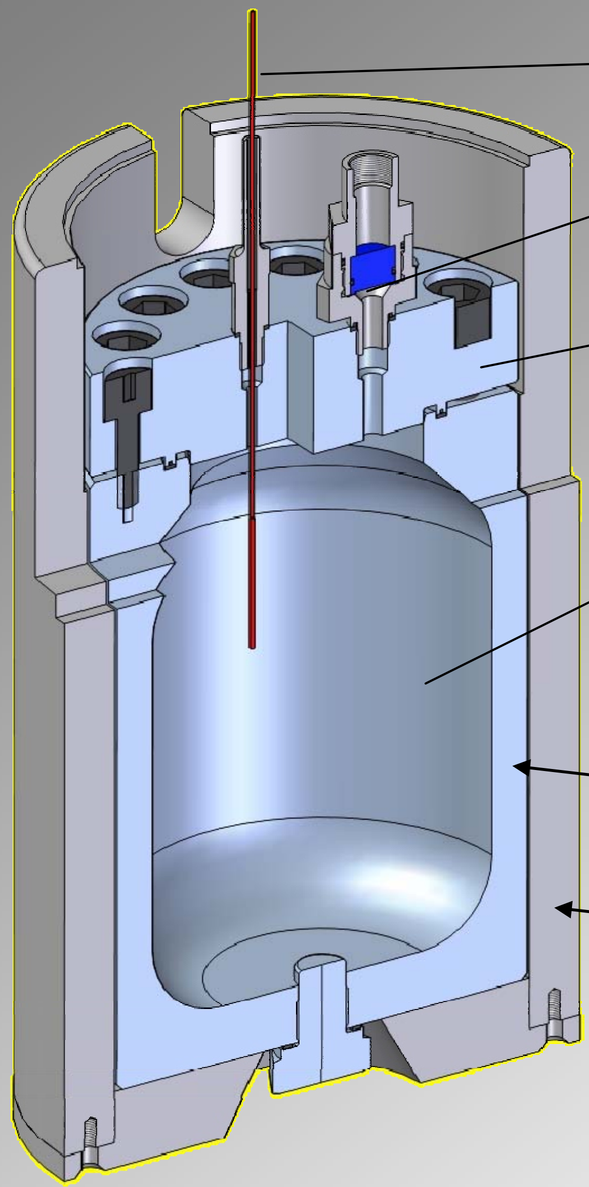
Hazardous properties

- 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

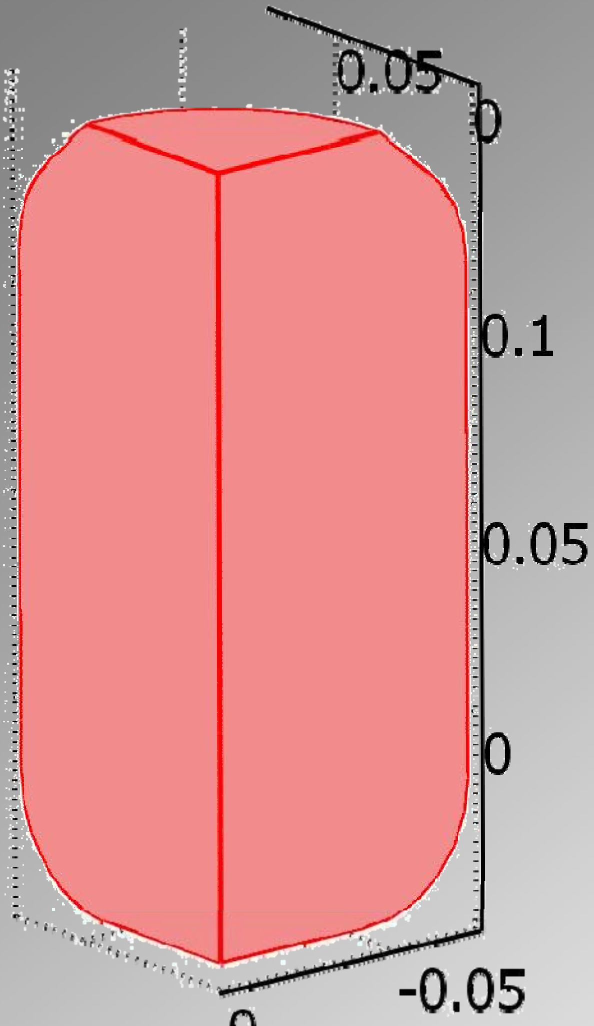


$$2C_2F_4 \leftrightarrow c-C_4F_8 \qquad \Delta H_R = -103\left(\frac{kJ}{mol_{TFE}}\right)$$

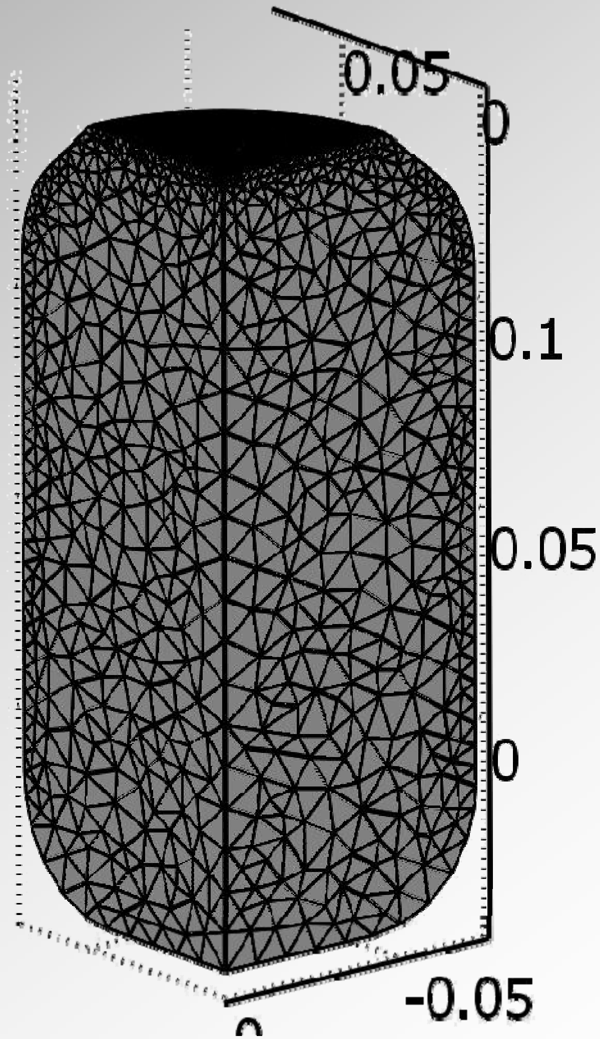
Experiments with 3-dm³ autoclave



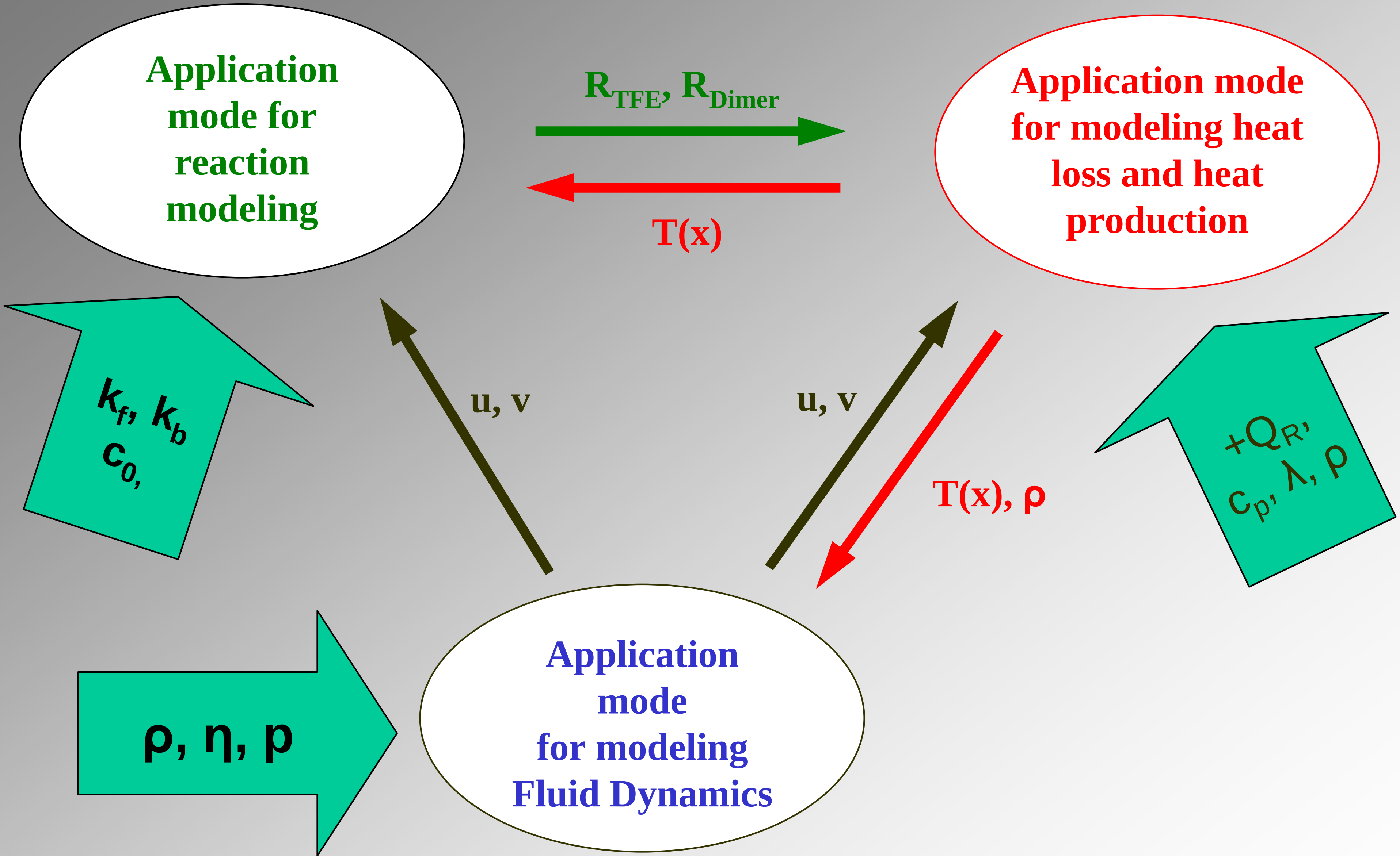
Outlook: 3D modeling



- 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



– Heat transfer by conduction and convection

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

– Species transfer by diffusion and convection

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

$$with \qquad R = reaction \;\; rate \;\; c_1$$

– Impulse transport by Navier-Stokes approach

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

$$with: \quad \mathbf{u} \; is \; the \; velocity \;\; field$$

$$\mathbf{F} \; is \; the \; volume \;\; force \;\; field$$

$$\mathbf{I} \; is \; the \; identity \;\; matrix \;\; for \; the \; viscous \;\; stress \;\; tensor$$

Outlook: 3D modeling

Computational results for a 3-dm^3- 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

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

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

New 2-stage kinetics was determined

backward reaction

$$c-C_4F_8 \xrightarrow{b} 2C_2F_4$$

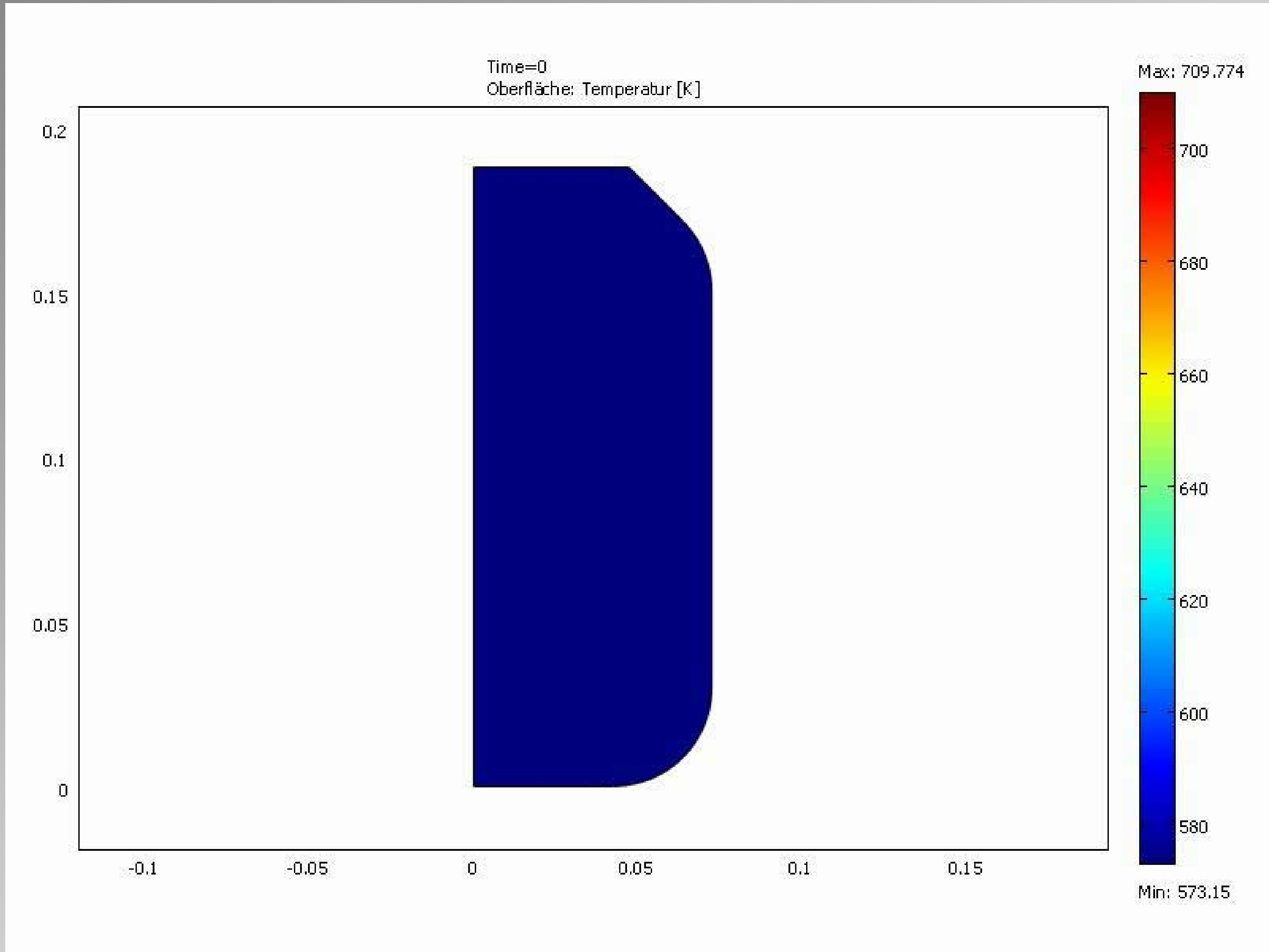
1. order reaction

$$k_f = 2{,}1\cdot 10^{16}\left[\frac{\mathrm{m^3}}{\mathrm{mol\cdot s}}\right]\cdot\exp^{\left(\frac{-310961[\mathrm{J/mol}]}{RT}\right)}$$

$$r_b = c_{c-C_4F_8}\cdot k_b$$

Film NS-Model 3-dm³

Computational results for a 3-dm³- autoclave (300°C; 5,0 bara)



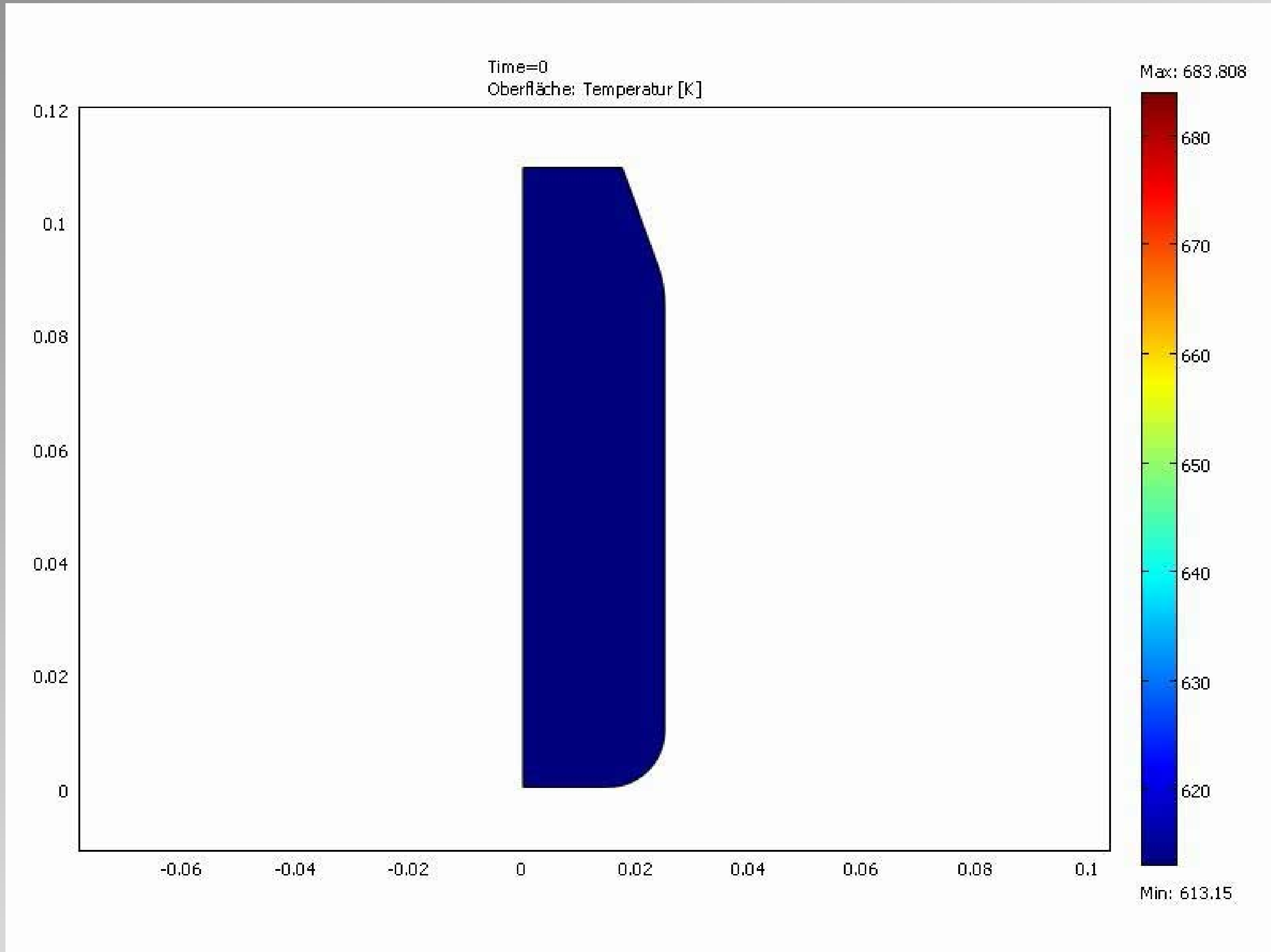
= 436°C

= 300°C

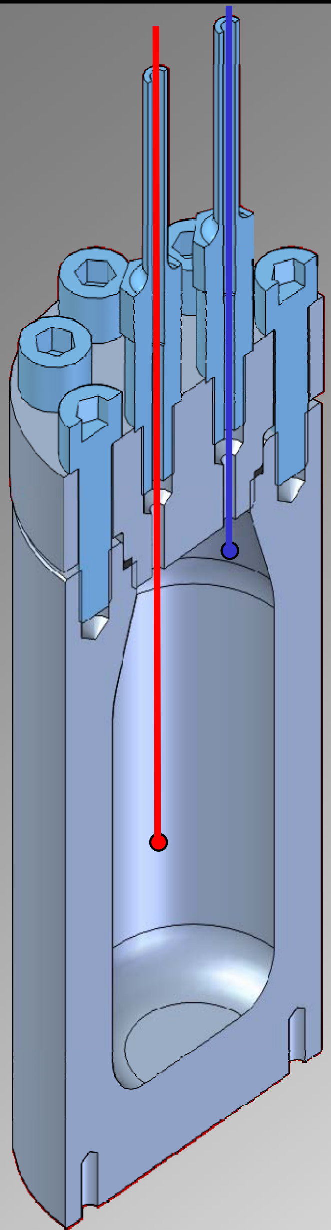
Feedback Effekte: Modellierung ←→ Experiment???

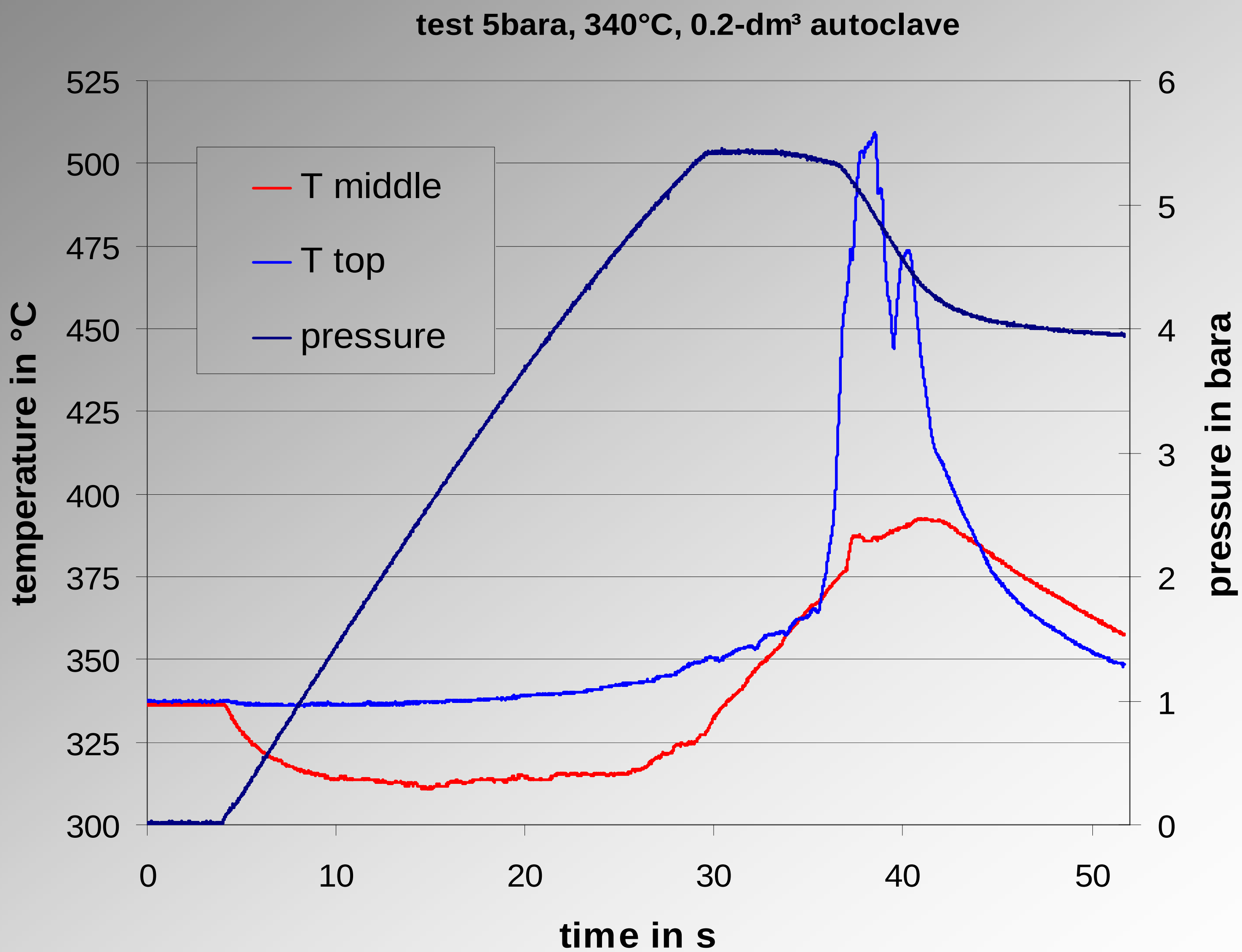
- FEM – modeling showed thermal layering → even in a0.2-dm³ autoclave, inner height of 120 mm

- Experiments with thin thermocouples were carried out

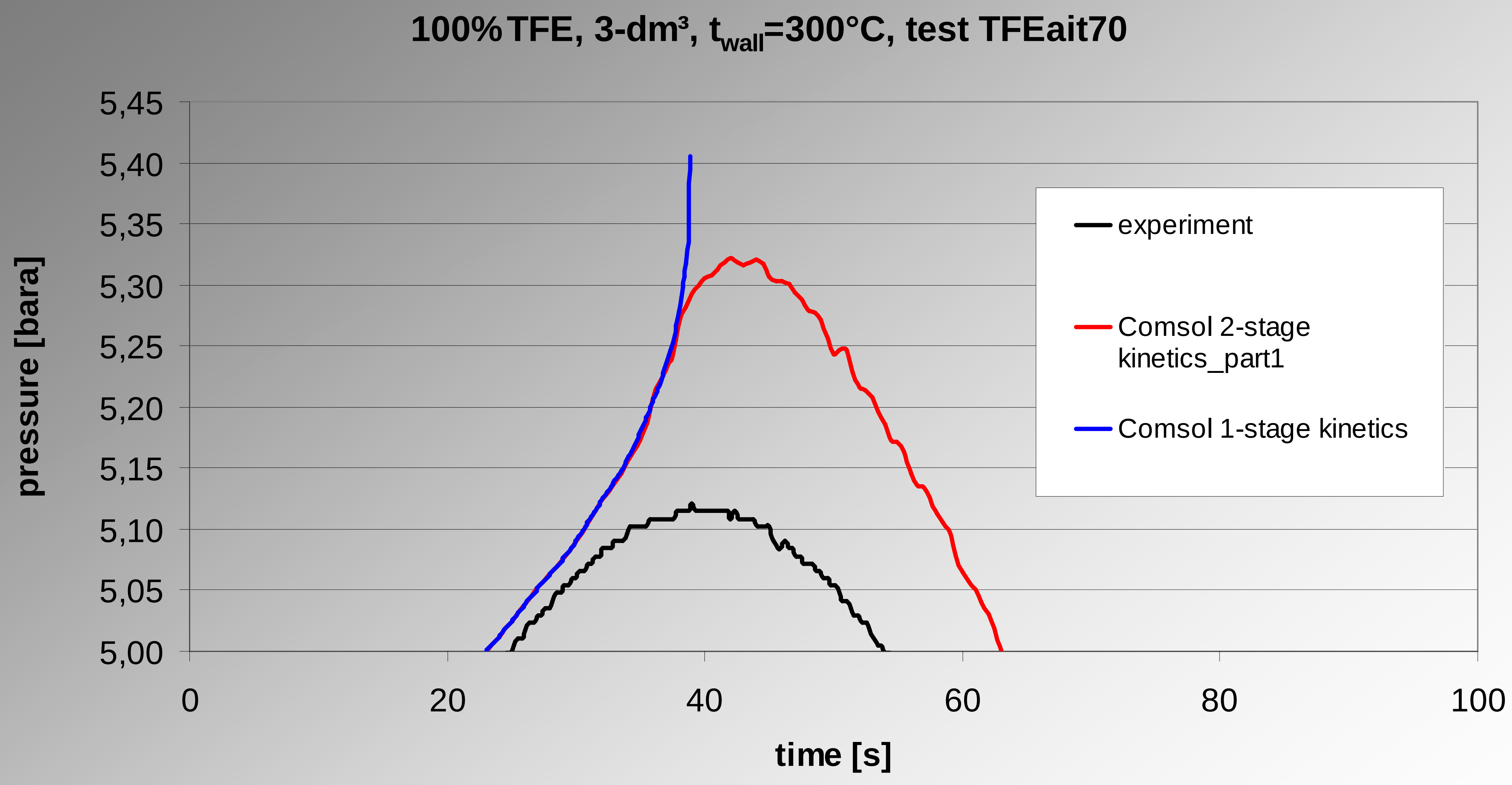


Feedback effects:
additional tests for temperature layering

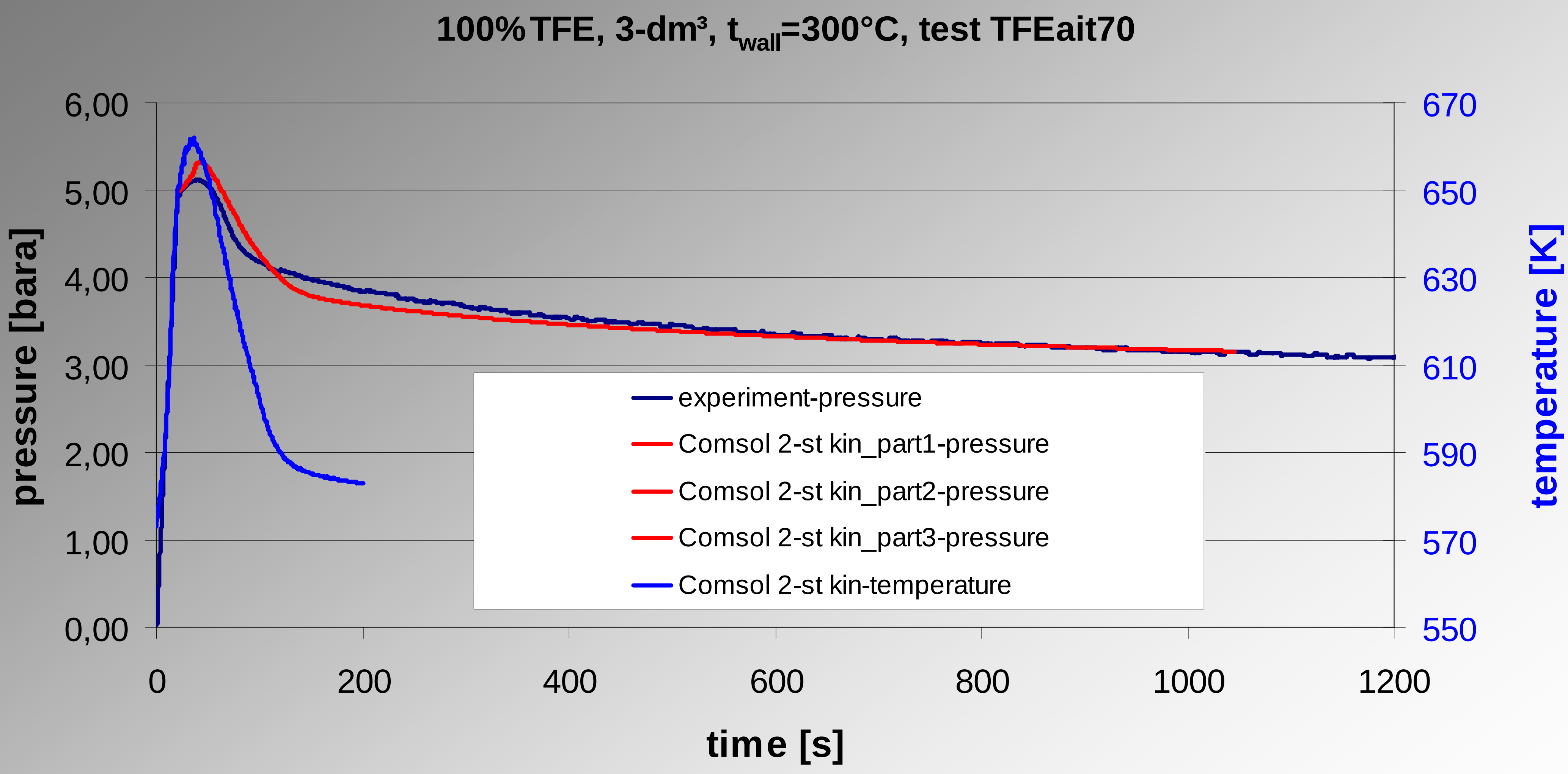




Advantage of 2-stage-kinetics

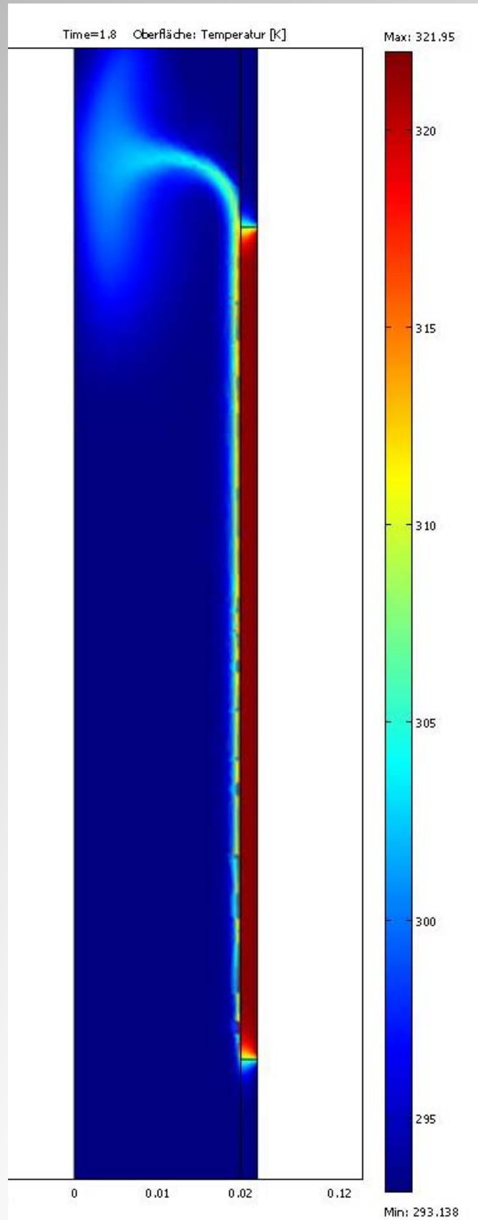


Navier-Stokes approach



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!