Improvements in the Modeling of the Self-ignition of Tetrafluoroethylene

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Content

I. Introduction to topic and motivation

II. Numerical Model with REL and Comsol Multiphysics

III. Results of different numerical approches

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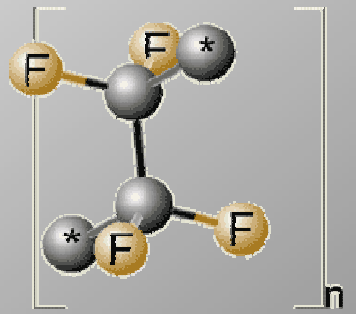
Introduction to TFE

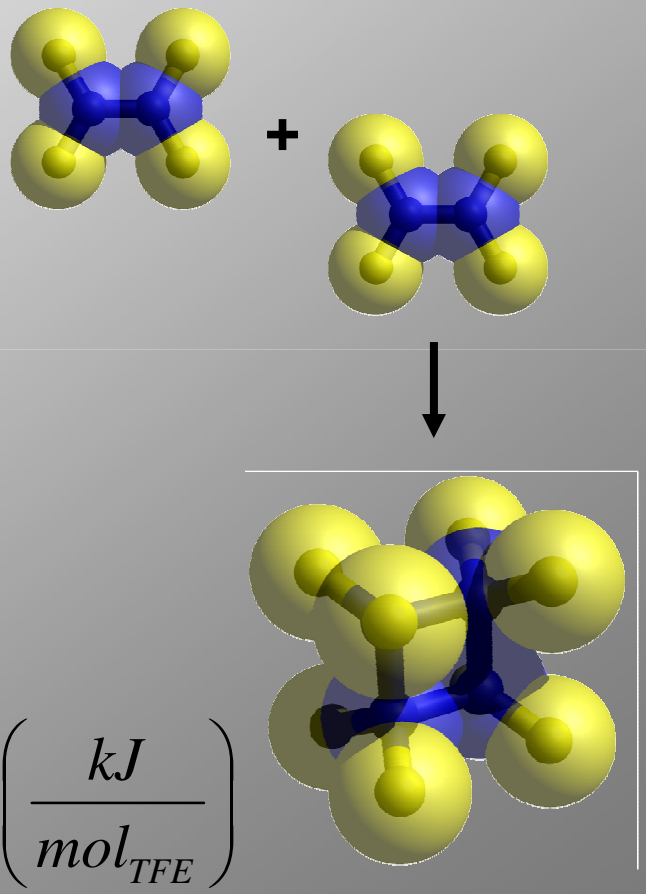
- Tetrafluoroethylene (TFE, C_2F_4) is monomer of Polytetrafluoroethylene (PTFE) and other copolymers (100.000 t/year)



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

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



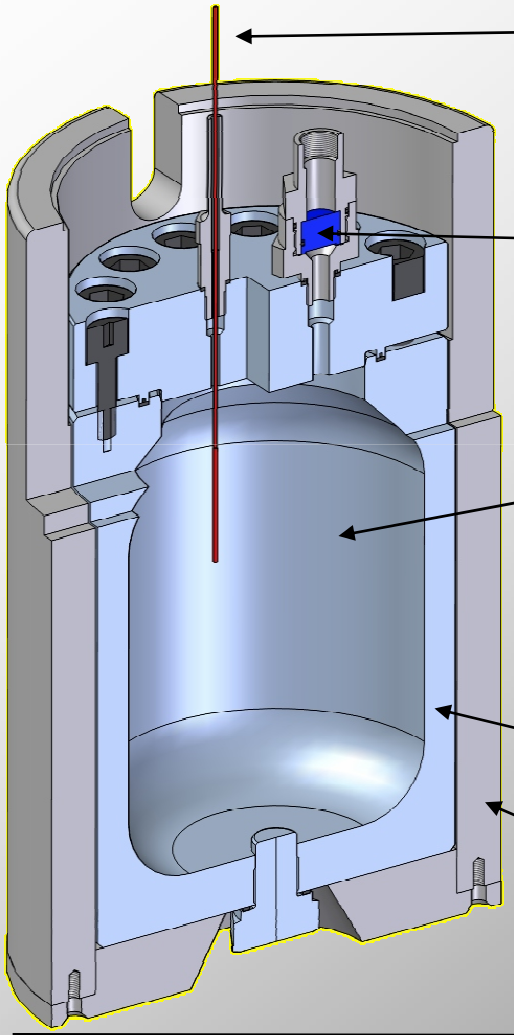
$$2C_2F_4 \leftrightarrow c-C_4F_8 \qquad \Delta H_R = -103\left(\frac{kJ}{mol_{TFE}}\right)$$

- 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

0.2-dm³ autoclave



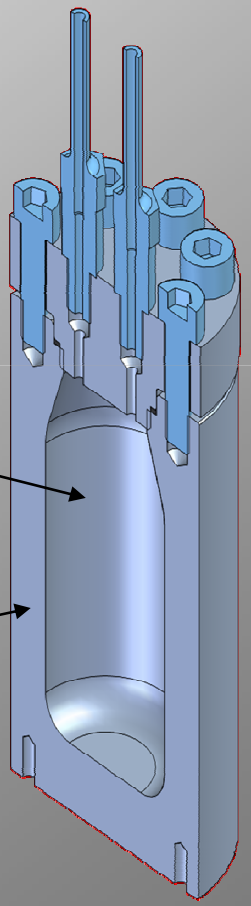
thermocouple for gas temperature

pressure transducer

internal volume (cylindrical reaction chamber)

Steel vessel

Aluminium (with heating jacket)



1st Model: Dimerization – Reaction

forward reaction

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

2. order reaction

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

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

New 2-stage kinetics was determined

backward reaction

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

1. order reaction

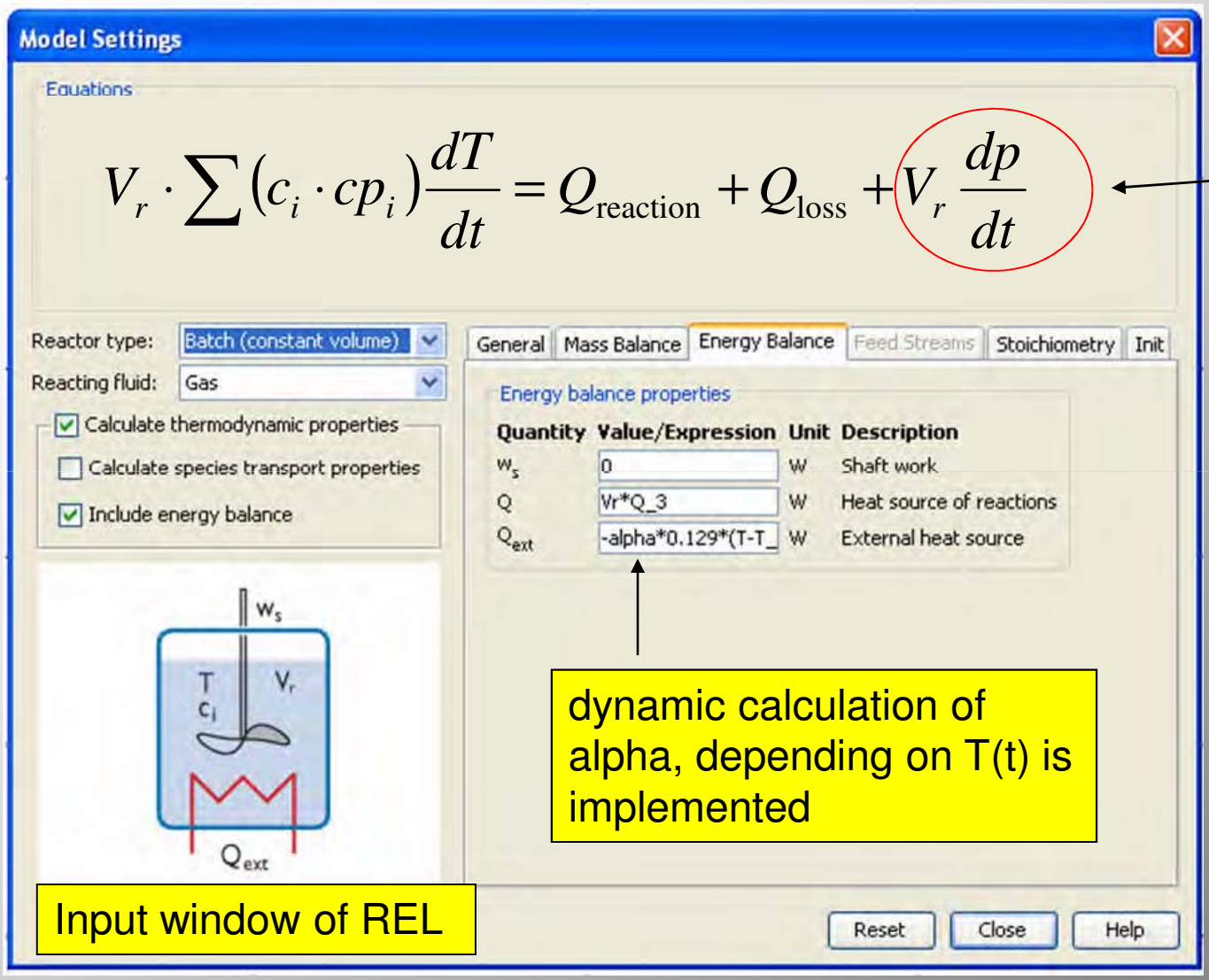
$$k_f = 2{,}1\cdot 10^{16}\left[\frac{\mathrm{m^3}}{\mathrm{mol}\cdot\mathrm{s}}\right]\cdot\exp\left(\frac{-310961[\mathrm{J/mol}]}{RT}\right)$$

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

Enhanced reaction net in REL and COMSOL CFD Model

Reaction	RO	A0 in [m³ mol-1 s-1] bzw. [s-1]	Ea in [J/mol]	ΔH_r^0 acc. NIST [kJ/mol]	ΔH_r^0 acc. REL (NASA Polynoms)
C2F4+C2F4 → C4F8	2	8.28E+04	105000	-166 (-116…-171)	-161,5
C4F8(c) → 2*C2F4	1	2.10E+16	310871	166 (116…171)	161,5
C4F8(c) → C3F6(e)+CF2	1	1.58E+17	332580	154,3	164
C3F6(e) → C2F4 + CF2	1	1.58E+13	346008	308,7	288
C3F6(c) → C2F4 + CF2	1	1.78E+13	161501	308,7	288
C3F6(e) → C3F6 (c)	1	1.00E+13	139767	-	-
C2F4 → 2*CF2	1	5.01E+16	301285	297	290,6
C4F8(c) + CF2 → C3F6(e)+ C2F4	2	1.00E+08	133032	-142,7	-126,5
C4F8(i) → 2* C2F4	1	1.00E+16	374070	309	-
C4F8(i) → C3F6(e)+ CF2	1	1.20E+16	384962	297,3	-

Reaction Engineering Lab Model



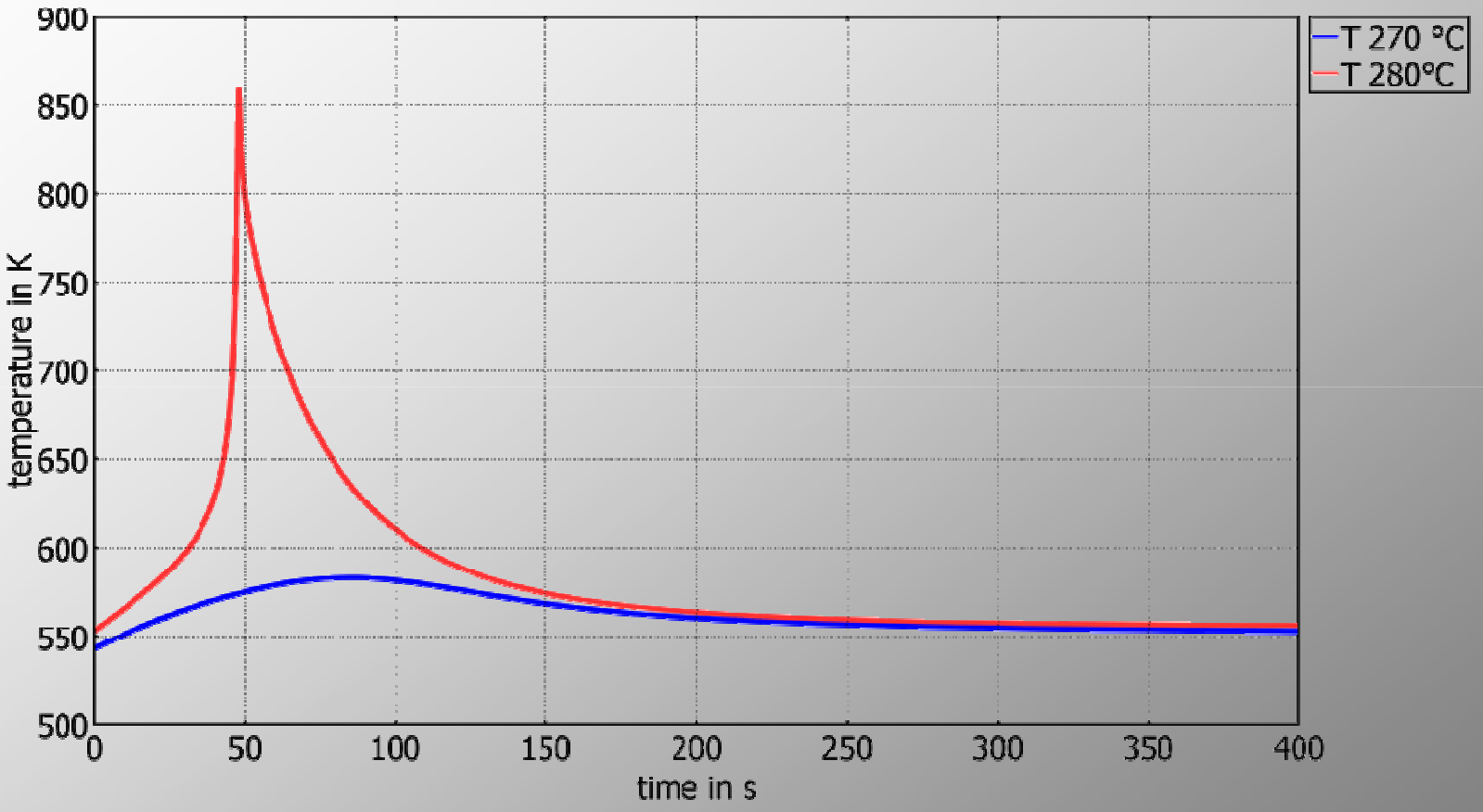
Pressure work is considered

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

Input window of REL

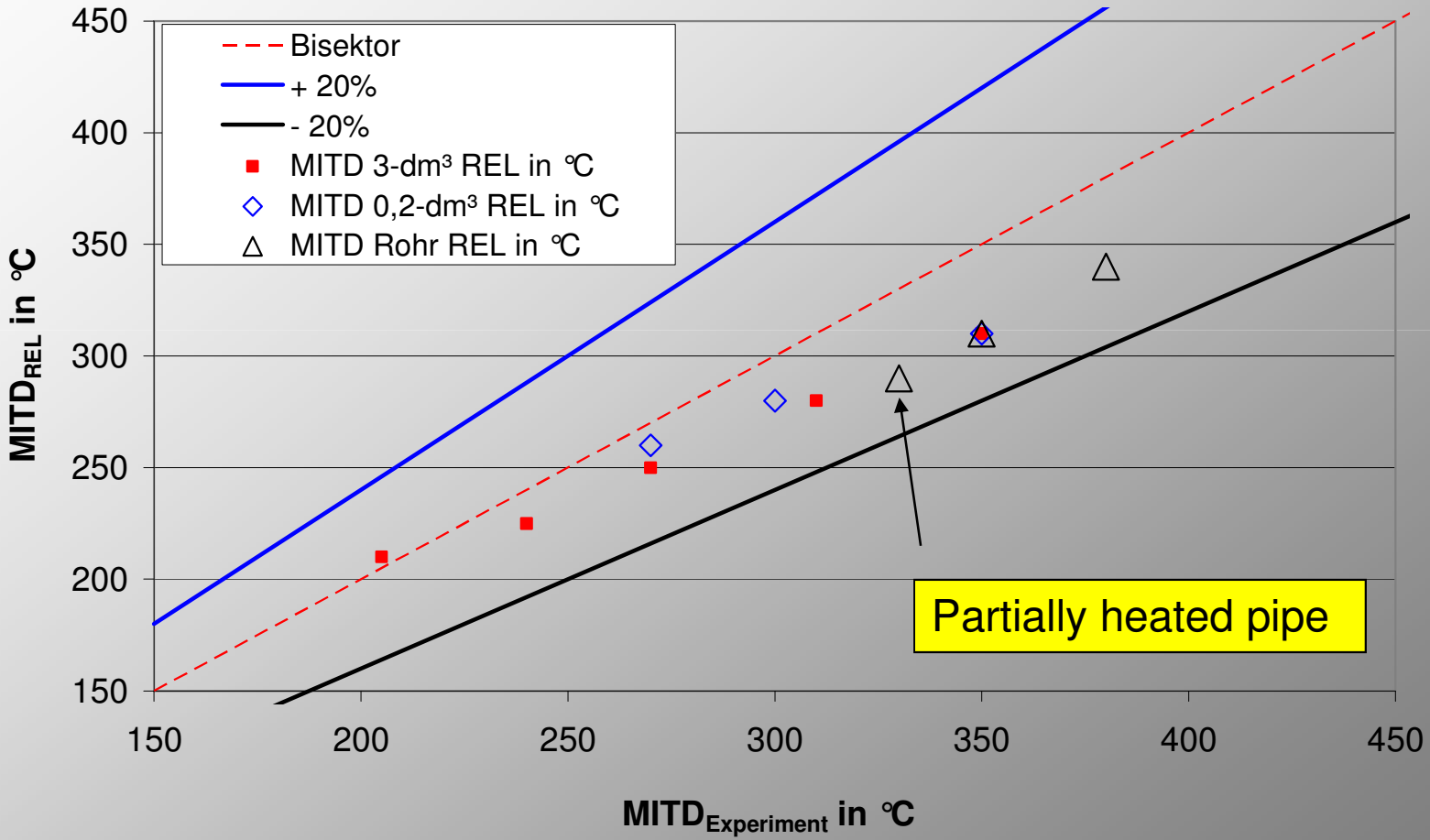
Reaction Engineering Lab Model

Prediction of the MITD with the REL method



experimental MITD = 310 °C, 5 bar, 0.2-dm³

Comparison of REL results and experimental values



Conclusions from REL method

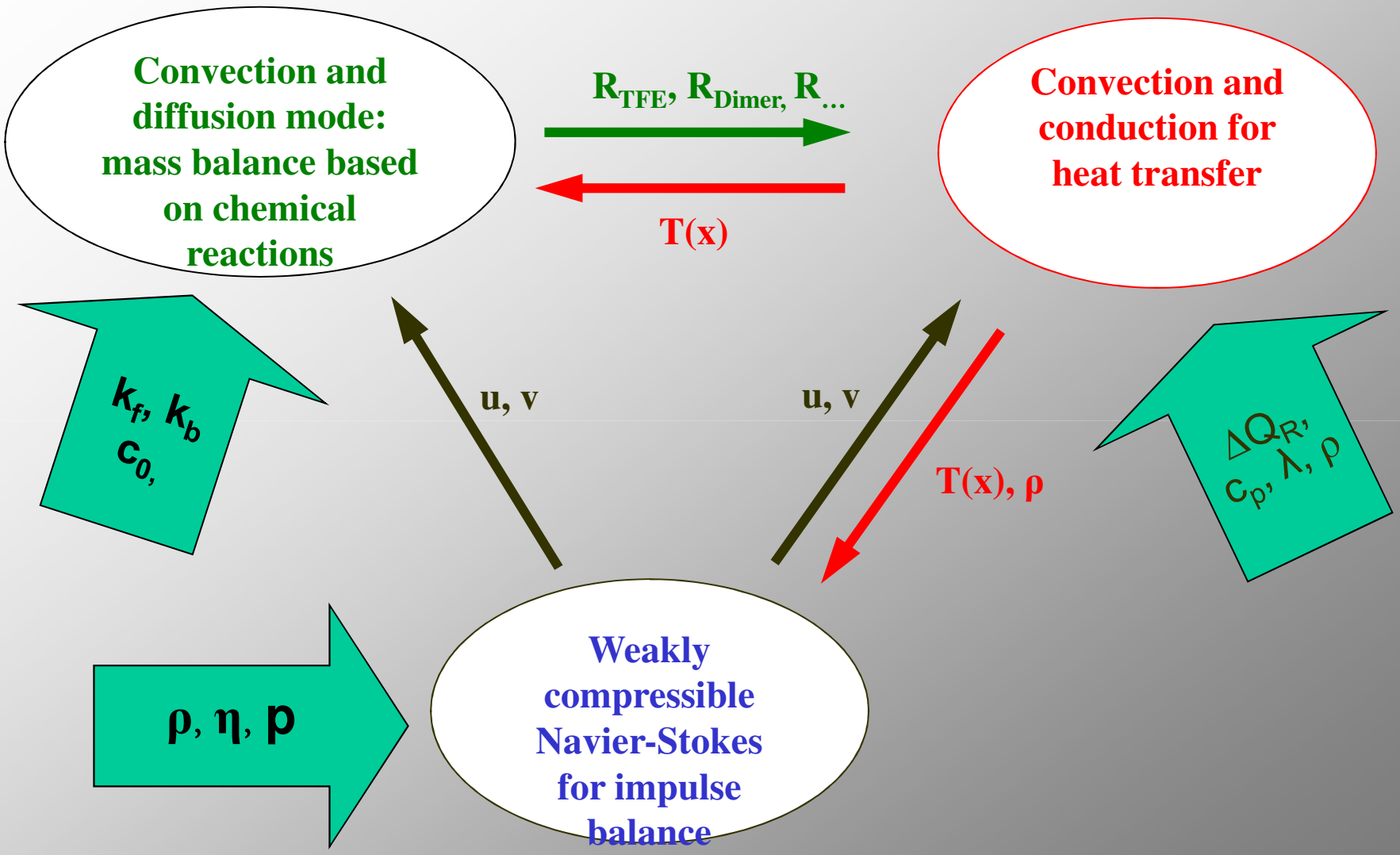
Pro

- 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

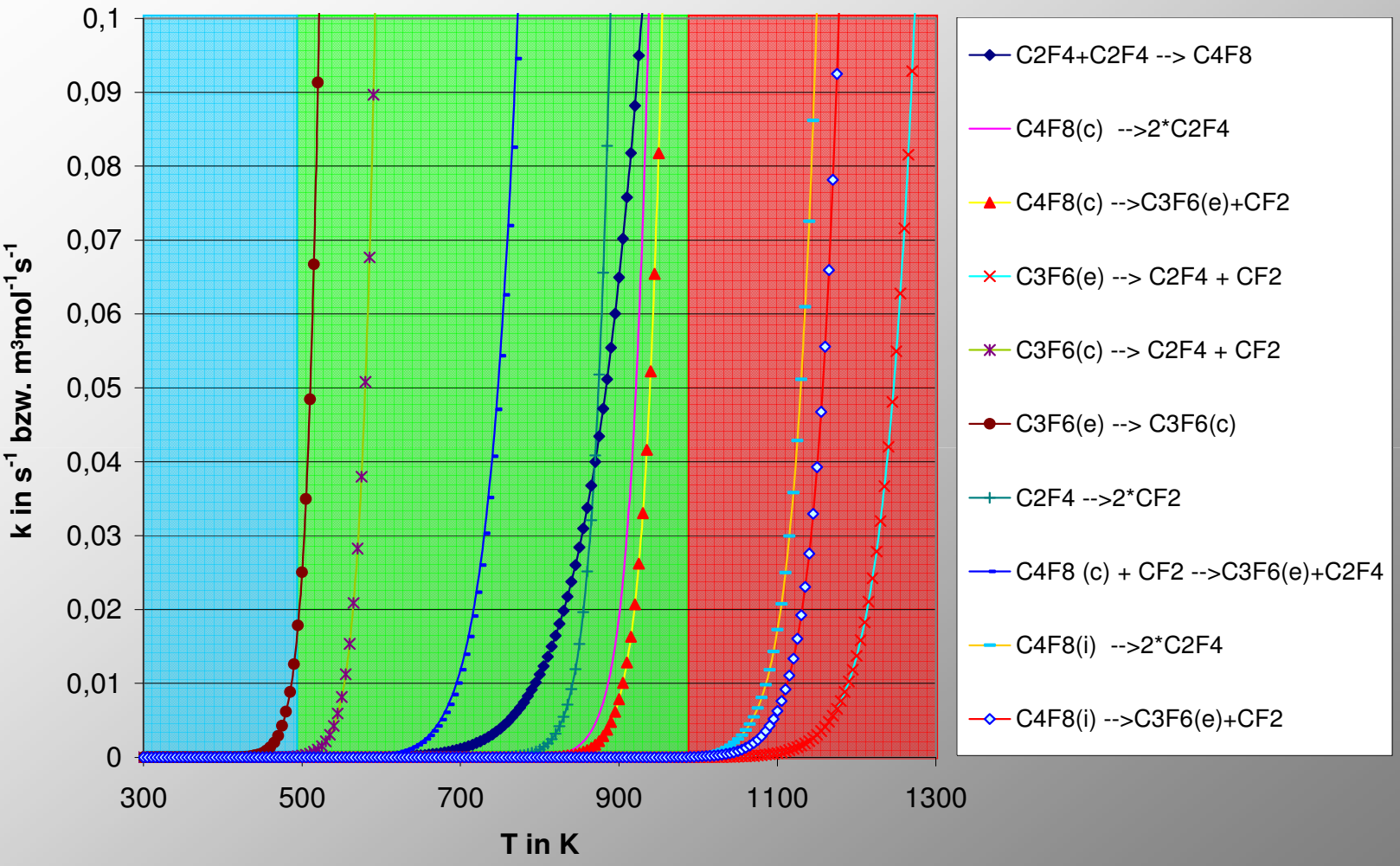
Contra

- No fluid dynamic considered (buoyancy)
- Geometry specification can only be considered in calculation of alpha
- Prediction of MITD might be to conservative

Application modes in Multiphysics



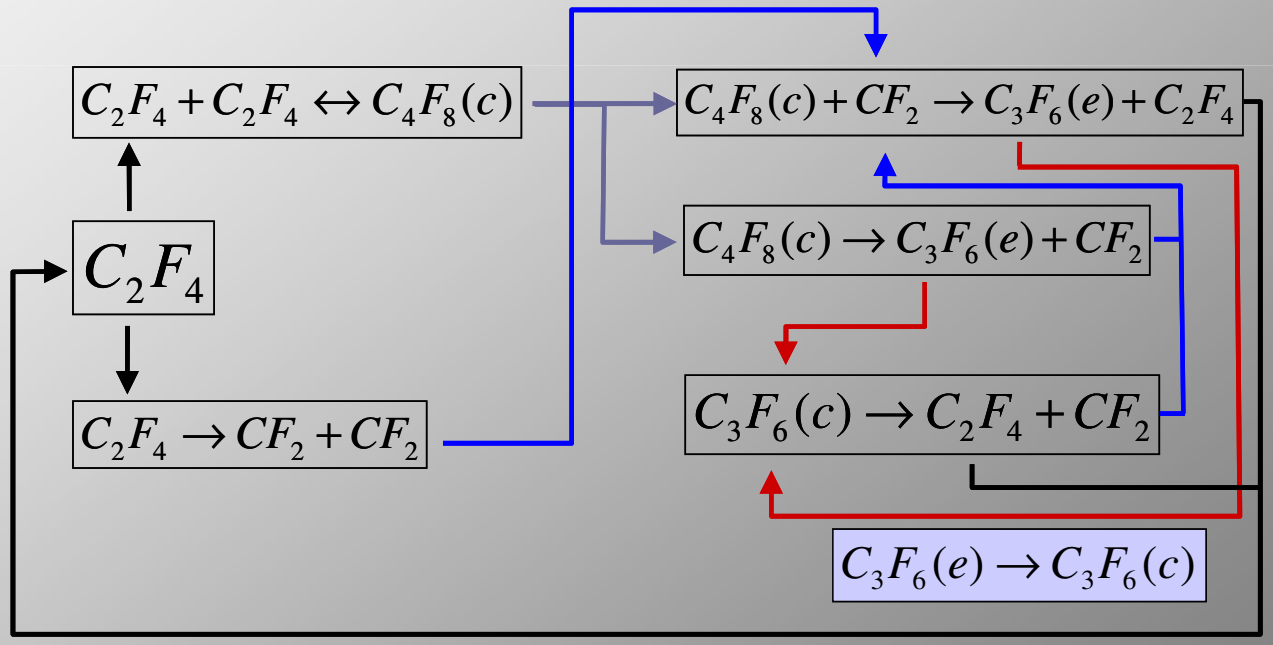
FEM Model: Enhanced reaction net in COMSOL Multiphysics



additional reactions are important in the relevant temperature range (green)

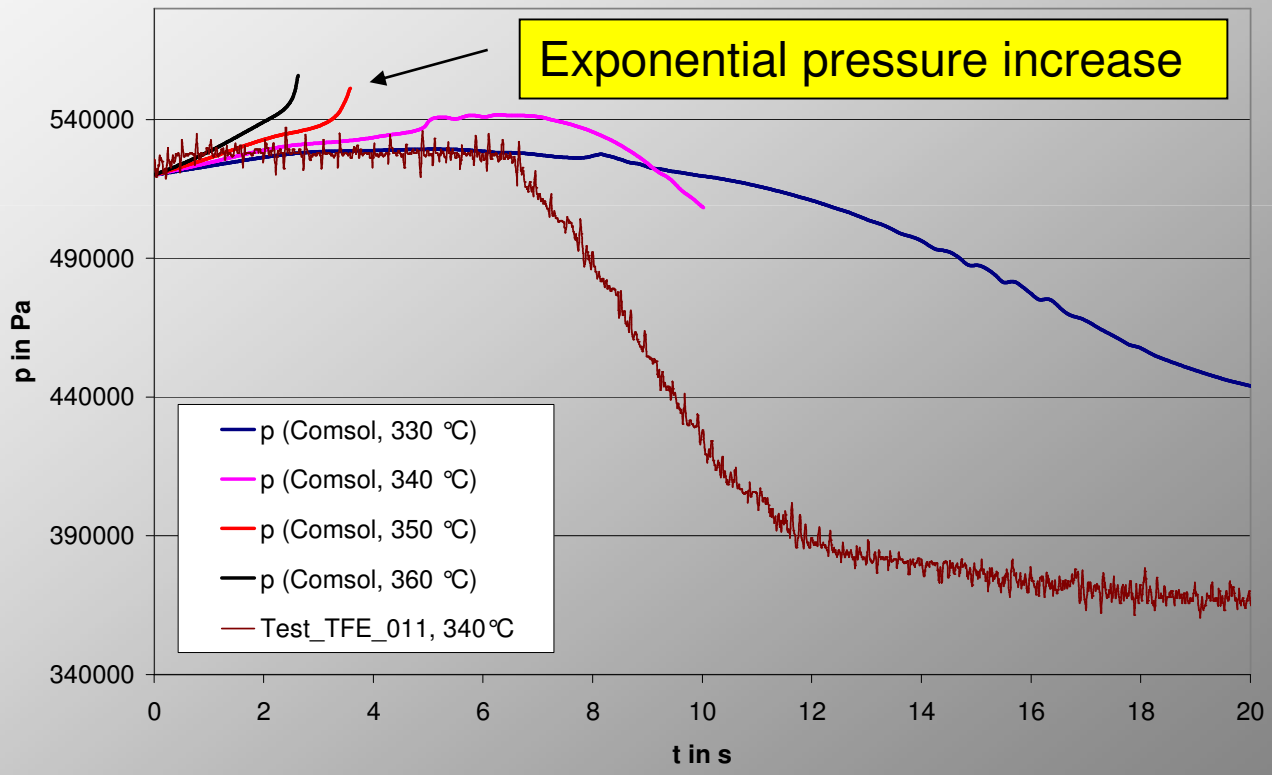
Enhanced reaction net in COMSOL CFD Model

- 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 reaciton



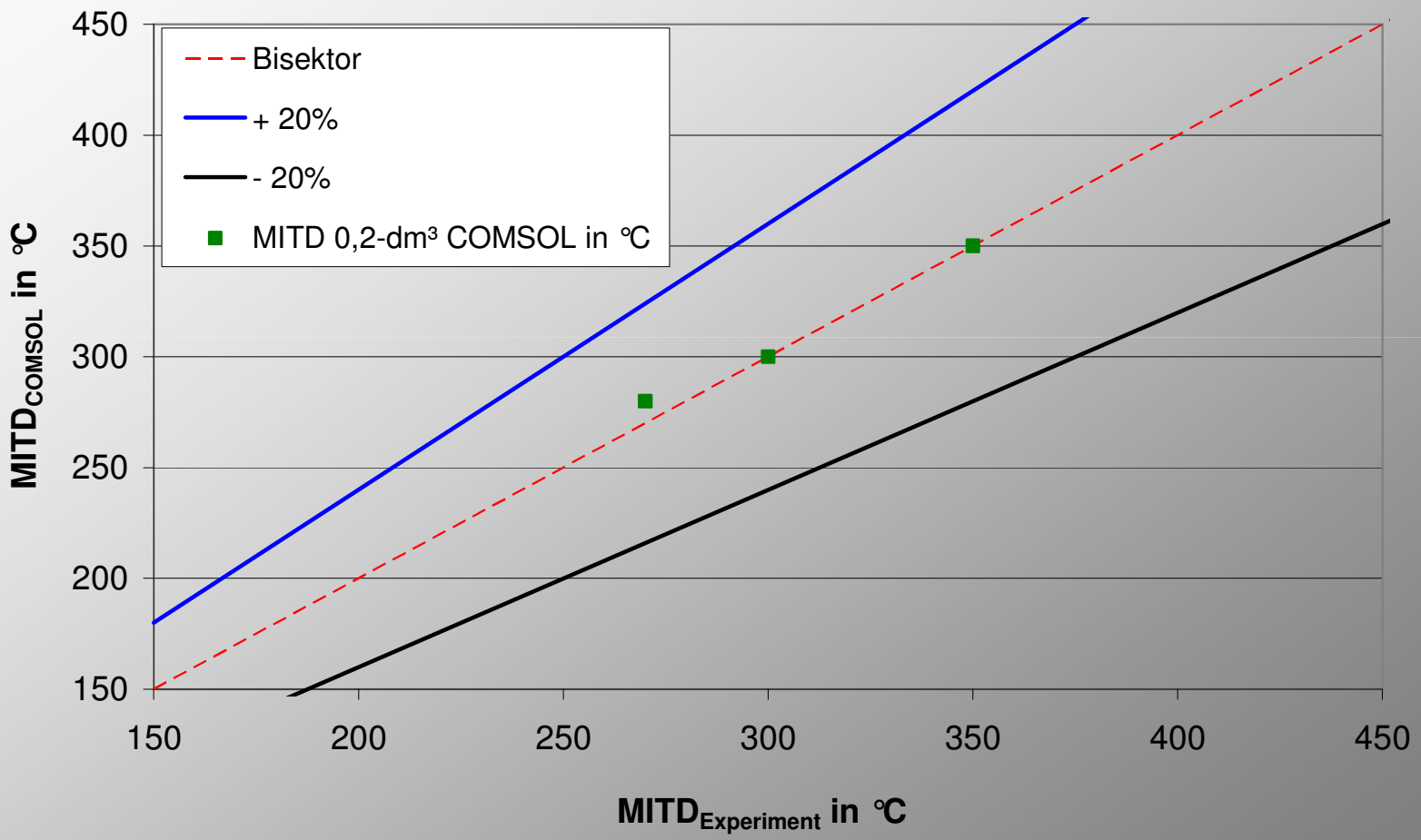
Enhanced reaction net in COMSOL CFD Model

- 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



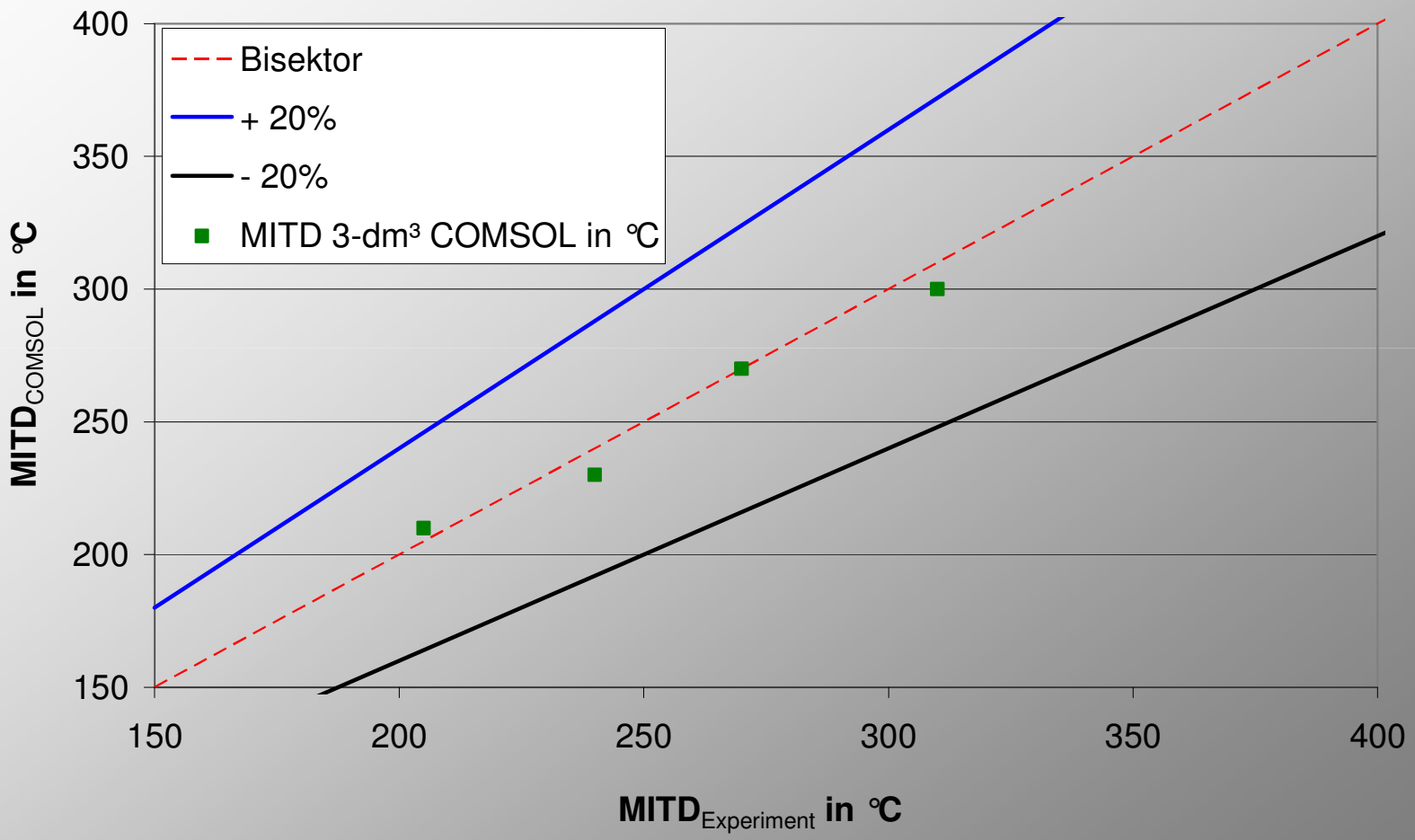
Enhanced reaction net in COMSOL CFD Model

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



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

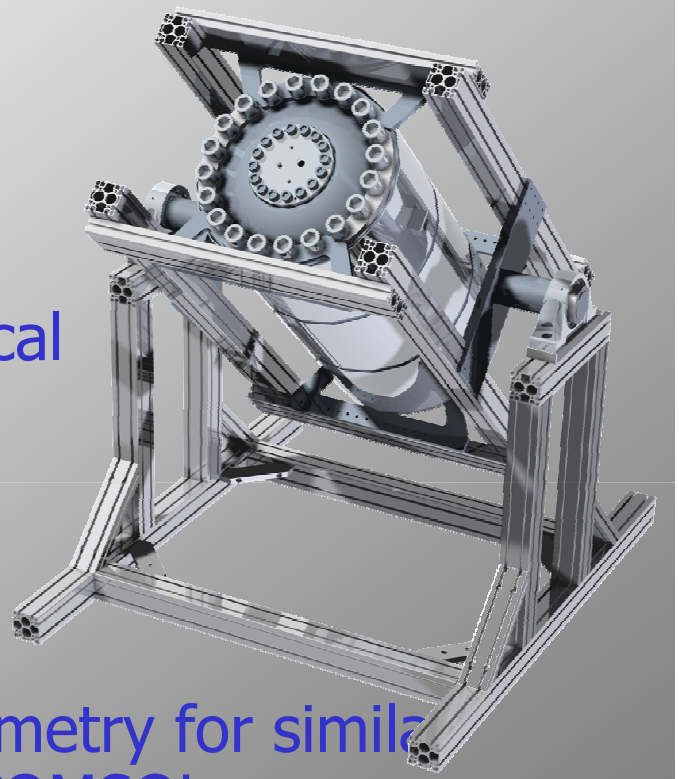
Contra

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

Outlook

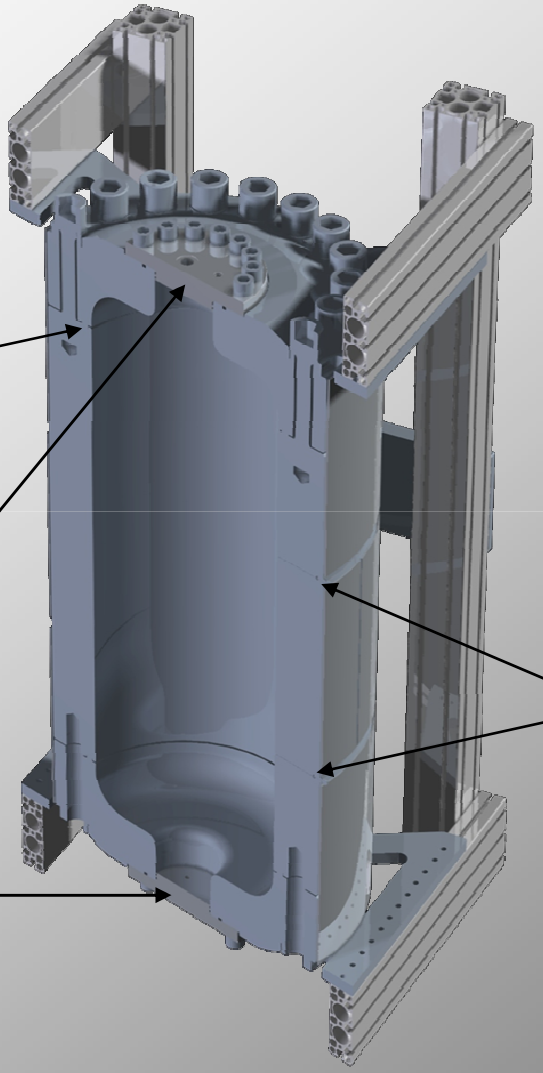
Validation in larger volumes

- 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 simila volumes could be found when using COMSOL Multiphysics

100-dm³ vessel: construction



Permanent sealing with graphite gasket

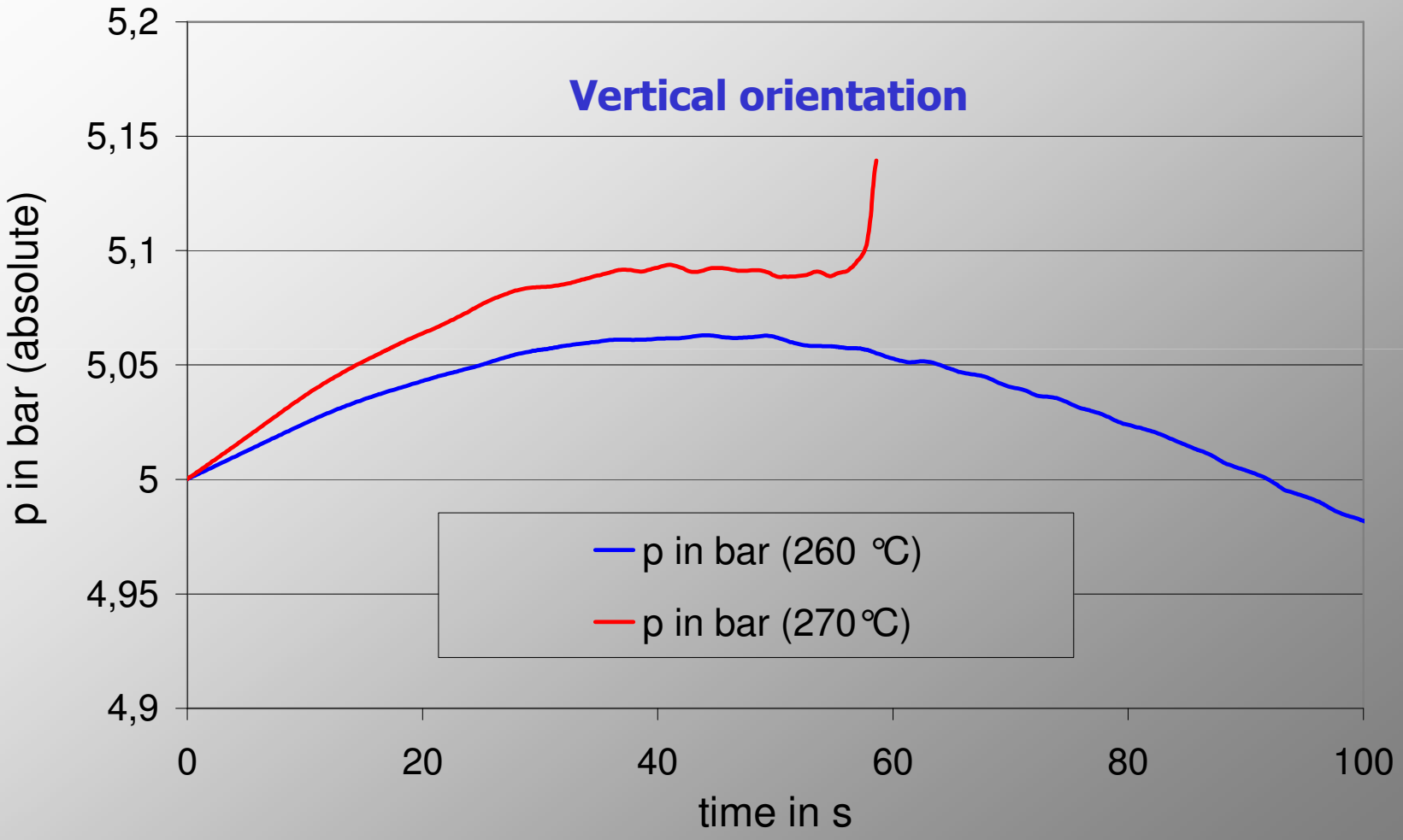
Easy removable lid

From existing 6,5-dm³ autoclave

Trough put for 4 thermocouples, 90° offset

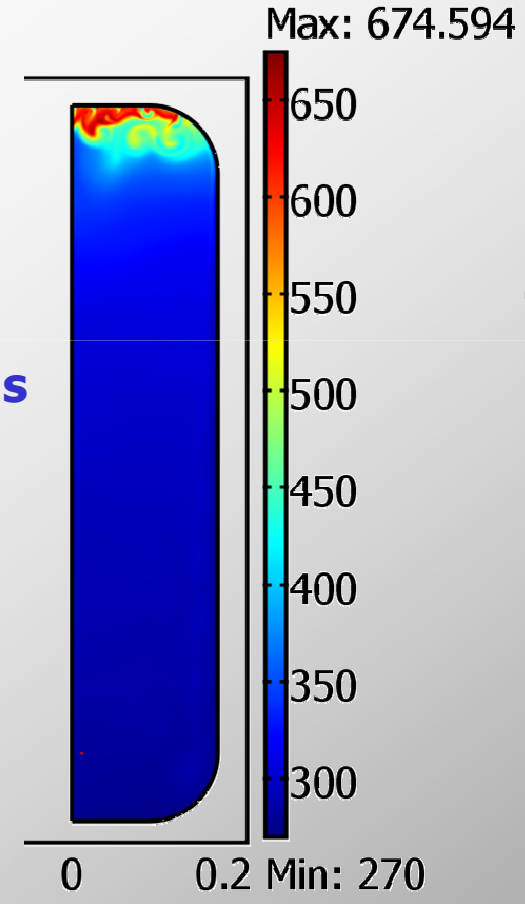
100-dm³ vessel: Simulation of MITD, 5 bar TFE

Ignition criterion based on exponential pressure increase



100-dm³ vessel simulation: MITD dependence on geometry

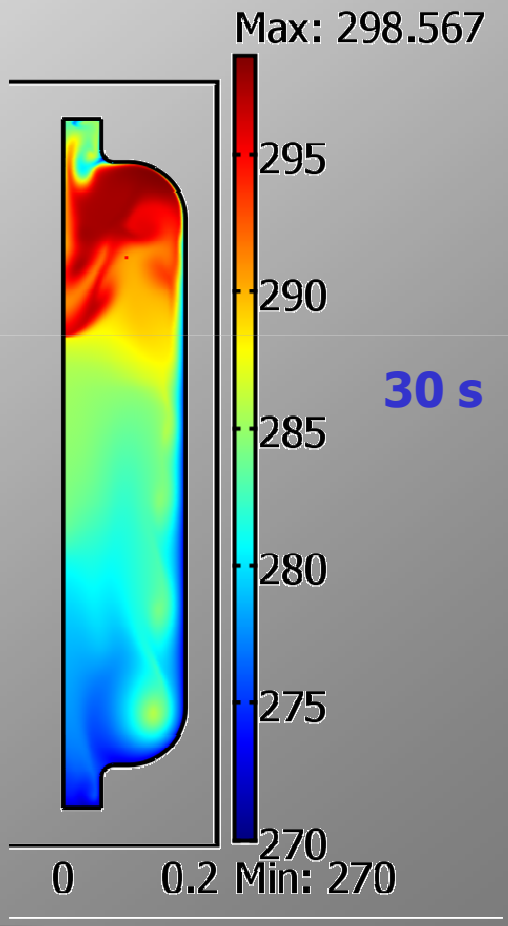
Simplified geometry



58 s

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

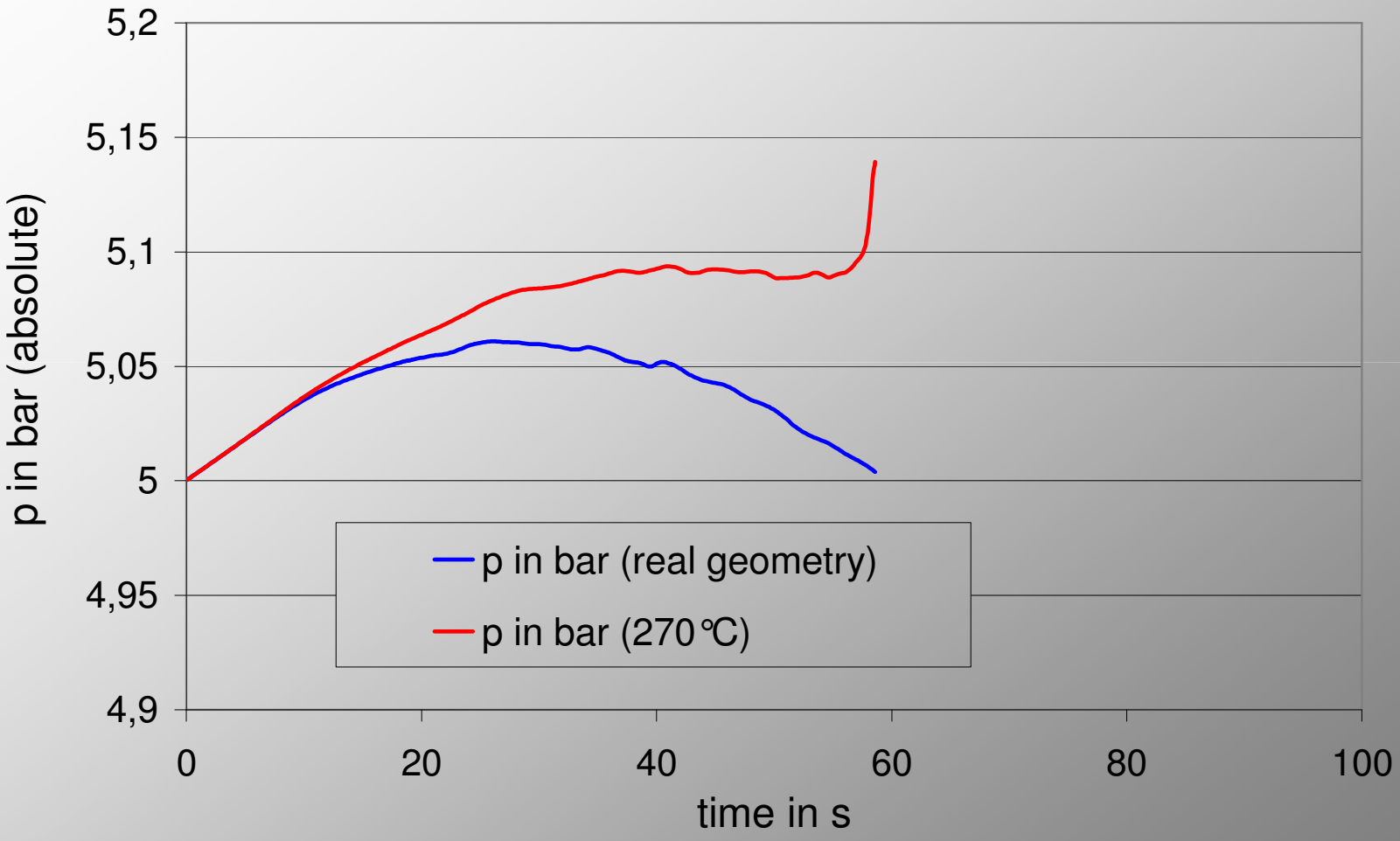
real geometry



30 s

100-dm³ vessel simulation: MITD dependence on geometry

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



Prediction of MITD for 100-dm³-vessel
(simple geometry)

MITD dependence on pressure for 100-dm³-vessel