University of Applied Sciences and Arts Northwestern Switzerland
School of Life Sciences

Modelling of a high phi-factor calorimeter for safety analysis

Reaction Calorimetry User Symposium

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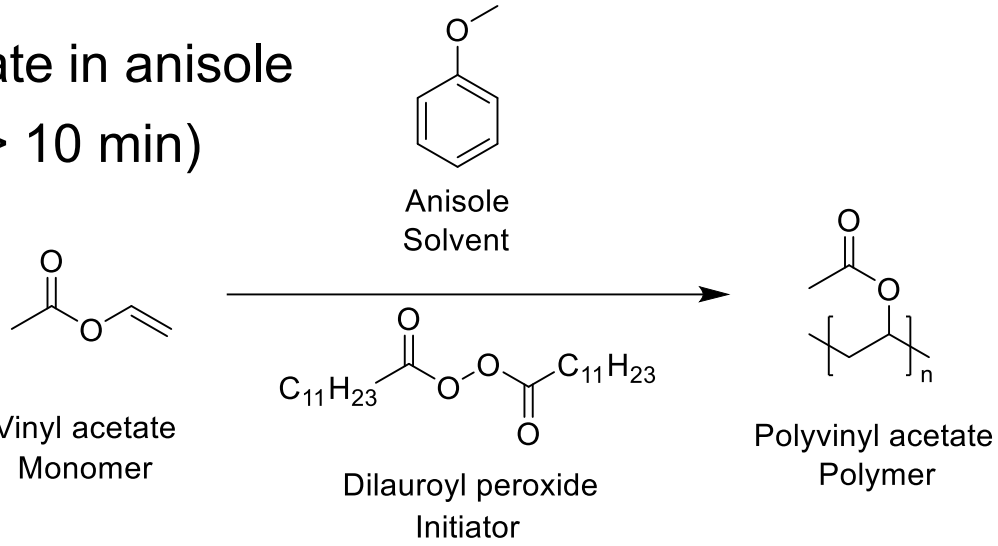
28. October 2025

Reminder: Presentation by Prof. Dr. Andreas Zogg

- Polymerization of vinyl acetate in anisole
  - **Type C reaction**: Slow (> 10 min)

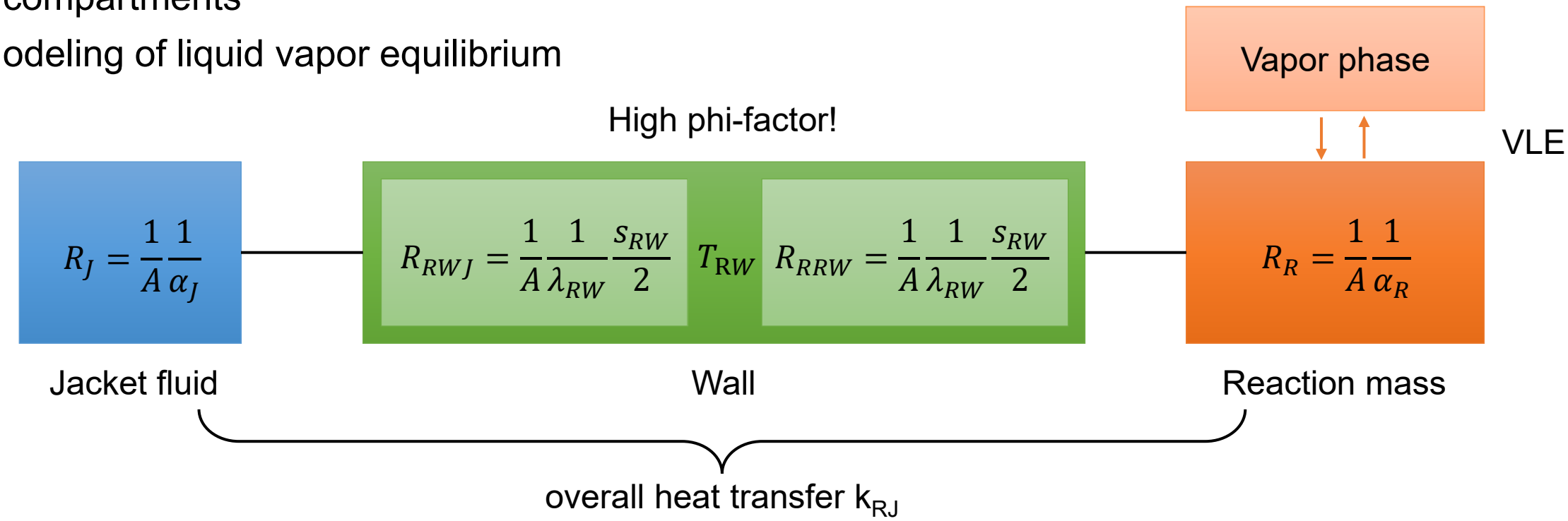


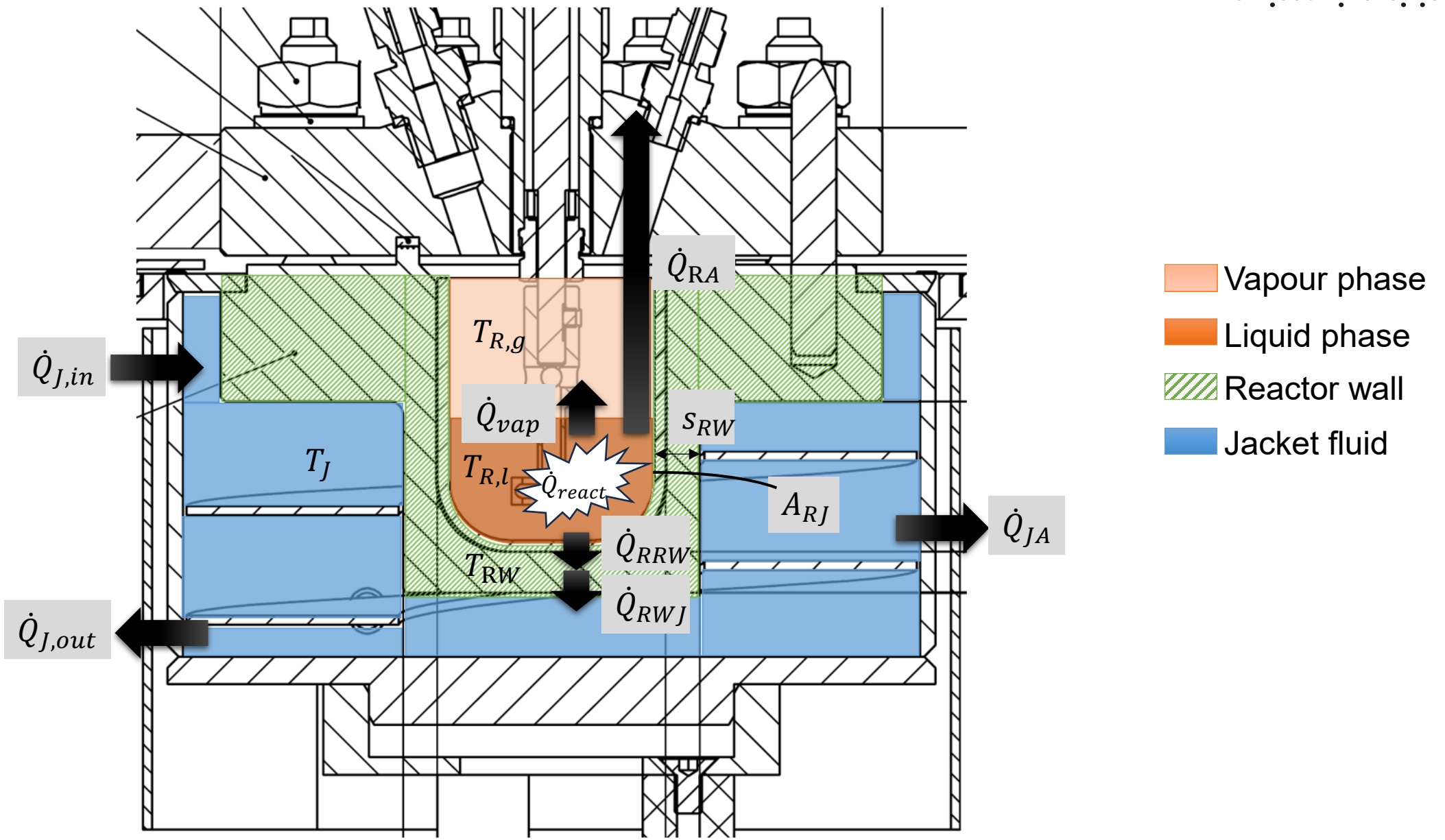
- **High phi-factor calorimeter** (autoclave)
  - Max. 300 bar and max. 250 °C
  - Reactor volume: **125 ml**
  - Phi – factor / Thermal inertia factor $\Phi = \frac{mass\ of\ reactor + mass\ of\ reaction\ mass}{mass\ of\ reaction\ mass}$

Modelling of calorimeter

- Model build in Matlab / Simulink
- Calculation of temperatures and pressure
- 3 compartments
- Modeling of liquid vapor equilibrium

α: heat transfer coefficient [W/K/m2]
λ: thermal conductivity [W/m/K]
s: wall thickness [m]
A: heat exchange area [m2]
R: thermal resistance [K/W]

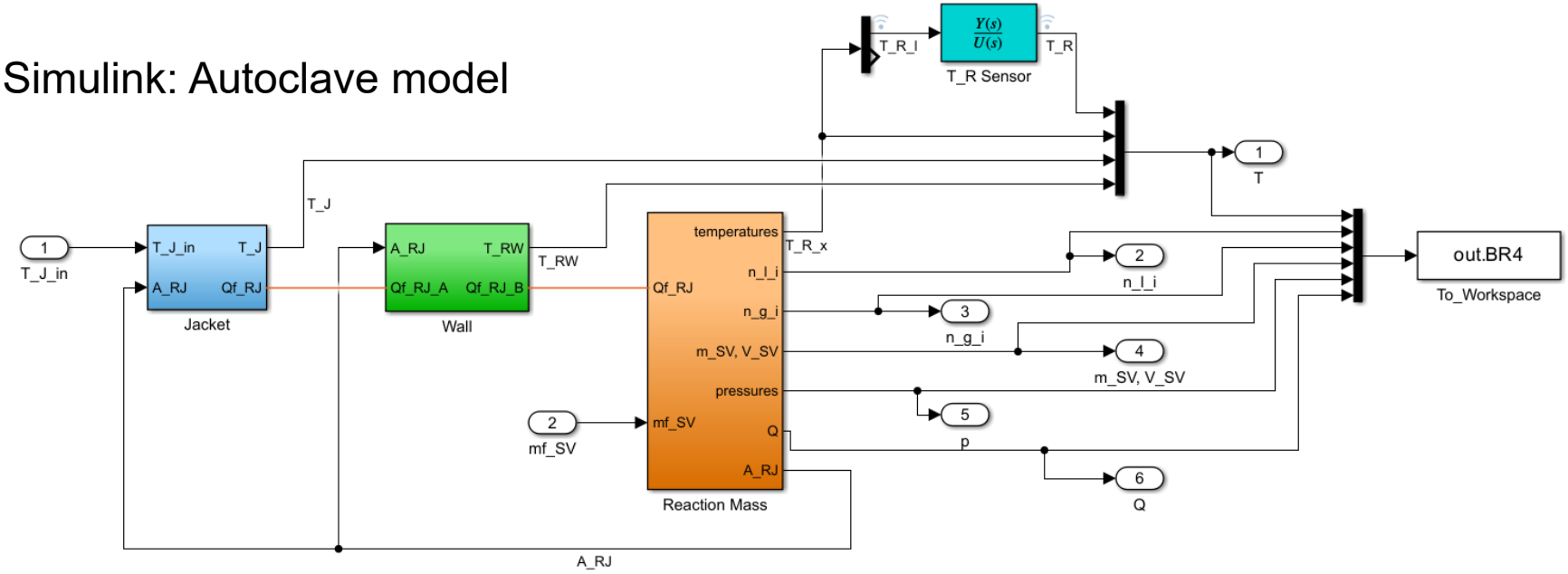



$\dot{Q}_{RA}$
$T_{R,g}$
$\dot{Q}_{J,in}$
$\dot{Q}_{vap}$
s_{RW}
T_J
$T_{R,l}$
$\dot{Q}_{react}$
A_{RJ}
$\dot{Q}_{JA}$
$\dot{Q}_{RRW}$
T_{RW}
$\dot{Q}_{RWJ}$
$\dot{Q}_{J,out}$
Vapour phase
Liquid phase
Reactor wall
Jacket fluid

Matlab / Simulink

- Simulink is a graphical programming language and is closely related to Matlab.
- Simscape is a Toolbox for Simulink that allows streams with physical properties in contrast to Simulink's solely numeric calculations.

Simulink: Autoclave model



Matlab / Simulink

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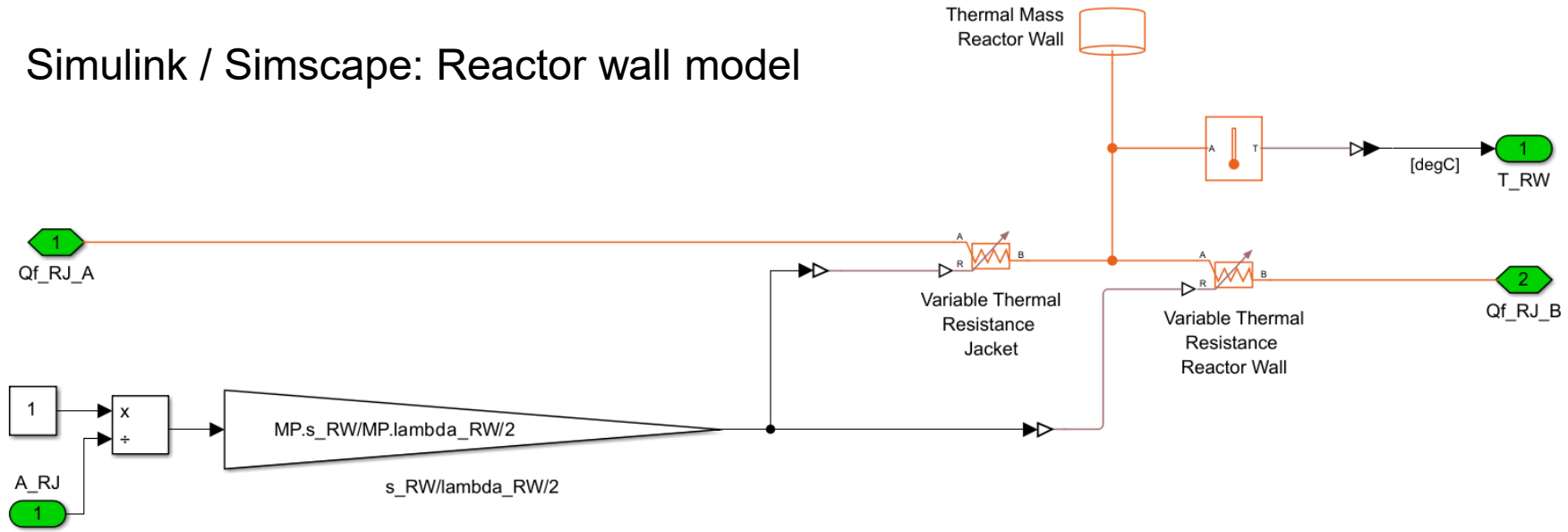
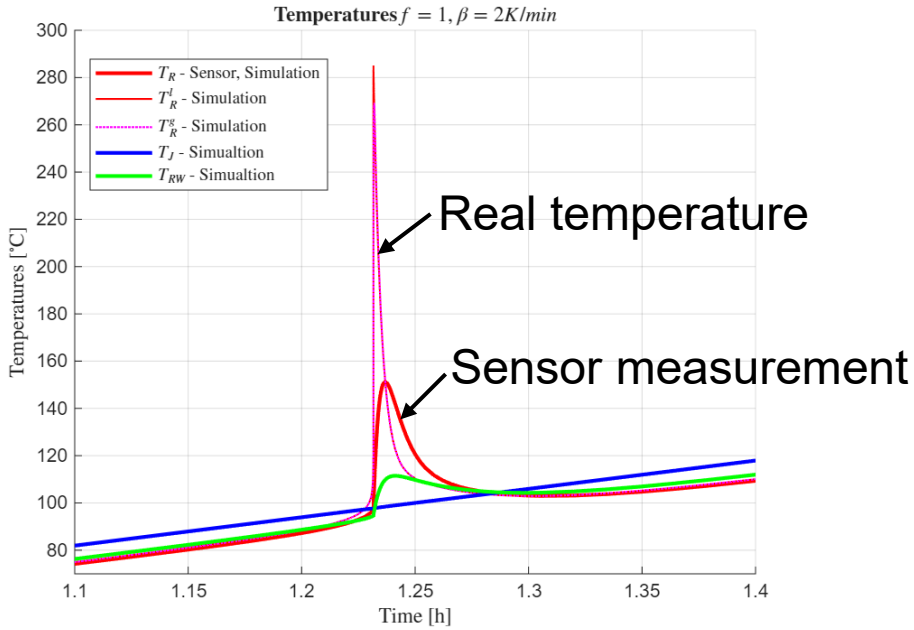
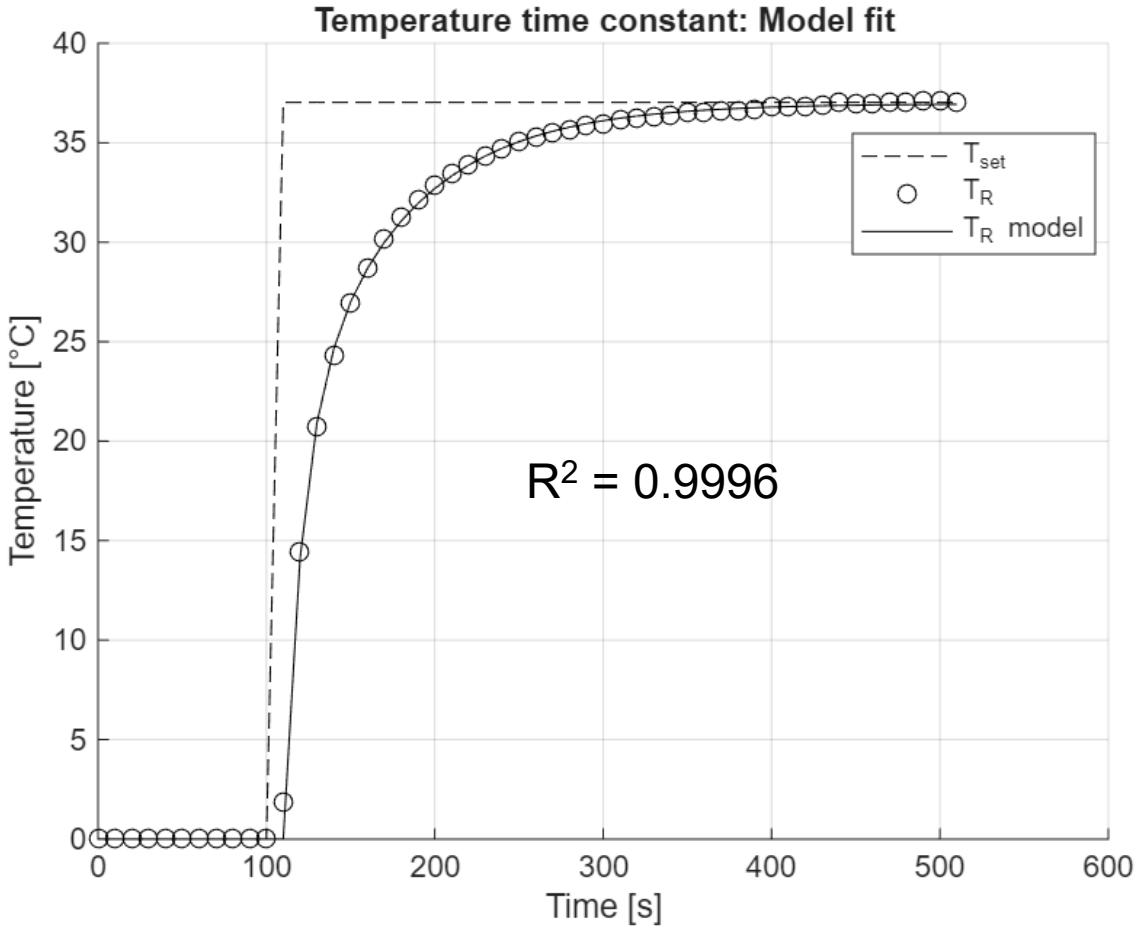
Simulink / Simscape: Reactor wall model



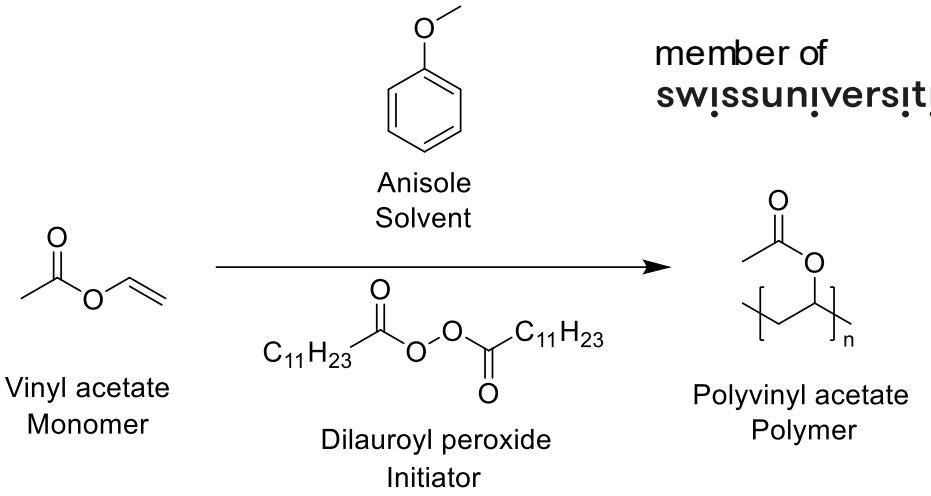
Time constant of temperature sensor

- Sensors do have a delay until they reach the actual value.
- The time constant of a temperature sensor can be determined by quickly submerging it into a hot fluid.





Model of reaction - Kinetics



– Reaction model was fitted to DSC data.

1. n'th order rate law: high activation energy → suspected autocatalytic reaction
2. Fit autocatalytic model (Benito-Perez)[1] → much lower activation energy

$$-r_A = k_0 \cdot e^{\frac{EA}{R}\cdot\left(\frac{1}{T_0}-\frac{1}{T}\right)} \cdot C_A^n$$

n'th order model

$$-r_A = k_1 \cdot e^{\frac{EA_1}{R}\cdot\left(\frac{1}{T_0}-\frac{1}{T}\right)} \cdot C_A + k_2 \cdot e^{\frac{EA_2}{R}\cdot\left(\frac{1}{T_0}-\frac{1}{T}\right)} \cdot C_A \cdot C_C$$

Simplified Benito-Perez (autocatalytic)

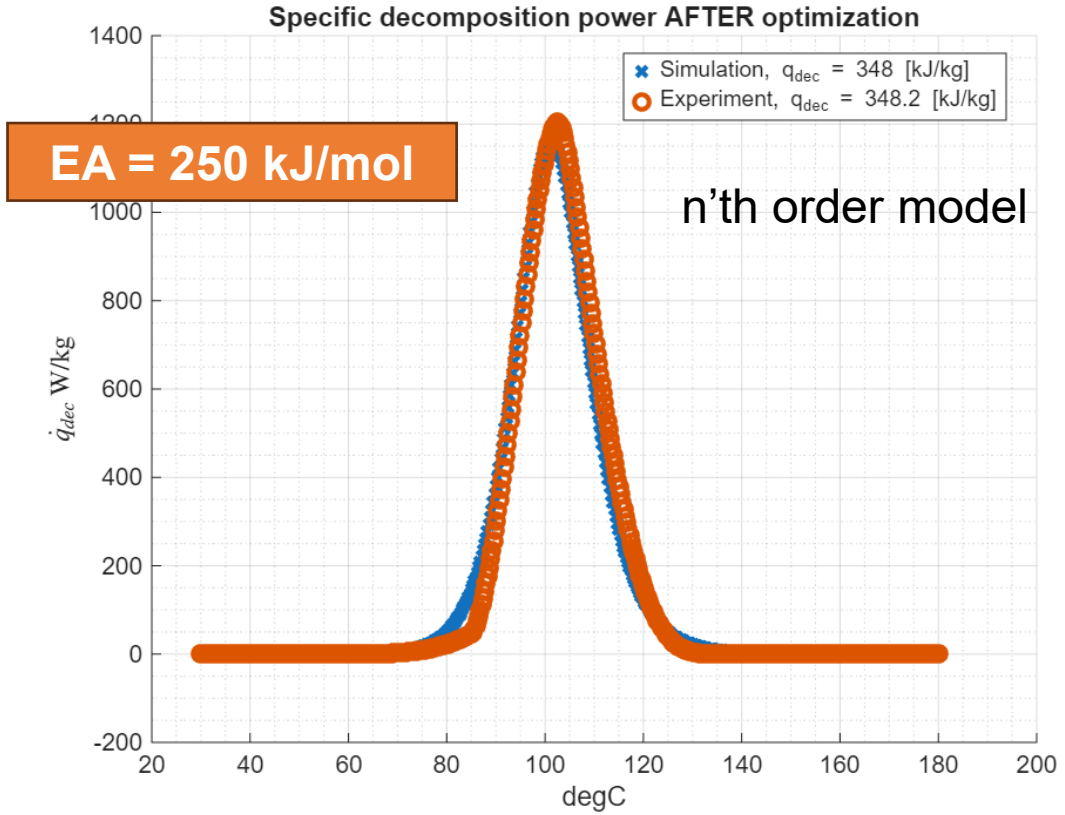
C_A concentration of vinyl acetate, C_C concentration of product

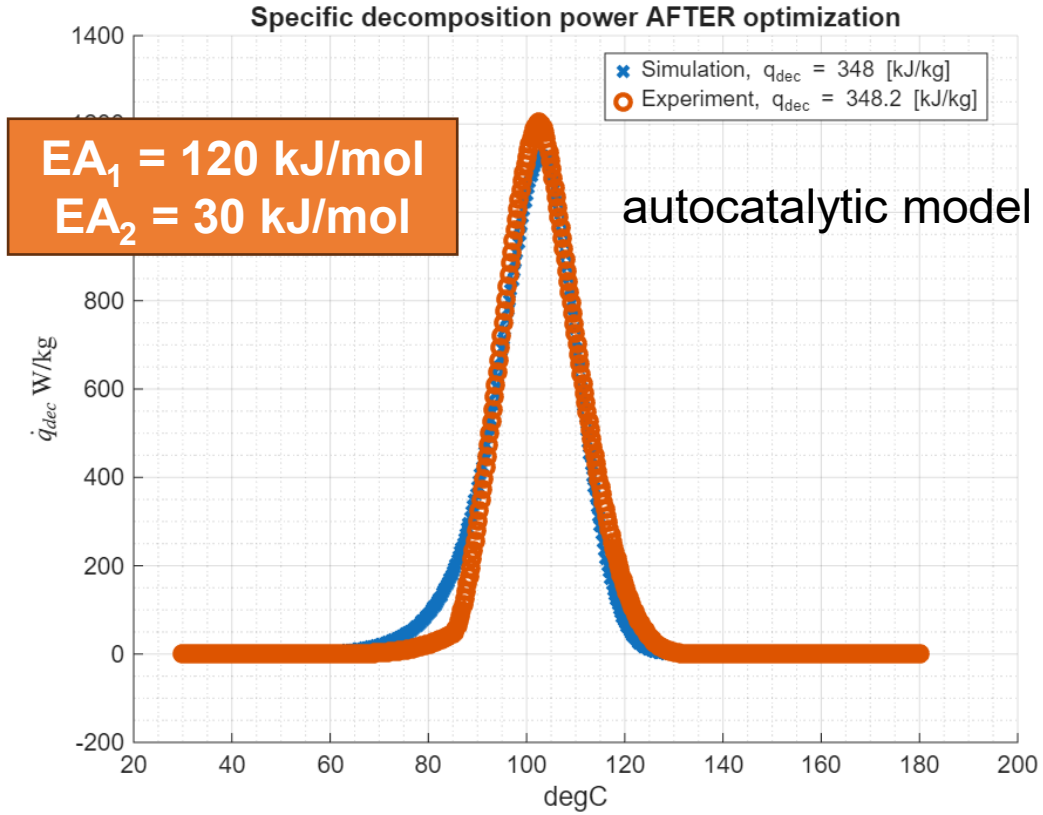
– DLP was not considered in the kinetic model, therefore the models are only valid for the DLP concentration that was used in the DSC.

1. F. Stoessel, *Thermal Safety of Chemical Processes: Risk Assessment and Process Design* (John Wiley & Sons, Incorporated, Newark, Second, completely revised and extended edition., 2020).

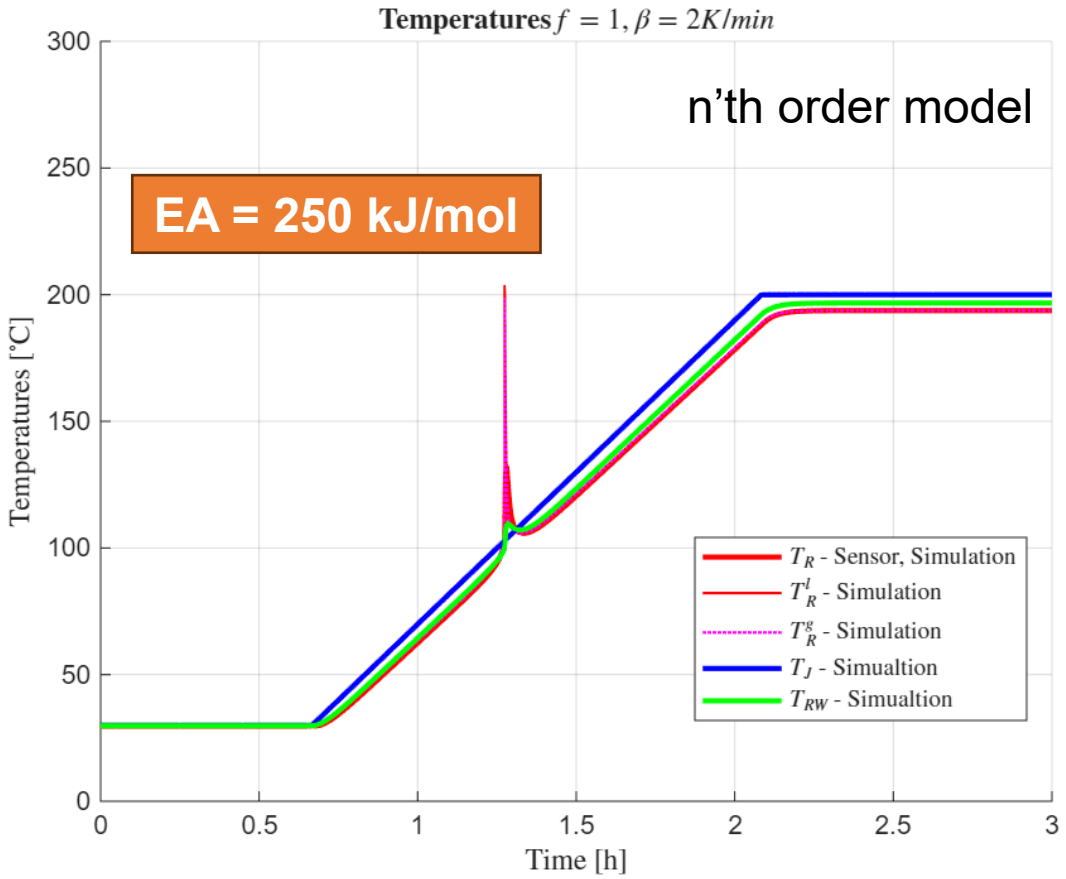
Model of reaction - DSC fit

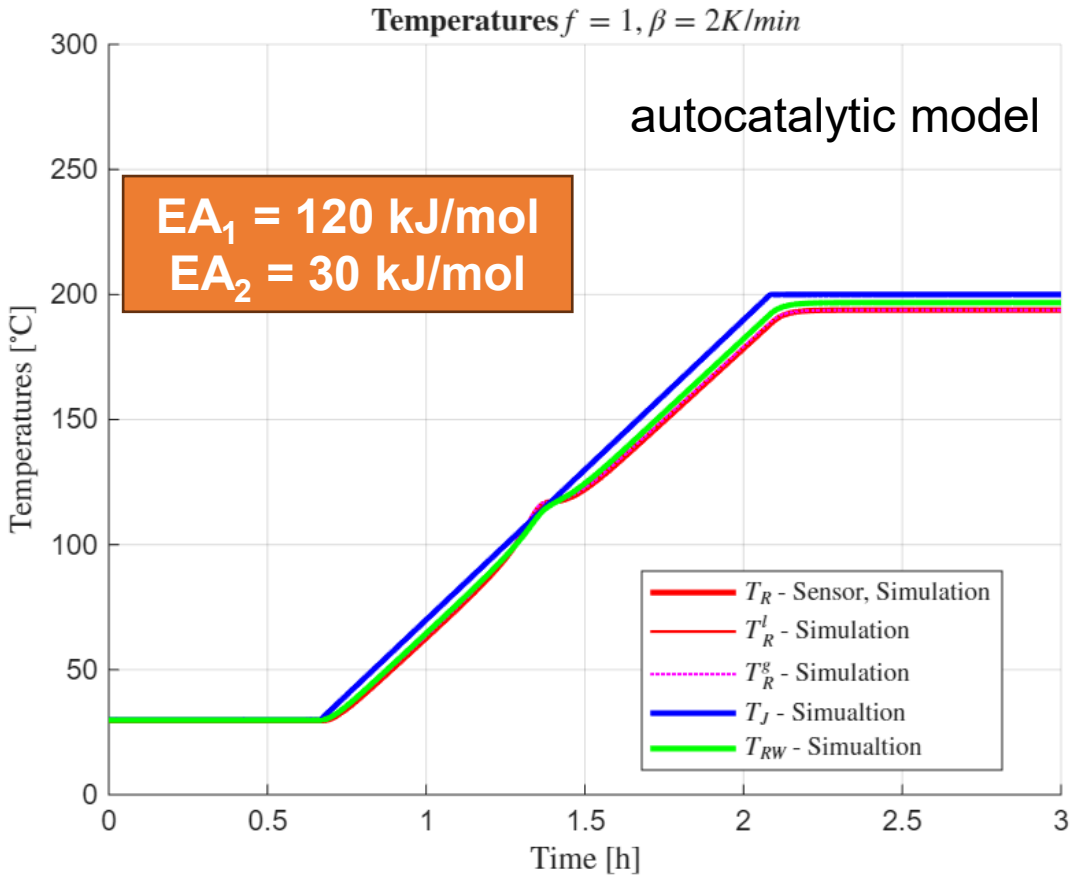
– Thermokinetic model fitted to two DSC measurements (only DSC one shown).





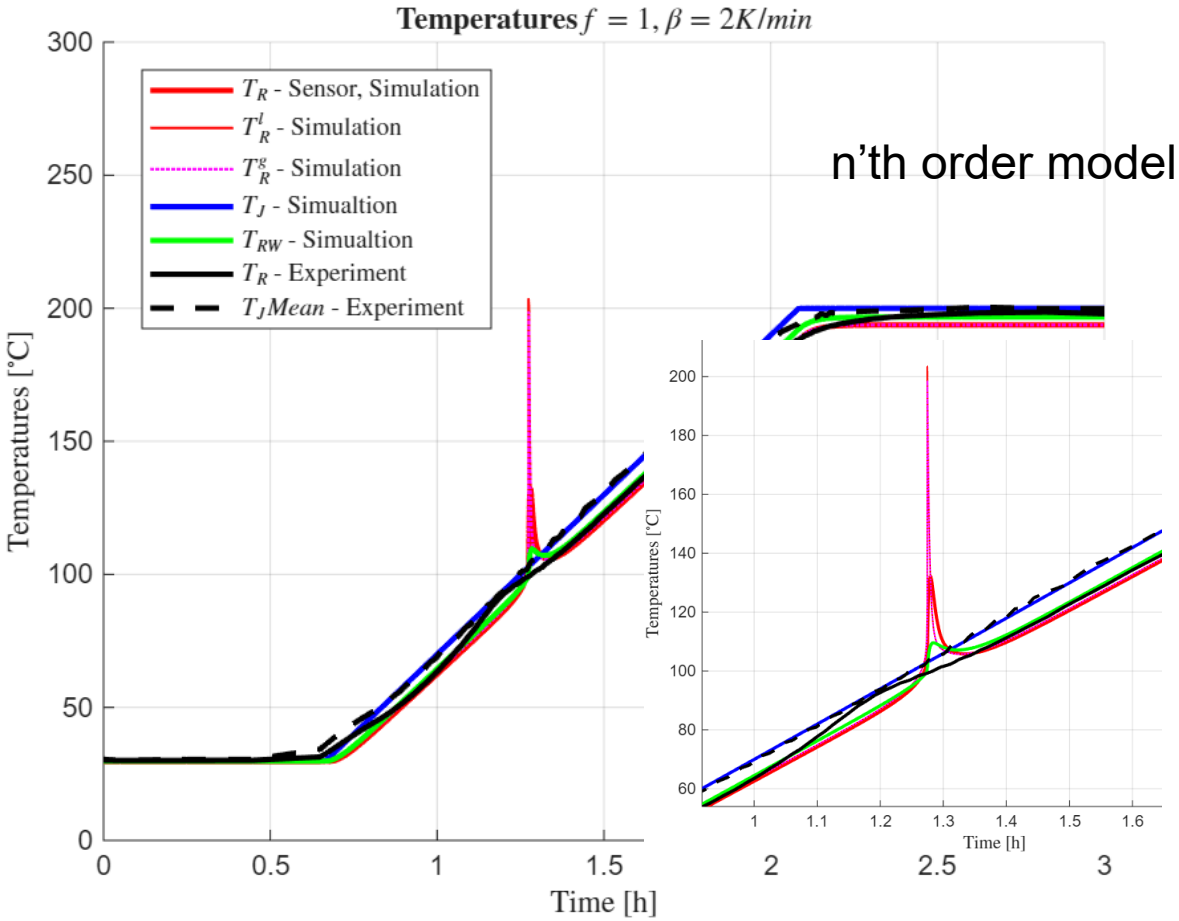
Model of reaction – Simulation of reaction in the autoclave



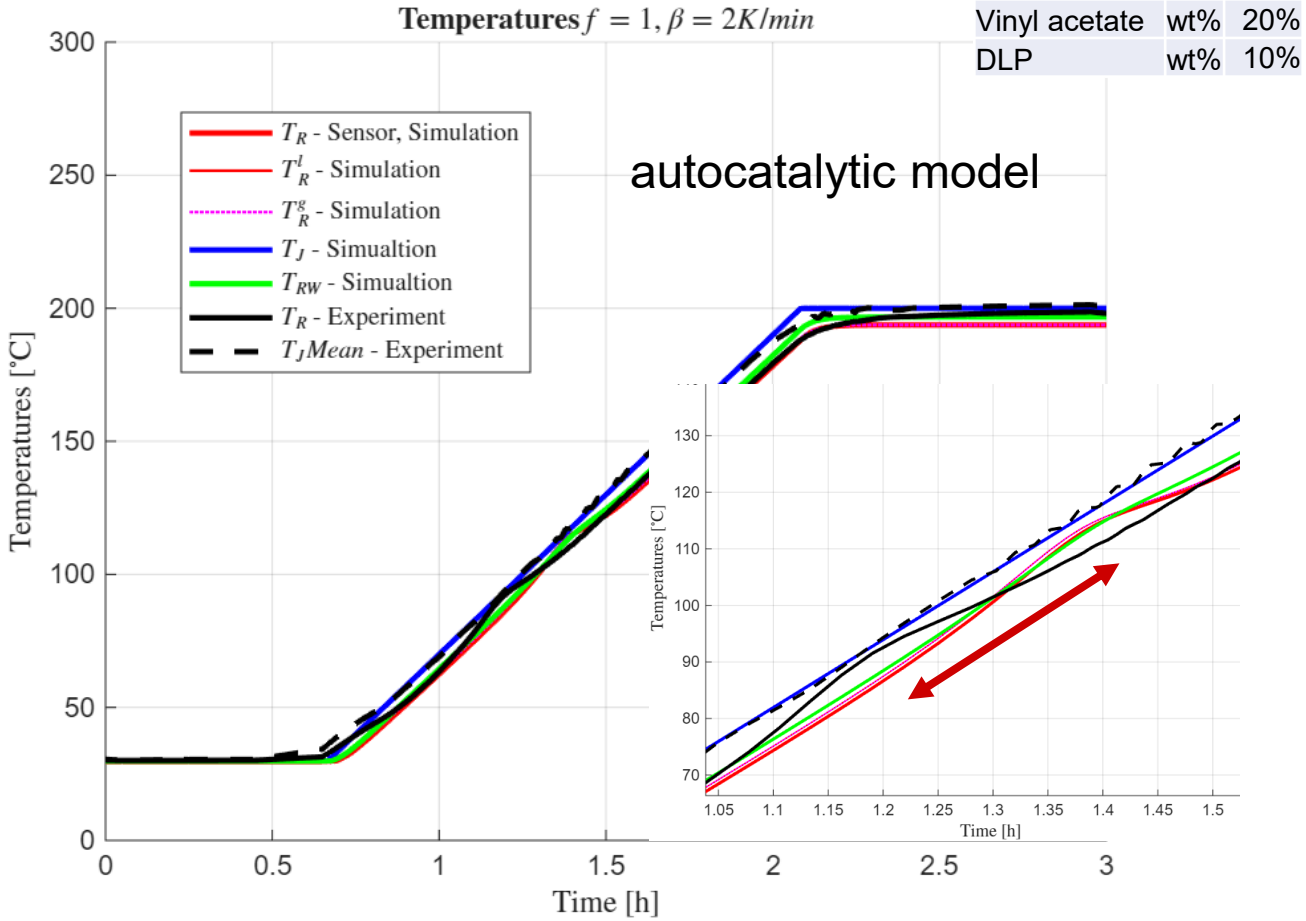


Model validation – Polymerization Experiment 2K/min

Anisol	wt%	70%
Vinyl acetate	wt%	20%
DLP	wt%	10%



n'th order model

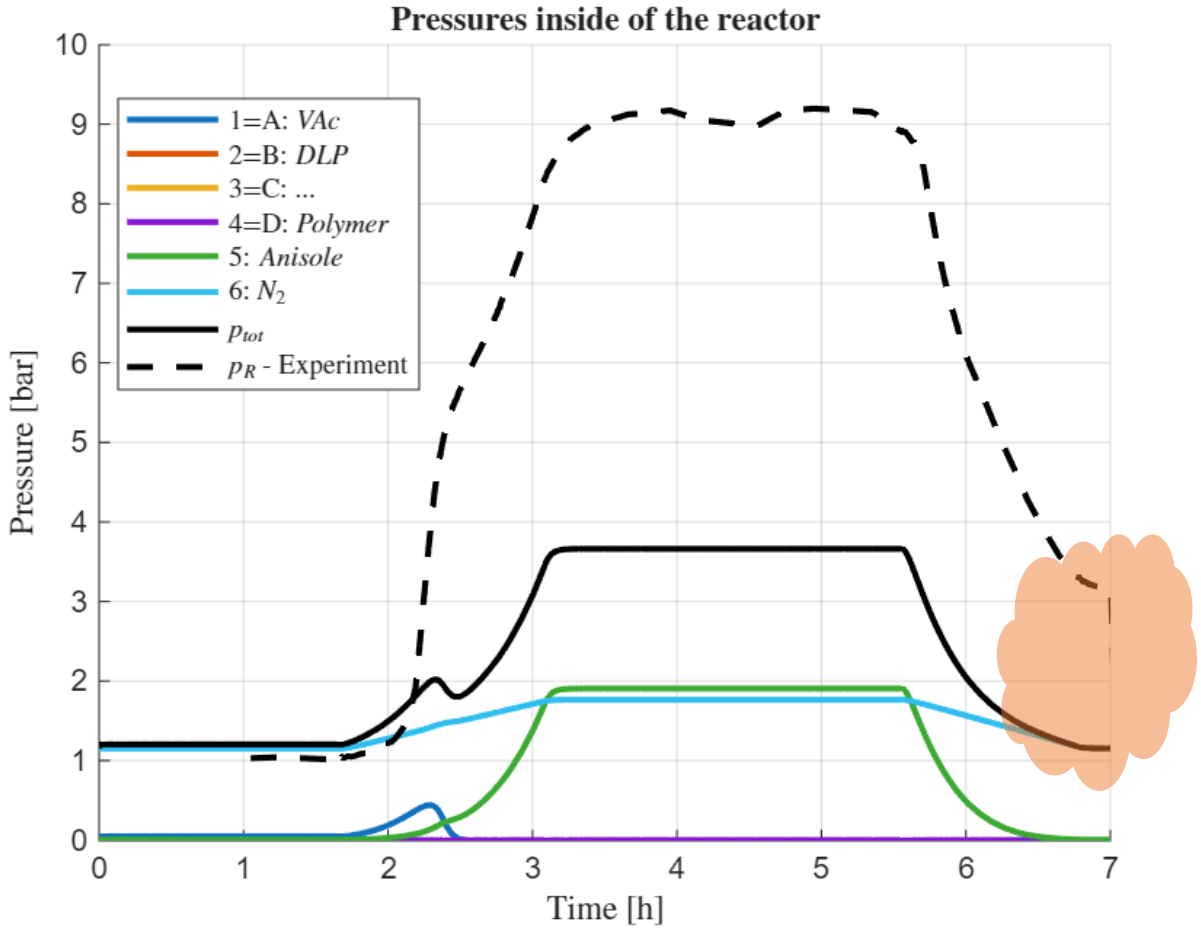


autocatalytic model

Model validation – Polymerization Experiment 2K/min

- Pressure is much larger at 200°C and does not decrease to initial pressure after cooling.
- The reaction mass forms foam when shaken.

→ Decomposition gas formed during reaction.

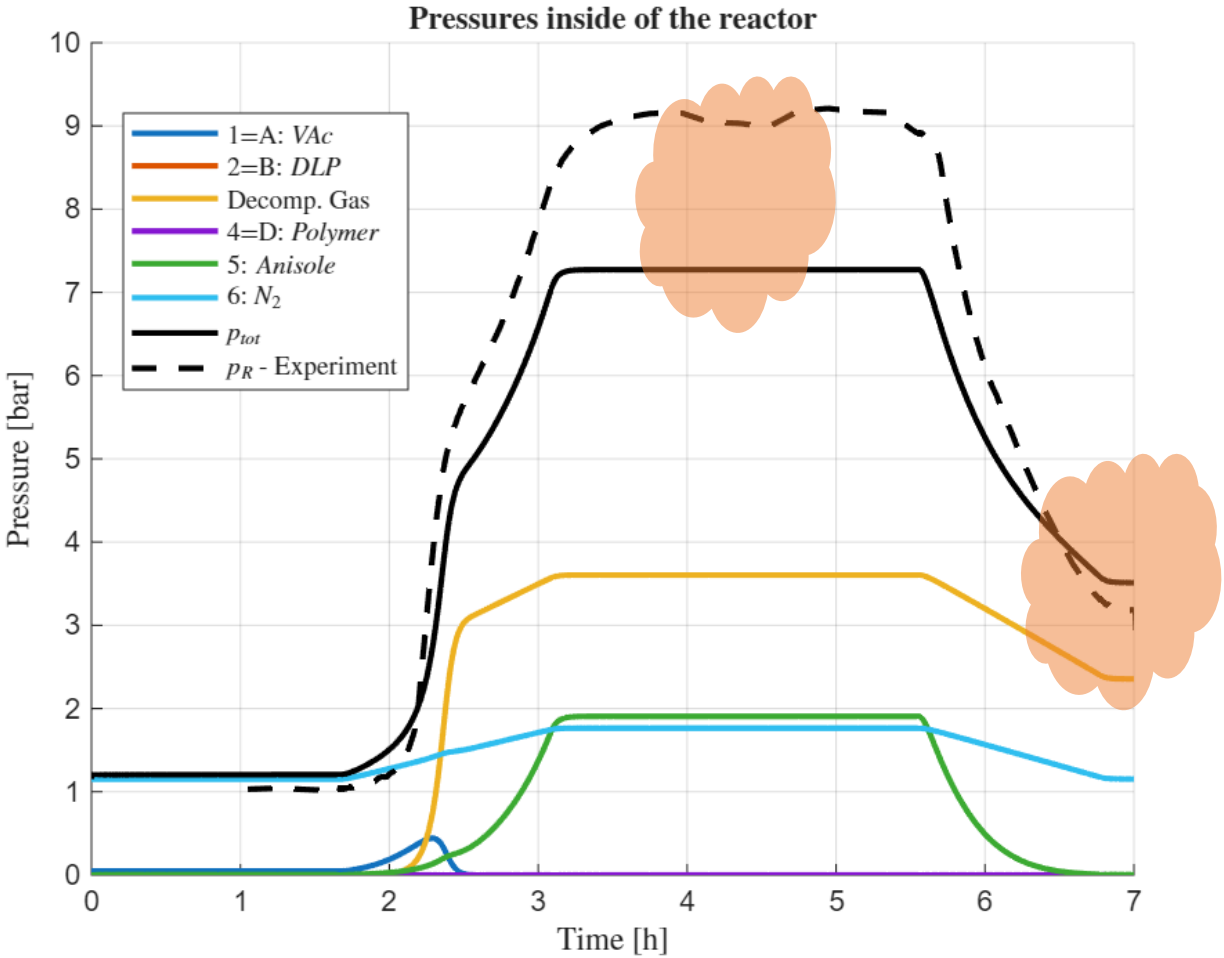


Model validation – Gas formation

- First approach:
  - $n_{gas}(t) = k \cdot X(t)$
  - X thermal conversion
  - At full conversion and 30°C:

    $n_{gas,end}$ via ideal gas law
  - $n_{gas,end} = k \cdot 1$
  - No dissolution of gas in liquid phase

→ measured pressure at elevated temperature is much higher → significant solubility of gas

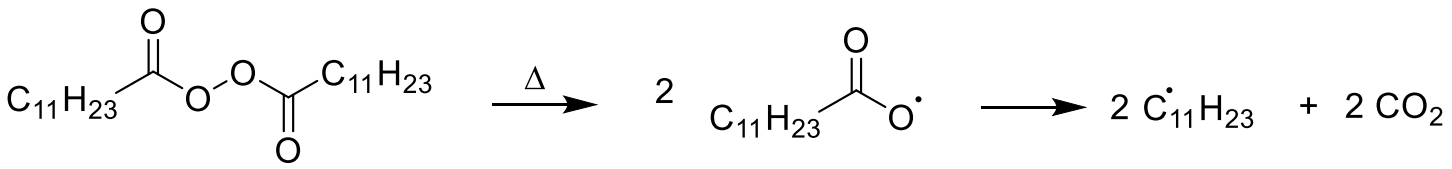


Decomposition of dilauroyl peroxide (DLP)

- Simulated pressure is much lower than the measured pressure.
- After cooling down to start temperature the pressure does not decrease to the initial pressure.

→ Hypothesis: Gas must be formed during the reaction

- Literature suggests formation of CO_2 after DLP decomposition.[1]

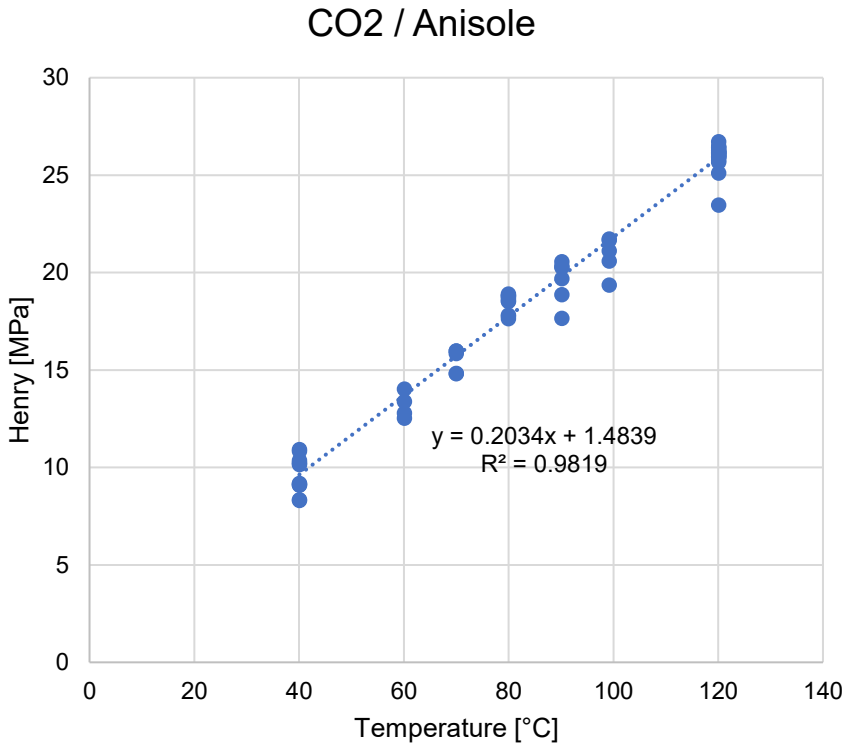


Dilauroyl peroxide
Initiator

1. J. E. Guillet, J. C. Gilmer, *Can. J. Chem.* **47**, 4405–4411 (1969).

Vapor / liquid equilibrium of CO_2 and anisole

- Henry's law
  - The partial pressure of compound p_1 is dependent of its concentration in the liquid phase x_1 and the Henry coefficient H_{12}.
  - $p_1 = x_1 \cdot H_{12}(T, p)$
- In literature VLE measurement data is given for CO_2 in anisole from 40 to 120°C.[1, 2, 3]

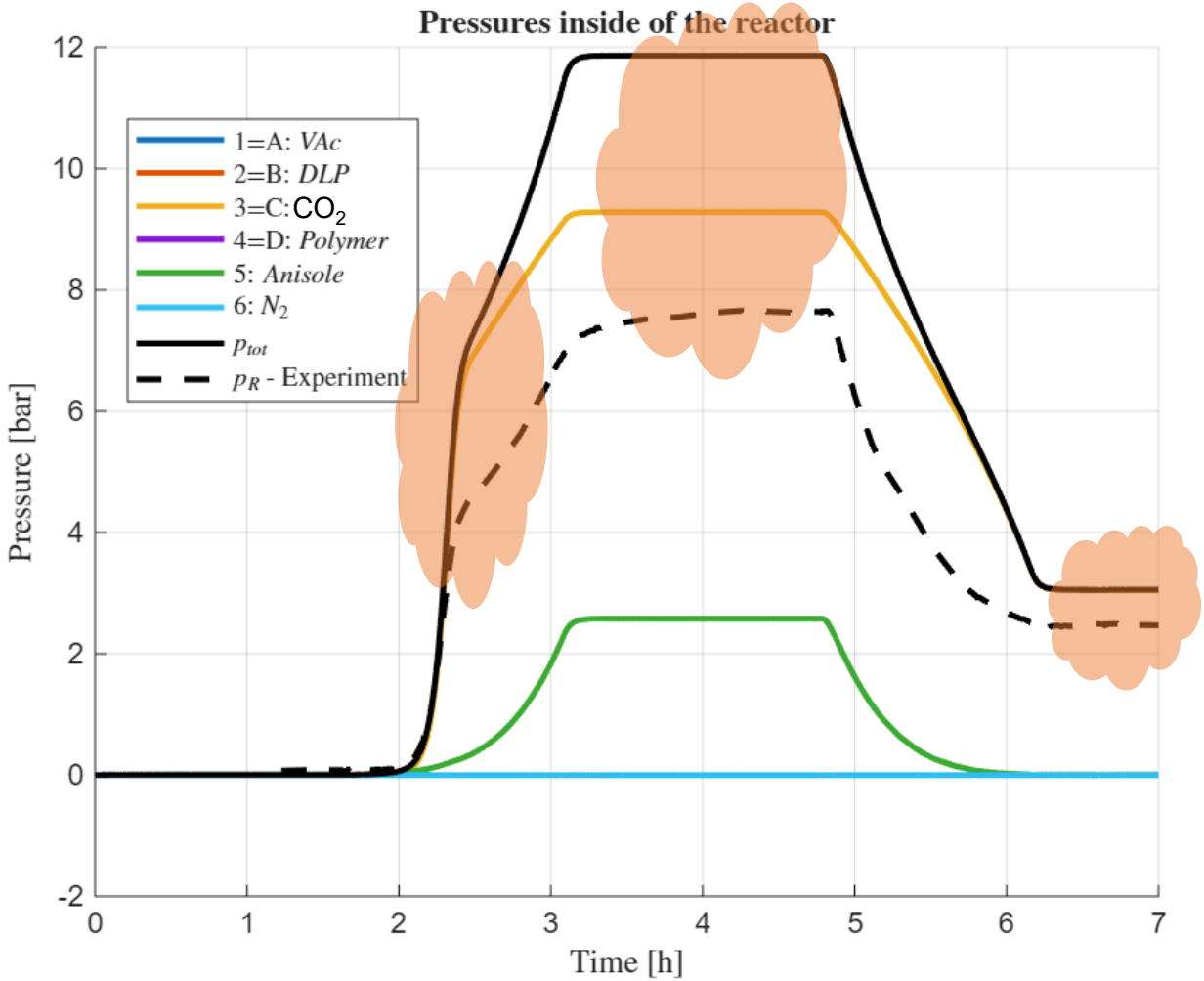


1. C. H. Kim, A. B. Clark, P. Vimalchand, M. D. Donohue, *J. Chem. Eng. Data*. **34**, 391–395 (1989).
2. S. D. Park, C. H. Kim, C. S. Choi, *J. Chem. Eng. Data*. **36**, 80–84 (1991).
3. D. Walther, G. Maurer, *J. Chem. Eng. Data*. **38**, 247–249 (1993).

Model validation of DLP decomposition

- Measurement: 10% DLP in anisole, no polymerization
  From 30°C to 200°C, β = 2 K/min
- Decomposition of DLP using Henry's law for CO_2.
- The henry coefficient is extrapolated linearly for temperatures outside the temperature range of the literature data.

→ Model must be investigated further.



Conclusions & Outlook

- **Autocatalytic model** showed more realistic simulations than n’th order model.
- More polymerization experiment with different concentrations are needed to validate the kinetic model further.
- The formation of gas is not yet fully understood. Work must be continued on **VLE** and **decomposition of DLP**.
- Decomposition of DLP could be further investigated using a **gas flow** measurement after release the pressure after reaction and **analyzing** the gases.

Thanks a lot

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